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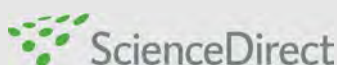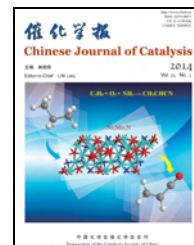
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Article

Acidic ionic liquid-catalyzed esterification of oleic acid for biodiesel synthesis

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A R T I C L E   I N F O

A B S T R A C T

Acidic ionic liquids (ILs) are used as environmentally-friendly and promising acid catalysts for biodiesel synthesis owing to their beneficial characteristics such as high catalytic activity, high selectivity, and ease of recycling. In this paper, seven different acidic ILs were examined as catalysts in the synthesis of biodiesel from the esterification of oleic acid with methanol. It was found that the stronger the acidity of the IL, the higher its esterification activity. The introduction of a SO_3H group into the IL greatly increases its Brönsted acidity and results in a bifunctional nature of the ILs for use as either a catalyst or environmentally-friendly solution in the esterification reaction. All of these effects contribute to product formation. Of all the tested acidic ILs, 1-sulfobutyl-3-methylimidazoliumhydrosulfate ([BHSO₃MIM]HSO₄) exhibited the best catalytic performance. The [BHSO₃MIM]HSO₄-catalyzed esterification of oleic acid with methanol was systematically explored, and the reaction conditions were optimized using a response surface methodology. The optimum molar ratio of methanol to oleic acid, catalyst amount, reaction temperature, and reaction time were 4:1, 10% (based on the mass of oleic acid), 130 °C, and 4 h, respectively, under these conditions, and a yield of methyl oleate (biodiesel) of 97.7% was achieved. Furthermore, [BHSO₃MIM]HSO₄ retained around 95.6% of its original catalytic activity after 10 successive reuses (4 h per period of use), showing excellent operational stability. In addition, the use of [BHSO₃MIM]HSO₄ for biodiesel synthesis from waste oils containing 72% of free fatty acids was examined, and yields as high as 94.9% after 6 h were obtained. Clearly, [BHSO₃MIM]HSO₄ shows considerable potential for the synthesis of biodiesel.

1. Introduction

With the development of the global economy and increasing environmental pollution problems, the energy crisis caused by increasing global demand for energy becomes steadily more serious [1]. The environmental problems caused by the use of fossil fuels are also of great concern [2]. Because a large amount of carbon dioxide is produced from fossil fuel use and released into the atmosphere, the earth's surface temperature increases, resulting in the melting of ice sheets and a rise in sea levels. This has prompted many researchers to search for sources of efficient, safe, and renewable green energy. Biodiesel, a monoalkyl ester of fatty acids with 12–24 carbon atoms, has recently gained considerable attention in this context

[3]. It was reported that the use of 100% pure biodiesel (B100) could reduce carbon dioxide emissions by 78.5% compared with petroleum-based diesel [4]. Biodiesel is easy to transport and store because of its high flash point. The cetane number of biodiesel is high and consequently its combustion properties are good. Besides, biodiesel has other advantages such as low sulfur content, low pollution, and good lubrication performance [5]. These factors all lead to biodiesel being considered as a new type of green and renewable energy [6–8].

Esterification reactions are one way of producing biodiesel. In recent years, many investigations on catalysts for the esterification step have demonstrated the use of solid superacids [9–11], heteropoly acids [12,13], or cation-exchange resins with strong acidity [14,15] as catalysts. These catalysts can displace sulfuric acid and thereby solve process problems such as equipment corrosion and environmental pollution. However, the preparation of these catalysts is relatively complicated, they are difficult to recycle, and the production cost of the catalysts is high. Therefore, it is necessary to develop an environmentally-friendly, efficient, and novel catalyst for the synthesis of biodiesel by esterification.

Ionic liquids (ILs) are salts consisting of organic cations and inorganic or organic anions, and remain liquid at room temperature or at relatively low temperatures (< 100 °C), generally known as room temperature ILs [16]. Recently, the use of ILs for biodiesel synthesis has been extensively studied [17–20], where the ILs have been used as either liquid acid catalysts or environmentally-friendly solvents. ILs have both high acidic densities, similar to those of liquid acid catalysts, and non-volatility, similar to that of solid acid catalysts. The IL structure and acidity can be tailored by altering the cation or anion. Additionally, ILs as catalysts can be readily separated from the products and can also show high thermal stability. Therefore, ILs are expected to be a type of designer green solvent, having significant potential [21,22]. To date, the use of ILs as catalysts for esterification reactions has remained largely unexplored, with only a few reports available [23–26]. In the present study, the effects of various acidic ILs as catalysts on the synthesis of biodiesel from the esterification of oleic acid with methanol were examined, and the reaction conditions were optimized. In addition, the use of acidic ILs for biodiesel synthesis from waste oils containing a high content of free fatty acids was successful.

2. Experimental

2.1. Materials

1-Butyl-3-methylimidazoliumhydrosulfate ([BMIM]HSO₄), *N*-ethylpyridinium hydrosulfate ([EPy]HSO₄), tetraethylammonium hydrosulfate ([TEAm]HSO₄), 1-sulfobutyl-3-methylimidazolium hydrosulfate ([BHSO₃MIM]HSO₄), 1-butyl-3-methylimidazoliumperchlorate ([BMIM]ClO₄), 1-ethylpyridiniumbromide ([EPy]Br), and tetraethylammoniumchloride ([TEAm]Cl) were purchased from Lanzhou AoKe Chem. Co. Ltd (Lanzhou, China) and were of >98% purity. Methyl oleate (>99% purity) and methylheptadecanoate (>97% purity) were

purchased from Sigma-Aldrich (St. Louis, USA) and TCI (Tokyo, Japan), respectively. Oleic acid and other chemicals were also obtained from commercial sources and were of the highest purity available.

2.2. Effects of various acidic ILs on the esterification of oleic acid with methanol

Oleic acid (2.82 g, 0.01 mol), methanol (0.64 g), and various acidic ILs as catalysts (0.28 g) were mixed in a 50 ml round bottom flask, and then the mixture was kept at 80 °C in an oil bath (reflux condensation, magnetic stirring at 500 r/min). Aliquots (50 μl) were withdrawn and centrifuged, and the supernatant liquid (5 μl) was mixed with 200 μl methylheptadecanoate (internal standard) prior to GC analysis.

