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Contributed Paper

Optimization of Oleic Acid Esterification for Biodiesel Production using Brønsted Acidic Ionic Liquid as a Catalyst

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ABSTRACT

Biodiesel preparation from the esterification of oleic acid with methanol catalyzed by Brønsted acid ionic liquid $[H_{NMP}]CH_3SO_3$ was investigated, and the effects of the amount of catalyst, molar ratio of methanol to oleic acid, reaction time and temperature on the esterification reaction were examined. The maximum oleic acid conversion was obtained by using a Box-Behnken experimental design. It was found that optimum response for oleic acid conversion was 97.35%, which can be obtained using methanol/oleic acid molar ratio of 11.23:1, catalyst dosage of 10.48%, reaction time at 2.81 h and reaction temperature at 52.86 °C. Oleic acid conversion at optimum conditions using recycled $[H_{NMP}]CH_3SO_3$ displayed few loss in catalytic activity after five runs.

Keywords: biodiesel, ionic liquid $[H_{NMP}]CH_3SO_3$, oleic acid, esterification, optimization

1. INTRODUCTION

The preparation of esters from esterification has attracted wide spread attentions due to their extensive applications in food, cosmetics, plasticizers, pharmaceutical, plastic derivatives, chemical industry and so on [1-2]. The most significant and valuable product obtained by esterification of long chain fatty acids is biodiesel [3]. In general, the esterification reaction can be catalyzed by homogeneous acid [4], such as H_2SO_4, HCl, and organic sulfonic acids, which are traditionally selected as the acid catalyst [5]. However, homogeneous acid-catalyzed reactions can generate environmental and corrosion problems, which together impact against their applications for continuous processing. Thus, the researchers have attempted to develop effective and eco-friendly catalysts for the esterification of free fatty acids (FFAs) to produce biodiesel. For example, solid super acids [6], heteropolyacids (HPAs) [7], metal oxides [8], and enzymes [9] have been exploited for biodiesel production.

Ionic liquids (ILs) have been diffusely utilized as green solvents and catalysts in virtue of their good thermal stability, outstanding solubility, inappreciable volatility, tunable physical and chemical properties, and reusability [10-11]. The esterification reactions catalyzed by ILs are attracting more and more attentions because of their facile separation of products, downsizing the process equipment. Accordingly, the use of ILs catalysts in the esterification reactions is exceedingly important in developing cleaner and more economically improved processes for biodiesel production. N-methyl-2-pyrrolidonium methyl sulfonate ([NMP][CH_3SO_3]), is a halogen-free Brønsted acid ionic liquid with acidic counterion, which influence its catalytic performance in reactions. The acetates were successfully produced from the reaction between carboxylic acids with alcohols. Furthermore, the higher acidity of [NMP][CH_3SO_3] led to higher conversion of FFAs to biodiesel in an esterification process compared to other ionic liquids [12].

Response surface methodology (RSM) is a method for designing experiment, appraising the effects of process parameters on the response and optimizing the process [13]. The amount of catalyst, methanol to oleic acid molar ratio, reaction time and reaction temperature [14] have important influence on synthesis of biodiesel. RSM with Box-Behnken design (BBD) was used to optimize oleic acid conversion [15]. RSM allows the user to gather massive information from a few experiments [16]. The use of RSM is able to observe the effects of individual variables and their combinations of interactions on the response [17].

In this work, the esterification of oleic acid with methanol catalyzed by [H_{NMP}]CH_3SO_3 was investigated, and the effect of the catalyst dosage, molar ratio of methanol to oleic acid, reaction time and temperature on the esterification reaction were examined. RSM was employed to optimize the levels of catalyst amount, molar ratio of alcohol to acid, reaction time and temperature.

2. MATERIALS AND METHODS

2.1 Materials and Reagents

Oleic acid, 1-Methyl-2-pyrrolidonium, methane sulfonic acid, ethyl acetate, ethyl ether, methanol, concentrated sulfuric acid, tetrafluoroboric acid, phosphoric acid, KOH were from Aladdin Reagent Co., Ltd (Shanghai, China). [Hmim]HSO_4 was purchased from Shanghai Chengjie Chemical Co., Ltd. Brønsted acidic ionic liquids [H_{NMP}]CH_3SO_3, [H_{NMP}]HSO_4, [H_{NMP}]BF_4, [H_{NMP}]H_2PO_4 were prepared in our laboratory according to the literature method [12,18]. Deionized water was prepared in our laboratory.

