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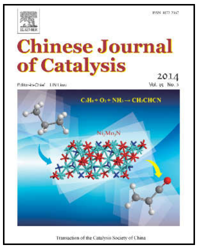

Article

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

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ABSTRACT

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 ($[BHSO_3MIM]HSO_4$) exhibited the best catalytic performance. The $[BHSO_3MIM]HSO_4$-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, $[BHSO_3MIM]HSO_4$ 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 $[BHSO_3MIM]HSO_4$ 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, $[BHSO_3MIM]HSO_4$ 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

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[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]HSO_4), *N*-ethylpyridinium hydrosulfate ([EPy]HSO_4), tetraethylammonium hydrosulfate ([TEAm]HSO_4), 1-sulfobutyl-3-methylimidazolium hydrosulfate ([$BHSO_3$MIM]HSO_4), 1-butyl-3-methylimidazoliumperchlorate ([BMIM]ClO_4), 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 [$BHSO_3$MIM]HSO_4-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 [$BHSO_3$MIM]HSO_4 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 [$BHSO_3$MIM]HSO_4 catalyst

Oleic acid (2.82 g, 0.01 mol), methanol (1.28 g), and 0.28 g [$BHSO_3$MIM]HSO_4 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 [$BHSO_3$MIM]HSO_4 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 [$BHSO_3$MIM]HSO_4 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 = $m_{(MO)}$×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 SO_3H-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: [$BHSO_3MIM$]HSO_4 > [BMIM]HSO_4 > [EPy]HSO_4 > [TEAm]HSO_4 > [BMIM]ClO_4 > [TEAm]Cl > [EPy]Br. Among the ILs tested, [$BHSO_3MIM$]HSO_4 showed the highest catalytic activity and gave the highest yield of 72.4% after reaction for 4 h. With [BMIM]HSO_4 acting as the catalyst, a relatively good yield of 60% was also achieved at a reaction time of 4 h. Hence, [$BHSO_3MIM$]HSO_4 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 [$BHSO_3MIM$]HSO_4-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.

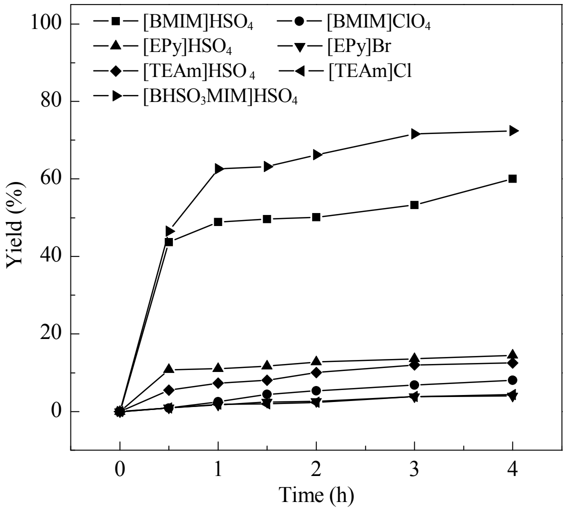

Fig. 1. Effect of various acidic IL catalysts on the esterification of oleic acid with methanol. Reaction conditions: 2.82 g oleic acid, 0.28 g IL catalysts (10% based on the mass of oleic acid), molar ratio of methanol to oleic acid = 2:1, 80 °C, 500 r/min.

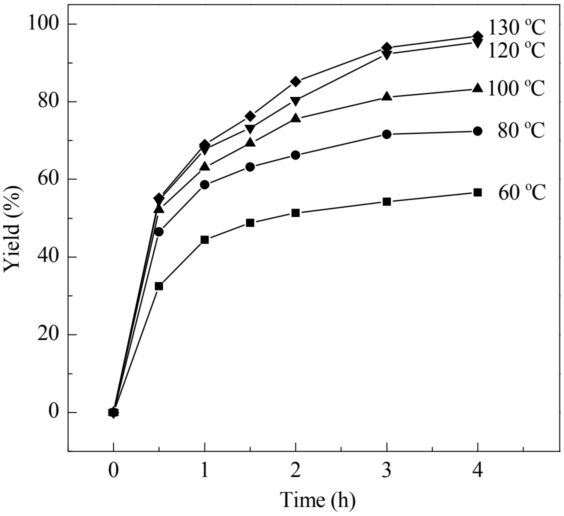

Fig. 2. Effect of reaction temperature on [$BHSO_3MIM$]HSO_4-catalyzed esterification of oleic acid with methanol. Reaction conditions: 2.82 g oleic acid, 0.28 g [$BHSO_3MIM$]HSO_4, molar ratio of methanol to oleic acid = 2:1, 500 r/min.