2.3. Optimization of [BHSO₃MIM]HSO₄-catalyzed synthesis of methyl oleate via the esterification of oleic acid with methanol

Oleic acid (2.82 g, 0.01 mol) was added to a 50 ml round bottom flask, followed by the addition of a known amount of methanol and [BHSO₃MIM]HSO₄ catalyst. The mixture was heated at a predetermined temperature in an oil bath (reflux condensation, magnetic stirring at 500 r/min). After completion of the reaction, the reaction mixture was biphasic, and the desired product (methyl oleate) stayed mainly in the upper phase. Samples (50 μl) were withdrawn from the upper phase and centrifuged, and then the supernatant liquid (5 μl) was mixed with 200 μl methylheptadecanoate (internal standard) prior to GC analysis.

2.4. Operational stability of the [BHSO₃MIM]HSO₄ catalyst

Oleic acid (2.82 g, 0.01 mol), methanol (1.28 g), and 0.28 g [BHSO₃MIM]HSO₄ catalyst were mixed in a 10 ml round bottom flask at 130 °C for 4 h (reflux condensation, magnetic stirring at 500 r/min). After completion of the reaction, the by-product water and excess methanol were removed from the mixture by evaporation, and then the IL catalyst [BHSO₃MIM]HSO₄ was further separated from the product by centrifugation. After thorough washing with *n*-hexane followed by air-drying, the IL catalyst obtained was used in the next cycle. The activity of the [BHSO₃MIM]HSO₄ catalyst in the first reaction cycle was assigned a relative activity of 100%. Samples (100 μl) were withdrawn from the reaction mixture at specified times for each batch and centrifuged, and the supernatant liquid (5 μl) was mixed with 200 μl methylheptadecanoate (internal standard) prior to GC analysis.

2.5. GC analysis

The reaction mixtures were assayed using a Shimadzu GC 2010 (Tokyo, Japan) instrument equipped with an HP-5 capillary column (0.53 mm × 15 m Agilent Technologies, Inc., Santa Clara, USA) and a flame ionization detector. The column temperature was held at 180 °C for 1 min, raised to 186 °C at 0.8 °C/min, then kept at 186 °C for 1 min, followed by a further rise

to 280 °C at 20 °C/min. Nitrogen was used as the carrier gas with a flow rate of 12.5 ml/min. The split ratio was 1:25 (v/v). The injector and the detector temperatures were set at 250 and 280 °C, respectively. The retention times for methylheptadecanoate and methyl oleate were 4.49 and 5.73 min, respectively. The average error for this determination was < 1%. All reported data were averages of experiments performed in duplicate at least. The yield of methyl oleate was calculated as Yield = $m_{(MO)} \times 100\% / m$, where $m_{(MO)}$ is the amount of methyl oleate obtained, and m is the amount of initial oils.

3. Results and discussion

3.1. Effect of different acidic IL catalysts on the esterification of oleic acid with methanol

The activity of the IL catalyst is closely related to its anion acidity and its solubility towards the substrate. During the initial stage of the esterification reaction, the acidity of the IL plays an important role in the reaction and was significantly dependent on the anion characteristics of the IL. The more acidic the anion, the stronger the IL's acidity, and this property is responsible for a marked improvement in the yield of methyl oleate. Therefore, the SO₃H-functioned ILs with the highest acidity exhibited a much better catalytic activity in the esterification reaction than other acidic ILs. In addition, the cation of the IL also plays a crucial role in the reaction because the hydrophilicity of the IL can be tuned mainly by the cation. This affects the miscibility of the IL with the ester product, the degree of phase separation, and the reaction efficiency [27–29]. The seven different acidic ILs tested in this present study for use in the synthesis of methyl oleate (biodiesel) gave the results depicted in Fig. 1.

As can be seen in Fig. 1, the catalytic activity of the seven acidic ILs for the esterification of oleic acid with methanol displayed the following order: [BHSO₃MIM]HSO₄ > [BMIM]HSO₄ >

[EPy]HSO₄ > [TEAm]HSO₄ > [BMIM]ClO₄ > [TEAm]Cl > [EPy]Br. Among the ILs tested, [BHSO₃MIM]HSO₄ showed the highest catalytic activity and gave the highest yield of 72.4% after reaction for 4 h. With [BMIM]HSO₄ acting as the catalyst, a relatively good yield of 60% was also achieved at a reaction time of 4 h. Hence, [BHSO₃MIM]HSO₄ was considered to be the best IL catalyst for the reaction.
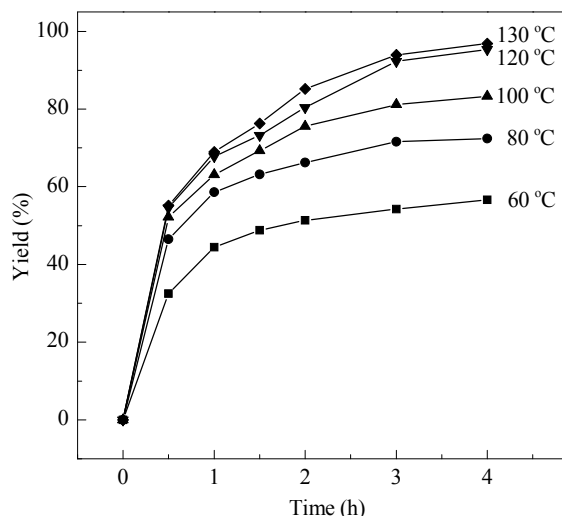
3.2. Effect of reaction temperature on the esterification of oleic acid with methanol

Reaction temperature is an important parameter for the esterification of oleic acid with methanol, with higher temperatures always leading to faster rates, together with a shift in the esterification reaction equilibrium towards the product. In a certain range of temperatures for the esterification reaction, the reaction rate and the yield clearly increase with an increase in reaction temperature. However, there is usually no substantial improvement in the product yield when the reaction temperature is increased further. In order to explore the effect of temperature on the reaction and to find the optimum reaction temperature, the [BHSO₃MIM]HSO₄-catalyzed esterification of oleic acid with methanol was carried out at different reaction temperatures (60–140 °C). The results obtained are illustrated in Fig. 2.