2.2 Catalytic Testing and Measurement of the Reaction Extension

All esterification reactions of oleic acid with methanol were carried out in a 100 mL round-bottom, three-necked flask equipped with a water-cooled reflux condenser and a magnetic stirrer. Figure 1 shows the batch reactor setup in this work. The product was directly measured by KOH-EtOH titration, acid value (AV) and the ratio of esterification were calculated according to the literature methods [13]. In this study, the initial AV (X_0) of oleic acids is 201.3± 0.5 mg KOH/g.

2.3 Comparison of Different Catalysts

For a catalyst dosage of 5%, methanol/ oleic acid molar ratio of 9:1, reaction time of 3 h and reaction temperature of 80 °C, the effects of [Hmim]HSO_4, [H_{NMP}]CH_3SO_3, [H_{NMP}]HSO_4, [H_{NMP}]BF_4, [H_{NMP}]H_2PO_4, H_2SO_4 and without catalyst on the oleic acid conversion were researched. And then, the most suitable catalyst was chosen by considering environmental impact and the number of sustainable cycles.

2.4 Experimental Design and Optimization by RSM

2.4.1 Single factor experiments

The effects of [H_{NMP}]CH_3SO_3 dosage (2.5%, 5%, 7.5%, 10%, 12.5%, 15%), methanol/ oleic acid molar ratio (6:1, 7:1, 8:1, 9:1, 10:1, 11:1, 12:1, 13:1, 14:1, 15:1), reaction temperature (40,

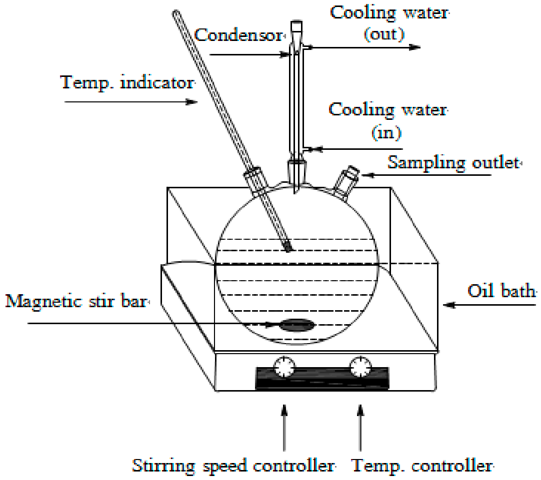


Figure 1. Schematic diagram of batch reaction system.

45, 50, 55, 60,65, 70, 75, 80, 85, 90, 100 °C) , and reaction time (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5 h), on the oleic acid conversion were studied.

2.4.2 Response surface methodology and statistical analysis

The optimum conditions for the synthesis of methyl oleate using ionic liquid $[H_{NMP}]CH_3SO_3$ as catalyst were confirmed by means of RSM. A Box-Behnken experimental design [19-20] was selected to evaluate the relationship between conversion of oleic acid with reactant ratio, amount of ionic liquid, reaction time and temperature. The independent variables and their levels, real values were shown in Table 1.

The quadratic equation model for predicting the optimal point was described according to Eq. (1):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \beta_{ij} x_i x_{ij} + \varepsilon \qquad (1)$$

where Y is the response variable, X_i is the coded levels of the independent variables, the term of β_0, β_i, β_{ii}, β_{ij} are the regression coefficient, the linear terms, the squared terms for the variable i, and the interaction terms between variables i and j, respectively. X_i, X_{ii} and X_{ij} represent the linear, quadratic and interactive terms of the coded independent variables, respectively. k is the total number of variables and optimized in the present experiment. ε is a random error. A software Design-Expert (Version 8.0.6, Stat-

Table 1. Parameter levels and coded values used in the experimental design.

Factors	Symbol	Range and level		
		-1	0	+1
Amount of catalyst (wt%)	X_1	8	10	12
Methanol/acid molar ratio	X_2	12	10	14
Reaction temperature (°C)	X_3	45	50	55
Reaction time (h)	X_4	2.5	3	3.5

Ease. Inc., USA) was used to analyze the data, perform analysis of variance and estimation of the regression equation.

2.5 Recycle Experiment for [H_{NMP}]CH_3SO_3

[H_{NMP}]CH_3SO_3 was reused in the esterification of oleic acid with methanol after washing with ethyl acetate; and the excess ethyl acetate was removed through reduced-pressure distillation.

3. RESULTS AND DISCUSSION

3.1 Effect of Six Different Catalysts on the Oleic Acid Conversion

The efficiency of [H_{NMP}]CH_3SO_3 was studied by comparison with other catalysts, such as 1-methylimidazole hydrogen sulfate salt ([Hmim]HSO_4), [H_{NMP}]HSO_4, [H_{NMP}]BF_4, [H_{NMP}]H_2PO_4, H_2SO_4 and without catalyst. 10 g oleic acid, 10.2 g methanol (molar ratio of methanol to acid = 9:1), and 0.5 g catalyst (5 wt% based on the mass of oleic acid) were mixed in a 100 ml round bottom flask, and then the mixture was kept at 80 °C in an oil bath (reflux condensation, vigorous magnetic stirring). At the end of the reaction, the unreacted methanol in the reaction mixture was removed by a rotary evaporator. The residual materials were then transferred into a funnel and settled for a certain time to obtain an efficient delamination. The upper layer product, which was mainly the desired methyl oleate, was directly measured by KOH-EtOH titration, and then, the acid value and the conversion were calculated.