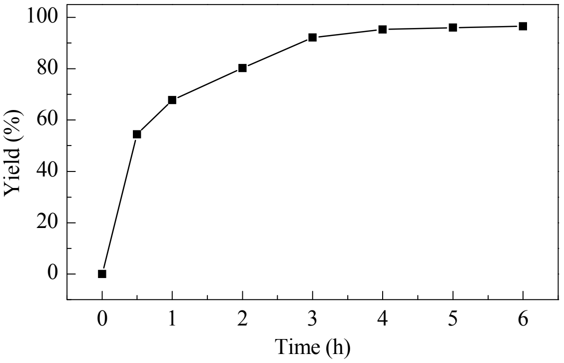

Fig. 3. Time course of the $[BHSO_3MIM]HSO_4$-catalyzed esterification of oleic acid with methanol. Reaction conditions: 2.82 g oleic acid, 0.28 g $[BHSO_3MIM]HSO_4$, molar ratio of methanol to oleic acid = 2:1, 120 °C, 500 r/min.

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 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.

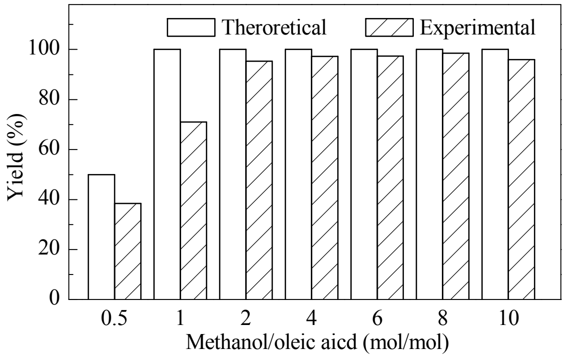

Fig. 4. Effect of molar ratio of methanol to oleic acid on the esterification reaction. Reaction conditions: 2.82 g oleic acid, 0.28 g $[BHSO_3MIM]HSO_4$, 120 °C, 4 h, 500 r/min.

3.5. Effect of $[BHSO_3MIM]HSO_4$ catalyst dosage on the esterification of oleic acid with methanol

As with other catalysts, the dosage of the IL catalyst $[BHSO_3MIM]HSO_4$ significantly affects the reaction rate. Within a certain range of IL concentration, when the dosage of $[BHSO_3MIM]HSO_4$ 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 $[BHSO_3MIM]HSO_4$ 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)

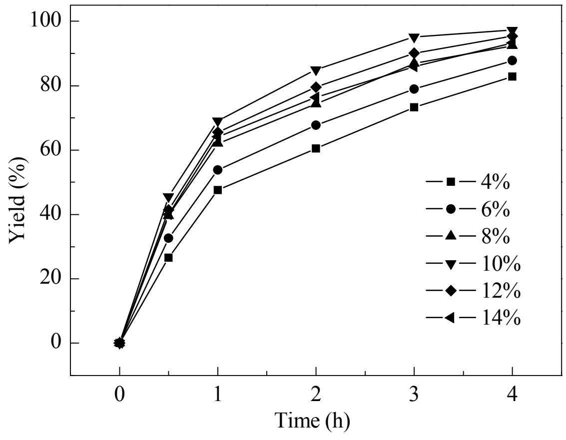

Fig. 5. Effect of dosage of IL catalyst on $[BHSO_3MIM]HSO_4$-catalyzed esterification of oleic acid with methanol. Reaction conditions: 2.82 g oleic acid, molar ratio of methanol to oleic acid = 4:1, 120 °C, 500 r/min.

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

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

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 temperature (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 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: $R^2 > 0.99$, $R^2_{\mathrm{adj}} > 0.99$, $R_{\mathrm{SN}} = 167$.