As is evident from the data depicted in Fig. 2, when the reaction temperature was lower than 120 °C, the yield of methyl oleate (biodiesel) significantly increased with increasing reaction temperature. When the reaction temperature was 120 °C, the relatively high yield of 95.3% was achieved at a reaction time of 4 h. Further increase of the reaction temperature (>120 °C) did not lead to a significant improvement in the product yield, indicating that the reaction was close to equilibrium. Taking the energy consumption and the product yield into account, 120 °C was selected as the optimum reaction temperature for the esterification of oleic acid with methanol.
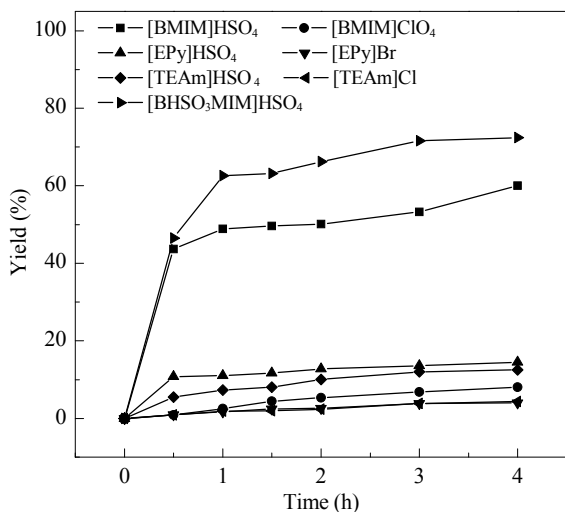
Fig. 1. Effect of various acidic IL catalysts on the esterification of oleic acid with methanol. Reaction conditions: 2.82 g oleic acid, 0.28 g IL catalysts (10% based on the mass of oleic acid), molar ratio of methanol to oleic acid = 2:1, 80 °C, 500 r/min.

Fig. 2. Effect of reaction temperature on [BHSO₃MIM]HSO₄-catalyzed esterification of oleic acid with methanol. Reaction conditions: 2.82 g oleic acid, 0.28 g [BHSO₃MIM]HSO₄, molar ratio of methanol to oleic acid = 2:1, 500 r/min.
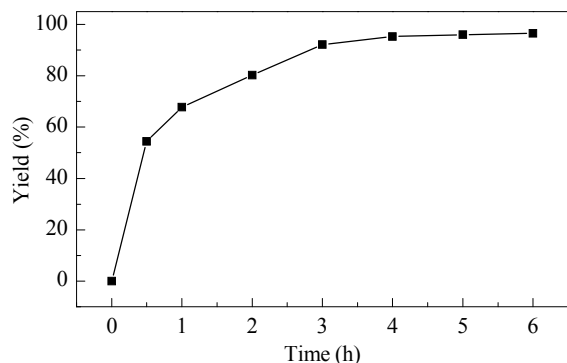
Fig. 3. Time course of the [BHSO₃MIM]HSO₄-catalyzed esterification of oleic acid with methanol. Reaction conditions: 2.82 g oleic acid, 0.28 g [BHSO₃MIM]HSO₄, molar ratio of methanol to oleic acid = 2:1, 120 °C, 500 r/min.
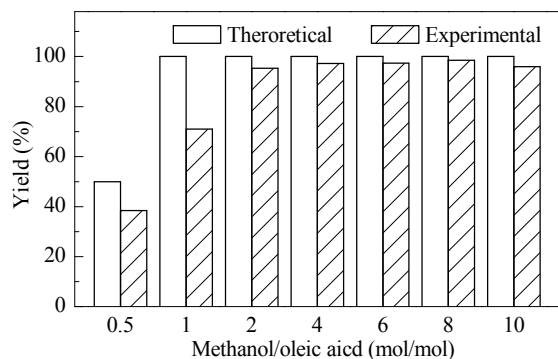
3.3. Effect of reaction time on the esterification of oleic acid with methanol

Reaction time is also an important factor influencing the esterification reaction. Generally, with an increase in reaction time, the reaction equilibrium will shift gradually to the products, and the yield of methyl oleate will be enhanced. However, when the reaction time exceeds the time required to attain equilibrium, the yield does not increase significantly with increasing reaction time. To find the optimal reaction time for the esterification, the time course of the reaction was plotted, as depicted in Fig. 3.

Figure 3 shows that the esterification process could be divided into three phases. In the first phase, the substrate oleic acid reacted rapidly with the excess of methanol, and more than 67.8% oleic acid was converted into methyl oleate within 1 h. In the second phase, the reaction rate gradually decreased in the period from 2 to 4 h, and a relatively high yield of methyl oleate (95.3%) was obtained at a reaction time of 4 h. In the third phase, the esterification reaction moved closer to equilibrium for reaction times >4 h, and the yield of methyl oleate showed no significant improvement at these extended reaction times. Therefore, the optimal reaction time for the esterification was considered to be 4 h.

3.4. Effect of molar ratio of methanol to oleic acid on the esterification of oleic acid

As shown in Fig. 4, when the molar ratio of methanol to oleic acid in the reaction system was <2:1, the yield of methyl oleate (biodiesel) at a reaction time of 4 h increased significantly with increasing methanol concentration. A slight improvement in the experimental yield at 4 h reaction time was observed when the molar ratio of methanol to oleic acid increased from 2:1 to 8:1, and this was close to the theoretical yield. It is well known that the esterification reaction is reversible, and an excess of methanol contributes to the esterification of oleic acid and increases the reaction rate. Nevertheless, when the molar ratio of methanol to oleic acid is greater than a certain value, the amount of methanol has little effect on the reaction rate. When
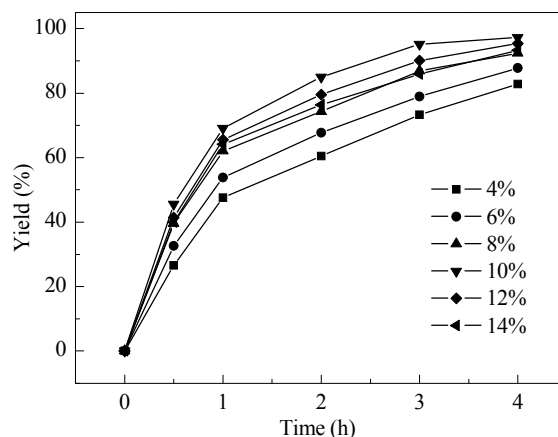

Fig. 4. Effect of molar ratio of methanol to oleic acid on the esterification reaction. Reaction conditions: 2.82 g oleic acid, 0.28 g [BHSO₃MIM]HSO₄, 120 °C, 4 h, 500 r/min.

the molar ratio of methanol to oleic acid was >8:1, the yield of methyl oleate even decreased slightly with increasing molar ratio. This was probably owing to the lowered IL concentration in the reaction system. Taking the energy consumption and the yield into consideration, the optimal molar ratio of methanol to oleic acid was shown to be 4:1.