As depicted in Figure 2, the oleic acid conversion was only 2.85% without the use of a catalyst. In other words, the chemical reaction takes place very slowly in the absence of a catalyst. H_2SO_4 had the best catalytic result with an oleic acid conversion of 65.87%. The catalytic activity of the five ILs for the esterification of oleic acid with methanol displayed the following order: [H_{NMP}]CH_3SO_3>[H_{NMP}]HSO_4>[Hmim]HSO_4>[H_{NMP}]BF_4>[H_{NMP}]H_2PO_4. Among the ILs tested, [H_{NMP}]CH_3SO_3 showed the highest catalytic activity and gave the conversion of 61.99%. With imidazolium IL [Hmim]HSO_4 acting as the catalyst, a relatively good conversion of 59.73% was also achieved under the same conditions. The lowest catalytic efficiency was depicted by [H_{NMP}]H_2PO_4, for which the oleic

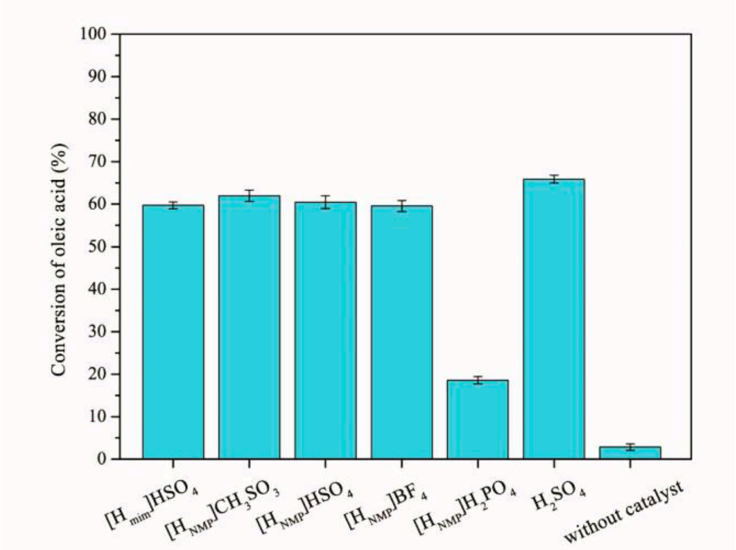
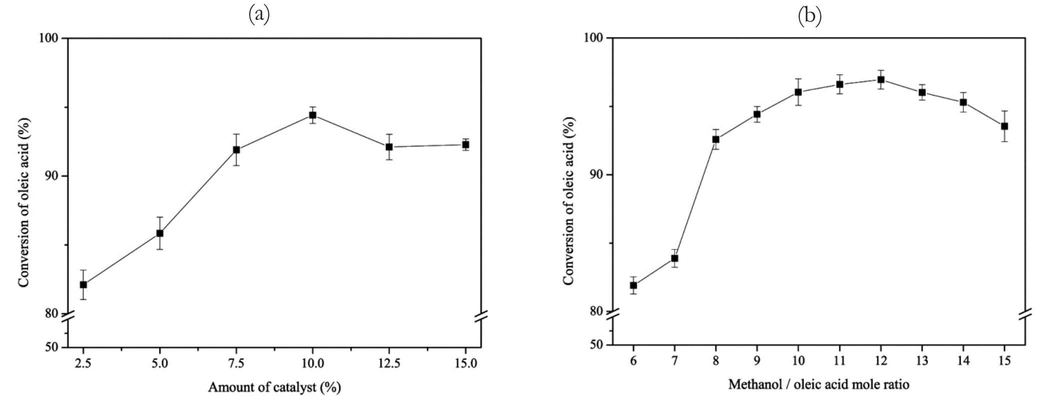


Figure 2. Effects of six different catalysts on the oleic acid conversion. (the reaction temperature: 80 °C, the catalyst amount: 5%, the molar ratio of methanol to acid: 9:1, the reaction time: 3 h).