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	**

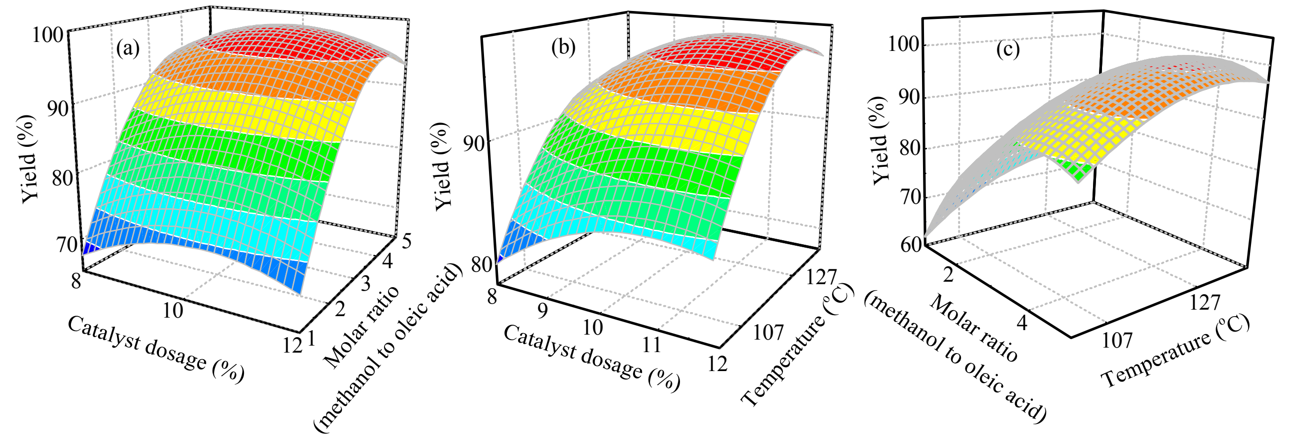

Fig. 6. (a) Effect of molar ratio and dose of the catalyst on esterification; (b) Effect of reaction temperature and dose of the catalyst on esterification; (c) Effect of reaction temperature and molar ratio on esterification.

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 [BHSO$_3$MIM]HSO$_4$ catalyst, the operational stability of [BHSO$_3$MIM]HSO$_4$ 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 [BHSO$_3$MIM]HSO$_4$ 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 [BHSO$_3$MIM]HSO$_4$ catalyst.

3.8. [BHSO$_3$MIM]HSO$_4$-catalyzed conversion of different feedstocks into biodiesel

The above results clearly demonstrate that the acidic IL [BHSO$_3$MIM]HSO$_4$ 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 [BHSO$_3$MIM]HSO$_4$-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. [BHSO$_3$MIM]HSO$_4$ 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 ºC. It is worth noting that [BHSO$_3$MIM]HSO$_4$ 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 [BHSO$_3$MIM]HSO$_4$-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 [BHSO$_3$MIM]HSO$_4$ is

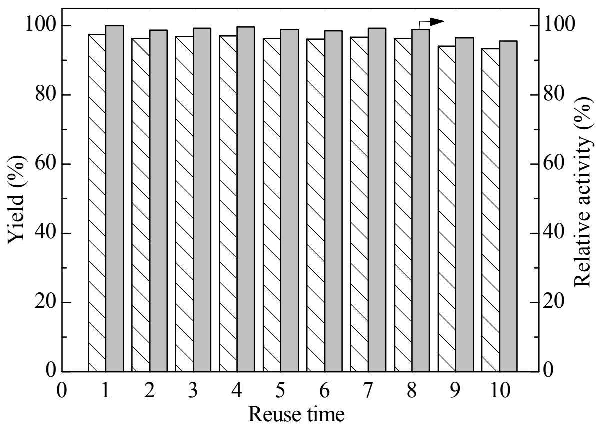

Fig. 7. Reusability of [BHSO$_3$MIM]HSO$_4$ for the esterification of oleic acid with methanol. Reaction conditions: 2.82 g oleic acid, 0.28 g [BHSO$_3$MIM]HSO$_4$, molar ratio of methanol to oleic acid of 4:1, 130 °C, 4 h, 500 r/min.

Table 5
Conversion of different feedstocks to biodiesel with $[BSO_3HMIM]HSO_4$.

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, $[BHSO_3MIM]HSO_4$ 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%. $[BHSO_3MIM]HSO_4$ 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, $[BHSO_3MIM]HSO_4$ shows great potential for converting different feedstocks into biodiesel. Moreover, the IL catalyst $[BHSO_3MIM]HSO_4$ 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

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

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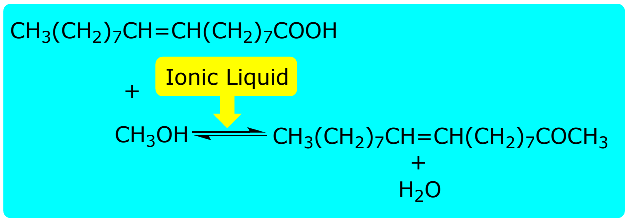

The esterification of oleic acid with methanol was successfully conducted with acidic ionic liquids as catalysts. $[BHSO_3MIM]HSO_4$ exhibited the best results and could also efficiently catalyze the conversion of waste oils to biodiesel.