3.5. Effect of [BHSO₃MIM]HSO₄ catalyst dosage on the esterification of oleic acid with methanol

As with other catalysts, the dosage of the IL catalyst [BHSO₃MIM]HSO₄ significantly affects the reaction rate. Within a certain range of IL concentration, when the dosage of [BHSO₃MIM]HSO₄ in the reaction system was increased, the reaction rate became markedly higher. However, when the dosage of catalyst exceeded a certain value, the reaction rate showed no significant increase with further increase in the dosage of IL catalyst, and might even have decreased. Figure 5 shows the effects of various concentrations of [BHSO₃MIM]HSO₄ catalyst (expressed as a percentage based on the mass of oleic acid) on the esterification of oleic acid with methanol.

The reaction rate and the yield of methyl oleate (biodiesel)

Fig. 5. Effect of dosage of IL catalyst on [BHSO₃MIM]HSO₄-catalyzed esterification of oleic acid with methanol. Reaction conditions: 2.82 g oleic acid, molar ratio of methanol to oleic acid = 4:1, 120 °C, 500 r/min.

Table 1
Factors and levels in the Box-Behnken experimental design for optimizing the synthesis of methyl oleate.

Name	Coded factor	Coded level		
		−1	0	1
Catalyst dosage (%)	A	8	10	12
Molar ratio of methanol to oleic acid	B	1:1	3:1	5:1
Temperature (°C)	C	100	120	140

were enhanced with increasing dose of [BHSO$_3$MIM]HSO$_4$ catalyst from 4% to 10%, and the maximum yield of 97.3% was achieved with 10% catalyst dose. However, a further increase in the catalyst dose lowered the yield. This might be attributable to the increased viscosity of the reaction system caused by adding a large amount of the IL catalyst, thereby affecting mass transfer and the reaction rate. The optimum dosage of the [BHSO$_3$MIM]HSO$_4$ catalyst was therefore 10%.

3.6. Optimization of the [BHSO$_3$MIM]HSO$_4$-catalyzed esterification of oleic acid with methanol using response surface methodology (RSM)

Based on the results of single factor experiments, catalyst dose, methanol to oil molar ratio, and reaction temperature were chosen as the variables for further optimization. The esterification of oleic acid with methanol by [BHSO$_3$MIM]HSO$_4$ was planned using a three-level, three factor Box-Behnken design. The experimental factors and levels are presented in Table 1.

Independent variables included catalyst dosage (A), methanol to oleic acid molar ratio (B), and reaction tempera (C) with their corresponding high, medium, and low levels being represented by coded values 1, 0, and −1, respectively. Methyl oleate yield was considered the response value, represented by Y. Table 2 shows the design matrix for the Box-Behnken experimental design together with the experimental results.

Details of the reaction were clarified through RSM and

Table 2
Arrangement and experimental results of the Box-Behnken experimental design for optimizing the synthesis of methyl oleate.

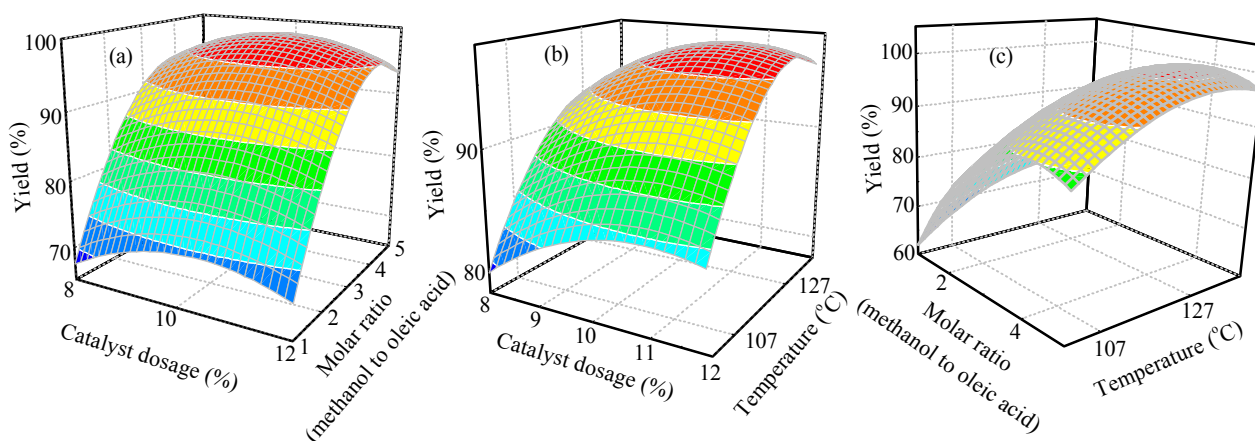| Entry	A	B	C	Y
1	−1	−1	0	67.3
2	−1	0	1	91.3
3	−1	0	−1	79.7
4	0	0	0	95.8
5	0	0	0	95.4
6	1	−1	0	70.0
7	1	0	1	92.9
8	0	0	0	95.5
9	1	1	0	93.2
10	0	−1	−1	62.0
11	0	0	0	96.2
12	0	1	−1	85.7
13	0	0	0	95.8
14	0	1	1	96.6
15	1	0	−1	82.0
16	−1	1	0	92.0
17	0	−1	1	73.4

shown in Tables 3 and 4. The 3D maps of the response surface are presented in Fig. 6.

The experimental values obtained from the Box-Behnken experimental design were regressed by using a quadratic polynomial equation, and the regression equation, expressed in terms of the coded factors defined in Table 1, is given as Eq. (1):

$$Y = 95.66 + 1.00A + 11.90B + 5.55C - 0.37AB - 0.18AC - 0.025BC - 3.97A^2 - 11.07B^2 - 5.27C^2 \quad (1)$$

The analysis of variance (ANOVA) for this model is present in Table 3, and the significance test for each regression coefficient of the established equation is shown in Table 4. From Table 3, it was found that the F-value of the regression model was 3197, which is more than $F_{0.05}(9, 4)$ of 6.00, and the P-value was very low ($P < 0.0001$), implying the significance of this model (P-values < 0.05 are generally taken to indicate that model terms are significant).

The F-value of the "Lack of fit" was 0.44, which was < $F_{0.05}(9, 3)$ of 8.1, while the P-value of "Lack of fit" was 0.74, > 0.05,

Table 3
Variance analysis for the established regression equation simulating the synthesis of methyl oleate.

Source	df	SS	SM	F-value	P-value
Model	9	2145	238	3197	<0.0001
Residual	7	0.52	0.075		
Lack of fit	3	0.13	0.043	0.44	0.74
Sum	16	2146			

Note: $R^2 > 0.99$, $R^2_{adj} > 0.99$, $R_{SN} = 167$.

Table 4
Significance test for each regression coefficient of the established regression equation simulating the synthesis of methyl oleate.

Factor	df	Coefficient estimate	Standard error	F-value	P-value	Significance
Intercept	1	95.74	0.12			
A	1	0.98	0.097	101.98	< 0.0001	**
B	1	11.85	0.097	15064.48	< 0.0001	**
C	1	5.60	0.097	3364.29	< 0.0001	**
A^2	1	−0.38	0.14	7.54	0.0286	*
B^2	1	−0.17	0.14	1.64	0.2408	
C^2	1	−0.13	0.14	0.84	0.3904	
AB	1	−4.03	0.13	918.15	< 0.0001	**
AC	1	−11.08	0.13	6934.89	< 0.0001	**
BC	1	−5.23	0.13	1545.9	< 0.0001	**

Fig. 6. (a) Effect of molar ratio and dose of the catalyst on esterification; (b) Effect of reaction temperature and dose of the catalyst on esterification; (c) Effect of reaction temperature and molar ratio on esterification.

suggesting that the Lack of fit of this regression equation was not significant. The adjusted R squared (R^2_{adj}) was above 0.99, indicating that this model could explain 74% of the response. Moreover, R^2 was above 0.99 (close to 1), implying that the actual values were very close to the predicted values and this showed that the model was reliable for predicting and analyzing the methyl oleate yield.

The optimum levels of the factors investigated can be deduced from Eq. (1), obtained from multiple regression analysis, and it was found that the maximum yield of methyl oleate was predicted to be 100%. Further, the model predicted that the maximum value would be obtained when the IL catalyst dosage was 9.7%, methanol to oleic acid molar ratio was 3.4:1, and the reaction temperature was 131.4 °C. To simplify operations, 10% catalyst, 4:1 molar ratio of methanol to oleic acid, and 130 °C were used, and the yield of methyl oleate was 97.7%, very close to the predicted value. This result clearly confirmed the validity of this model.

3.7. The operational stability of the [BHSO₃MIM]HSO₄ catalyst

The operational stability of the catalyst directly affects its application in semi-continuous and automated production processes. Catalysts having a high operational stability always exhibit excellent reusability, thereby reducing the costs of methyl oleate (biodiesel) production. To evaluate the recycling performance of the [BHSO₃MIM]HSO₄ catalyst, the operational stability of [BHSO₃MIM]HSO₄ was investigated by using the esterification of oleic acid with methanol as a model reaction under the optimized conditions described above. As is evident in Fig. 7, the IL catalyst [BHSO₃MIM]HSO₄ still retained about 95.6% of its original catalytic activity even after 10 cycles of successive reuse (4 h per cycle) and gave the relatively high yield of methyl oleate of 93.2%. The performance demonstrates the outstanding activity and excellent operational stability of the [BHSO₃MIM]HSO₄ catalyst.

3.8. [BHSO₃MIM]HSO₄-catalyzed conversion of different feedstocks into biodiesel

The above results clearly demonstrate that the acidic IL [BHSO₃MIM]HSO₄ is effective in catalyzing the esterification of oleic acid with methanol to methyl oleate. To expand the applicability of the IL catalyst for different feedstocks, the [BHSO₃MIM]HSO₄-catalyzed conversion of other feedstocks (palmitic acid and waste oils with high acid value) to biodiesel as investigated, and the results are summarized in Table 5. [BHSO₃MIM]HSO₄ was also capable of efficiently catalyzing the esterification of palmitic acid with methanol and gave 94.7% yield of methyl palmitate (biodiesel) after reaction for 4 h at 130 °C. It is worth noting that [BHSO₃MIM]HSO₄ afforded 88.5% yield of biodiesel at a reaction time of 4 h and 130 °C when waste oils with 72% free fatty acids (FFAs) were used as feedstock. It is well known that the esterification and transesterification reactions occur simultaneously in the [BHSO₃MIM]HSO₄-catalyzed conversion of waste oils with a high content of FFAs. Because the rate of transesterification was much lower than that of esterification, the reaction temperature for conversion of waste oils was raised from 130 to 140 °C, and the yield of biodiesel at a reaction time of 6 h was increased to 94.9%. Clearly, the acidic IL [BHSO₃MIM]HSO₄ is
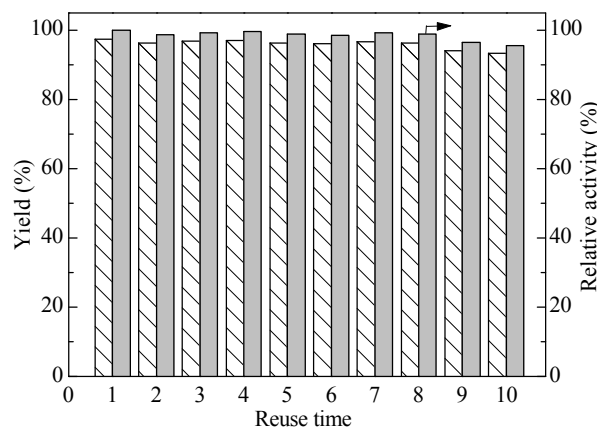
Fig. 7. Reusability of [BHSO₃MIM]HSO₄ for the esterification of oleic acid with methanol. Reaction conditions: 2.82 g oleic acid, 0.28 g [BHSO₃MIM]HSO₄, molar ratio of methanol to oleic acid of 4:1, 130 °C, 4 h, 500 r/min.

Table 5
Conversion of different feedstocks to biodiesel with [BSO$_3$HMIM]HSO$_4$.

Feedstock	T (°C)	Time (h)	Yield (%)
Oleic acid [a]	130	4	97.7
Palmitic acid [a]	130	4	94.7
Waste oils [b]	130	4	88.5
	140	6	94.9

[a] Molar ratio of methanol to fatty acid = 4:1, and the amount of the IL catalyst was 10% based on the mass of fatty acid.
[b] Waste cooking oils contained 72% FFAs. Molar ratio of methanol to oil was 8:1, and the amount of the IL catalyst was 10% based on the mass of waste oils.

able to efficiently catalyze the conversion of different feedstocks, especially waste oils with high acid value, into biodiesel.

4. Conclusions

The above-described results clearly showed that the stronger the acidity of IL, the higher its esterification activity. Among all the acidic ILs tested, [BHSO$_3$MIM]HSO$_4$ provided the best results for the synthesis of methyl oleate (biodiesel) from the esterification of oleic acid with methanol, and the yield of methyl oleate obtained reached 97.7%. [BHSO$_3$MIM]HSO$_4$ was also used for the esterification of palmitic acid with methanol and in the conversion of waste oils with high acid value (with 72% FFAs) to biodiesel. Clearly, [BHSO$_3$MIM]HSO$_4$ shows great potential for converting different feedstocks into biodiesel. Moreover, the IL catalyst [BHSO$_3$MIM]HSO$_4$ exhibited excellent operational stability. This system can provide a green, safe, and feasible means for the industrial production of biodiesel.

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Graphical Abstract

Acidic ionic liquid-catalyzed esterification of oleic acid for biodiesel synthesis

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The esterification of oleic acid with methanol was successfully conducted with acidic ionic liquids as catalysts. [BHSO$_3$MIM]HSO$_4$ exhibited the best results and could also efficiently catalyze the conversion of waste oils to biodiesel.

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$$
$$+ \; \text{Ionic Liquid}$$
$$CH_3OH \rightleftharpoons CH_3(CH_2)_7CH=CH(CH_2)_7COCH_3 + H_2O$$
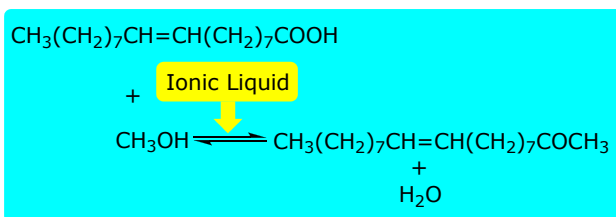
酸性离子液体催化油酸酯化合成生物柴油

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摘要: 酸性离子液体具有催化活性好、选择性高及易于回收等优点, 是一种应用前景非常好的环境友好的酸性催化剂, 在生物柴油合成反应中具有重大的理论意义和应用价值. 本文以油酸和甲醇为原料, 探讨了7种不同酸性离子液体在生物柴油合成反应中的催化效应. 研究表明, 离子液体酸性越强, 催化酯化活性越高; 引入磺酸基团可大大增强离子液体Brönsted酸性, 使其在酯化反应中发挥溶剂/催化剂的双重作用, 促进酯化反应向产物方向进行, 达到高产率, 因而1-丁基磺酸-3-甲基咪唑硫酸氢盐 ([BHSO$_3$MIM]HSO$_4$)催化效果最好. 此外, 系统研究了[BHSO$_3$MIM]HSO$_4$催化油酸与甲醇酯化反应, 并采用响应面法优化了反应条件. 结果发现, 该反应的最适醇酸摩尔比、催化剂用量、反应温度及反应时间分别为4:1, 10%(基于油酸的质量), 130 °C和4 h; 在此条件下, 生物柴油产率为97.7%. [BHSO$_3$MIM]HSO$_4$连续使用10批次后, 仍能保持初始催化活性的95.6%, 表现出极好的操作稳定性. 另外, 利用该离子液体催化游离脂肪酸含量为72%的废油脂生产生物柴油, 反应6 h可获得产率94.9%. 可见, [BHSO$_3$MIM]HSO$_4$在酯化生产生物柴油方面具有巨大的应用潜力.

关键词: 酸性离子液体; 生物柴油; 油酸; 甲醇; 酯化

1. 前言

随着全球经济发展和环境污染问题不断加剧, 全球能源需求不断增加, 由此引起了能源危机[1]. 化石燃料对环境造成的问题也令人堪忧[2], 二氧化碳大量释放, 地表温度增加, 导致冰川融化, 海平面上升. 因此越来越多的研究者开始寻找高效、安全、环保的可再生能源. C$_{12}$–C$_{24}$的脂肪酸单烷基酯简称生物柴油[3], 研究表明, 与石化柴油相比, 使用100%纯生物柴油(B100)可以减少78.45%的二氧化碳排放量[4]. 生物柴油闪点高, 便于运输和存储; 十六烷值高, 燃烧性能好; 含硫量低, 对环境污染小; 具有较好的润滑性能[5]. 因此, 生物柴油是一种新型绿色可再生能源[6,7].

酯化是一种合成生物柴油的方法, 近年来, 随着对酯化催化剂的深入研究, 人们发现采用固体超强酸[8,9]、杂多酸[10,11]和强酸性阳离子交换树脂[12,13]代替浓硫酸作为酯化催化剂, 虽然可以解决设备腐蚀和环境污染等问题, 但此类催化剂的制备过程较复杂, 催化剂不易再生, 且成本也较高. 因此, 开发环境友好的新型酯化催化剂是当前研究的热点.

离子液体是由有机阳离子和无机或有机阴离子构成的在室温或较低温度(<100 °C)下呈液态的盐类, 通常称为室温离子液体[14]. 离子液体在生物柴油合成研究中的应用[15–18]已相当广泛, 它作为一种新型的环境友好溶剂和液体酸催化剂, 同时拥有液体酸的高密度反应活性和固体酸的不挥发性, 其分子结构和酸性具有可调控性, 催化剂和产物易分离, 热稳定性高, 将有望成为真正意义上可设计的绿色溶剂, 而且具有很好的应用前景[19,20]和较大的工业化生产价值. 鉴于目前离子液体在酯化反应中的应用研究不多[21–24], 本文探讨了不同的酸性离子液体作为催化剂催化油酸与甲醇酯化合成生物柴油的催化活性, 并优化了其反应条件, 同时还考察了酸性离子液体在催化高酸值废油脂合成生物柴油过程中的使用效果.

2. 实验部分

2.1. 主要试剂

1-丁基-3-甲基咪唑硫酸氢盐([BMIM]HSO$_4$)、N-乙基吡啶硫酸氢盐 ([EPy]HSO$_4$)、四乙基铵硫酸氢盐 ([TEAm]HSO$_4$)、1-丁基磺酸-3-甲基咪唑硫酸氢盐 ([BHSO$_3$MIM]HSO$_4$)、1-丁基-3-甲基咪唑高氯酸盐 ([BMIM]ClO$_4$)、1-乙基吡啶溴盐([EPy]Br)和四乙基铵氯盐([TEAm]Cl)均购自兰州奥力科化工有限公司; 油酸甲酯为色谱纯, 购自Sigma公司; 十七碳酸甲酯(内标)为色谱纯, 购自TCI公司; 油酸、甲醇等其他试剂均为市售分析纯.

2.2. 不同酸性离子液体催化油酸与甲醇的酯化反应

在50 ml三口圆底烧瓶中加入2.82 g (0.01 mol)油酸、0.64 g甲醇和0.28 g催化剂, 混合均匀, 置于80 ℃的油浴中开始反应(冷凝回流, 磁力搅拌速度为500 r/min). 定时从反应液中取样50 μl, 高速离心(10000 r/min, 7 min), 取5 μl上清液与200 μl内标溶液(十七碳酸甲酯)混合振荡均匀, 取1 μl进行气相色谱分析.

2.3. [BHSO₃MIM]HSO₄催化油酸与甲醇酯化合成油酸甲酯的优化

在50 ml三口圆底烧瓶中加入2.82 g(0.01 mol)油酸, 然后加入一定质量比的催化剂和一定醇酸摩尔比的甲醇, 混合均匀, 置于反应温度下的油浴中开始反应(冷凝回流, 磁力搅拌速度为500 r/min). 反应结束后, 静置分层, 分出产物相. 定时从反应液中取样50 μl, 高速离心(10000 r/min, 7 min), 取5 μl上清液与200 μl内标溶液(十七碳酸甲酯)混合振荡均匀, 取1 μl进行气相色谱分析.

2.4. [BHSO₃MIM]HSO₄催化剂的操作稳定性

在10 ml圆底烧瓶中装入2.82 g油酸、1.28 g甲醇和0.28 g [BHSO₃MIM]HSO₄催化剂, 置于130 ℃油浴中开始反应(冷凝回流), 4 h后终止反应. 将反应混合液进行旋转蒸发除去未反应的甲醇和反应生成的水, 再将产物与离子液体通过离心进行分离, 得到的离子液体用适量正己烷清洗, 室温晾干后进行下一批次循环使用. 第一批次反应的[BHSO₃MIM]HSO₄催化剂的活性定义为相对活性100%. 从每批次的反应液中取样100 μl, 离心(10000 r/min, 7 min), 取5 μl上清液与200 μl内标溶液(十七碳酸甲酯)混合振荡均匀, 取1 μl进行气相色谱分析.

2.5. 气相色谱分析

采用日本岛津公司GC-2010型气相色谱仪进行分析, FID检测器, 毛细管色谱柱为美国Agilent公司HP-5(柱长15 m, 内径0.53 mm, 膜厚1.50 μm). 分析条件为气化室温度250 ℃, 检测室温度280 ℃, 柱温180 ℃, 维持1 min, 以0.8 ℃/min的速率升温至186 ℃, 维持1 min, 再以20 ℃/min的速率升高到280 ℃; 载气为氮气, 流速为12.5 ml/min; 分流比为25:1; 进样量为1 μl. 在该分析条件下, 十七碳酸甲酯和油酸甲酯的保留时间分别是4.488和5.734. 该分析方法条件稳定, 重现性好, 分析的最大相对误差为1%. 根据公式Yield = $m_{(MO)}$×100%/m计算甲酯产率, 其中$m_{(MO)}$为反应生成的甲酯质量, m为反应前油酸的质量.

3. 结果与讨论

3.1. 不同酸性离子液体催化剂对油酸酯化反应的影响

离子液体催化剂的活性与其阴离子的酸强度和离子液体溶解度密切相关. 反应初始阶段, 离子液体酸强度对反应起重要作用. 离子液体的酸性很大程度上决定于阴离子, 阴离子的酸性越强, 则离子液体酸性越强, 获得产物的产率也越高. 引入磺酸基团的离子液体酸性最强, 将其应用到酯化反应, 其催化活性是其它酸性离子液体不能比拟的. 同时, 离子液体的阳离子对反应也有决定性作用, 阳离子主要调控离子液体的亲水性, 离子液体与酯产物的互溶性决定了其与产物分相的难易程度, 而分相性能对催化效果有较大的影响, 从而影响催化活性[25–27]. 本实验考察了7种不同酸性离子液体催化油酸酯化合成油酸甲酯的进程曲线, 结果见图1. 由图可知, 7种离子液体催化剂的活性顺序为: [BHSO₃MIM]HSO₄ > [BMIM]HSO₄ > [EPy]HSO₄ > [TEAm]HSO₄ > [BMIM]ClO₄ > [TEAm]Cl > [EPy]Br. [BHSO₃MIM]HSO₄催化油酸酯化的活性最高, 反应4 h时, 所得产率为72.4%; 以[BMIM]HSO₄为催化剂时产率也较高(60%). 因此, 离子液体 [BHSO₃MIM]HSO₄为该反应的最佳催化剂.

3.2. 反应温度对油酸酯化反应的影响

温度是影响酯化反应的一个重要参数, 随着反应温度的升高, 反应速度加快, 同时有利于反应平衡向产物生成的方向移动, 提高酯化率. 为了确定 [BHSO₃MIM]HSO₄催化油酸酯化反应的最适温度, 研究了60–140 ℃油浴条件下油酸与甲醇的酯化反应, 结果见图2. 由图可知, 当反应温度低于120 ℃时, 甲酯产率随着温度的升高而显著增加; 当反应温度为120 ℃时, 反应4 h时, 产率为95.3%; 继续升高温度, 酯化产率增加并不显著, 表明反应已接近平衡. 综合考虑能耗与产率, 选择120 ℃为最佳反应温度.

3.3. 反应时间对油酸酯化反应的影响

反应时间也是影响酯化反应的一个重要参数, 随着反应时间的延长, 反应平衡向产物生成的方向移动, 油酸甲酯产率增加. 但超过反应的平衡时间时, 随着时间的延长, 酯化率将不再提高. 为了确定 [BHSO₃MIM]HSO₄催化剂催化油酸甲酯化的最适反应时间, 本实验研究了油酸甲酯化反应的过程曲线, 结果见图3, 可以看出, 酯化反应可以分为三个阶段: 第一阶段, 大量的甲醇与油酸迅速相互作用, 1 h内超过67.8%的油酸转化成油酸甲酯; 第二阶段, 酯化反应速率从2 h到4 h逐步减慢, 反应4 h时产率达95.3%; 第三阶段, 反应4 h后, 酯化反

应趋向平衡, 甲酯产率无明显增加. 因此选择4 h为最佳的反应时间.

3.4. 醇酸摩尔比对油酸酯化反应的影响

由图4可知, 当反应体系中醇酸摩尔比≤2时, 反应4 h, 油酸甲酯产率随着甲醇浓度的增加而显著增加. 当醇酸摩尔比在2–8时, 反应4 h, 油酸甲酯产率随着甲醇浓度的增加而继续增加, 但增加幅度不显著, 且均接近理论值, 这是由于酯化反应为可逆反应, 过量的甲醇有利于酯化反应, 因为甲醇过量可促进酯化反应速率, 有利于产物生成. 当醇酸摩尔比超过8时, 反应4 h, 油酸甲酯产率随醇酸摩尔比的增大而有所下降, 这是因为大量的甲醇存在会稀释油酸与离子液体的浓度. 综合考虑能耗和产率, 选择最适醇酸摩尔比为4:1.

3.5. [BHSO$_3$MIM]HSO$_4$用量对酯化反应的影响

[BHSO$_3$MIM]HSO$_4$作为离子液体催化剂, 与其他催化剂一样, 其催化反应速率直接取决于其浓度的大小. 在一定浓度范围内, [BHSO$_3$MIM]HSO$_4$催化剂用量越大, 反应速率越快. 但当其用量大于某一定值时, 增加催化剂的用量对反应速率就几乎没有影响, 甚至会降低反应速率. 图5考察了不同用量的[BHSO$_3$MIM]HSO$_4$催化剂对酯化反应的影响. 当[BHSO$_3$MIM]HSO$_4$催化剂用量在4%–10%时, 酯化反应速率随着催化剂用量的增加而增加, 产率提高, 且当[BHSO$_3$MIM]HSO$_4$添加量为10%时, 产率达到最大值97.3%. 随后, 继续增大催化剂用量, 酯化产率稍有下降. 加入大量的离子液体会使反应体系粘度升高, 从而降低了传质速率和反应速率. 因此, 该反应最适的[BHSO$_3$MIM]HSO$_4$用量为10%.

3.6. 采用响应面分析法对油酸酯化反应条件的优化

根据单因素实验结果, 选取催化剂用量、醇酸摩尔比和反应温度3个影响显著的因素作为响应面试验的3个因素, 采用统计软件Design-Expert中的响应曲面法建立三因素三水平的Box-Behnken模型对油酸酯化反应进行优化, 实验因素与水平见表1.

以催化剂用量(A)、醇酸摩尔比(B)和反应温度(C)为反应自变量, 其中自变量的编码值1, 0和–1分别代表自变量的高、中、低水平, 以产率为操作中的响应值, 由Y表示, 响应面试验方案及结果见表2. 实验4, 5, 8, 11和13为5个中心实验, 用以估计实验误差, 其他为析因实验.

通过Design-Expert软件进行数据处理, 建立二次响应面回归模型, 分析结果见表3和表4, 响应面图见图6.

各因素经回归拟合后, 得到回归方程如下:

$$Y = 95.66 + 1.00A + 11.90B + 5.55C - 0.37AB -$$

$$0.18AC - 0.025BC - 3.97A^2 - 11.07B^2 - 5.27C^2 \quad (1)$$

该模型进行方差分析结果见表3, 模型系数显著性检验见表4. 由表3可以看出: F回归 = 3197 > ($F_{0.05}$ (9, 4) = 6.00), $P < 0.05$, 表明模型显著; F失拟 = 0.44 < $F_{0.05}$ (9, 3) = 8.1, 失拟项P = 0.74 > 0.05, 模型失拟度不显著; 校正决定系数R^2_{adj} > 0.99, 说明该模型能解释74%响应值的变化; 复相关系数R^2 > 0.99 (接近1), 说明该模型拟合程度良好, 试验误差小, 可用此模型对该反应进行分析和预测.

对模型(3)解逆矩阵, 求得油酸甲酯产率的最大值为100%, 此时催化剂用量为9.7%, 醇酸摩尔比为3.4:1, 反应温度为131.4 ℃. 为方便实验操作, 选取催化剂用量为10%, 醇酸摩尔比为4:1, 反应温度为130 ℃, 所得油酸甲酯产率为97.7%, 与预测值接近, 说明该模型有效.

3.7. [BHSO$_3$MIM]HSO$_4$催化剂操作稳定性

催化剂的操作稳定性直接影响连续化、自动化生产过程, 具有较高操作稳定性的催化剂可反复利用多次, 从而降低油酸甲酯(生物柴油)的生产成本. 为考察催化剂的可重复利用性, 本文在上述优化条件下研究了[BHSO$_3$MIM]HSO$_4$在催化油酸与甲醇酯化反应中的操作稳定性. 由图7可知, [BHSO$_3$MIM]HSO$_4$催化剂循环使用10个批次(每批次使用4 h)后, 仍能保持其初始活性的95.6%, 反应4 h后仍获较高油酸甲酯产率(93.2%), 表明[BHSO$_3$MIM]HSO$_4$催化剂不仅具有很好的催化活性, 而且具有较高的操作稳定性.

3.8. [BHSO$_3$MIM]HSO$_4$催化不同原料转化为生物柴油

以上结果表明酸性离子液体[BHSO$_3$MIM]HSO$_4$能高效地催化油酸与甲醇酯化反应合成油酸甲酯(生物柴油). 为了进一步拓展该离子液体催化剂在不同原料中的适用性, 本文考察了[BHSO$_3$MIM]HSO$_4$催化棕榈酸和高酸值废油脂转化为生物柴油, 结果如表5所示. [BHSO$_3$MIM]HSO$_4$也可高效催化棕榈酸与甲醇的酯化反应, 在130 ℃反应4 h时, 获得94.7%棕榈酸甲酯(生物柴油). 值得注意的是, 以含72%游离脂肪酸的废油脂为原料, 在130 ℃时反应4 h, 得到88.5%生物柴油产率. [BHSO$_3$MIM]HSO$_4$催化含高游离脂肪酸的废油脂转化时发生酯化和转酯反应, 由于转酯反应速率明显慢于酯化反应速率, 因此提高反应温度至140 ℃, [BHSO$_3$MIM]HSO$_4$催化废油脂转化反应6 h, 得到生物柴油的产率提高至94.9%. 可见, 酸性离子液体[BHSO$_3$MIM]HSO$_4$能高效地催化不同原料, 尤其是高酸

值废油脂转化为生物柴油, 表现出巨大的应用潜力.

4. 结论

研究结果表明离子液体酸性越强, 其催化酯化活性越高. 在所研究的酸性离子液体中, [BHSO$_3$MIM]HSO$_4$催化油酸与甲醇酯化反应合成油酸甲酯(生物柴油)的效果最好, 得到油酸甲酯的产率高达97.7%. [BHSO$_3$-MIM]HSO$_4$不仅能有效地催化棕榈酸与甲醇的酯化反应, 还能高效地催化高酸值废油脂(含72%游离脂肪酸)转化为生物柴油, 表明该离子液体催化剂对不同原料生产生物柴油方面具有很好的适用性, 展示出巨大的应用潜力. 此外, 离子液体催化剂[BHSO$_3$MIM]HSO$_4$呈现出极好的操作稳定性. 这为工业化生产生物柴油提供了一种绿色安全的可行方法.