acid conversion was only 18.59%. These results indicated that for pyrrolidonium ILs, the ILs containing $[CH_3SO_3]^-$ anion showed the better catalytic activity, gaining the higher oleic acid conversion. The IL anion plays a key role in the Brønsted acidic nature of the ILs; the more acidic the conjugate acid of the anion, the stronger the IL's acidity, and this property is responsible for a marked improvement in the oleic acid conversion [21]. In this study, the catalytic efficiency of $[H_{NMP}]CH_3SO_3$ was close to that of H_2SO_4. However, the use of H_2SO_4 could bring about some drawbacks, such as strong corrosivity, environmental pollution and non-recyclability. By contrary, the IL $[H_{NMP}]CH_3SO_3$ displayed some advantages in these cases. First, it showed higher catalytic activity than other ILs. Second, the costs of 1-methyl-2-pyrrolidonium as a source of cations are more economical than those of 1-methylimidazole and 1-methylpyrrolidine [22]. Hence, $[H_{NMP}]CH_3SO_3$ was selected for further research.

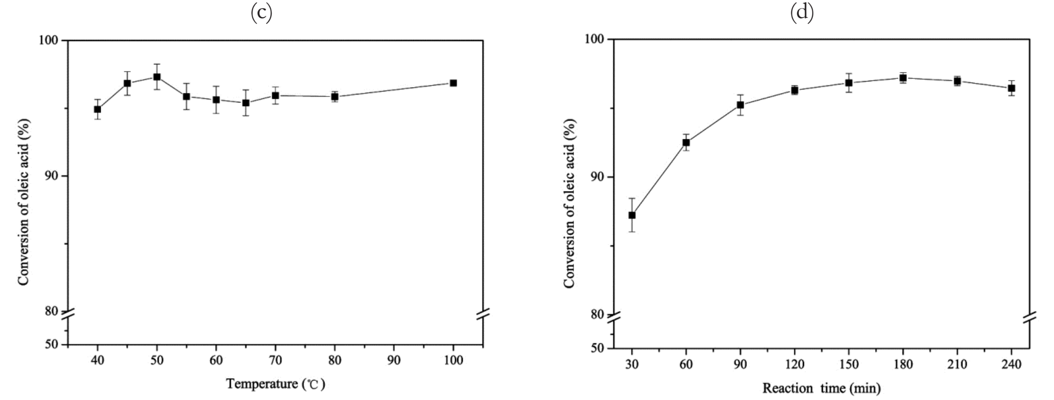
3.2 Single Factor Experiments

The effects of $[H_{NMP}]CH_3SO_3$ dosage, molar ratio, reaction temperature and time, on the oleic acid conversion were analyzed (Figure 3). In general, the dosage of catalyst



Amount of catalyst (wt.%). (the reaction temperature: 80°C, the molar ratio of methanol to acid: 9:1, the reaction time: 3 h)

Methanol/oleic acid molar ratio. (the reaction temperature: 80°C, the reaction time: 3 h, the catalyst amount: 10 %)



Reaction temperature (°C). (the catalyst amount: 10%, the molar ratio of methanol to acid: 12:1, the reaction time: 3h)

Reaction time (h). (the catalyst amount: 10%, the molar ratio of methanol to acid: 12:1, the reaction temperature: 50 °C)

Figure 3. Effects of four factors on the oleic acid conversion. (a) amount of catalyst ($[H_{NMP}]CH_3SO_3$), (b) methanol/oleic acid molar ratio, (c) reaction temperature, and (d) reaction time.

should influence the oleic acid conversion. In this study, a series of experiments were developed using different dosages of $[H_{NMP}]CH_3SO_3$. Initially, the rate of the esterification reaction increased with increasing $[H_{NMP}]CH_3SO_3$ dosage, reaching 96.93 % oleic acid conversion at 10 % dosage; furthermore, there was no obvious improvement beyond 10 % (Figure 3a). This might be due to the side effect which derived from the acidity of excessive $[H_{NMP}]CH_3SO_3$ [23]. In view of the preparation cost, 10 % was selected as the optimum catalyst dosage.

An excess of methanol is necessary for the esterification of oleic acid because it can increase the rate of methanolysis. The oleic acid conversion rapidly increased with increasing mole ratio up to 12:1, and decreased thereafter (Figure 3b). Further increasing this ratio would only hamper the reaction since the residual methanol tended to dilute the reaction mixture, leading to an inferior reactivity, and hence, a lower oleic acid conversion. This was in accordance with the literature reported earlier [21]. As a result, 12:1 was selected as the optimum molar ratio of methanol/oleic acid for this reaction.

As shown in Figure 3c, the oleic acid conversion fractionally increased when the temperature was increased from 40 to 50 °C. The highest oleic acid conversion of 97.32% was gained at 50 °C. However, the oleic acid conversion reduced when the temperature was increased from 50 to 65 °C. And then, the conversion slightly changed with temperature from 65 to 100 °C. The high temperature over 65 °C might increase the rate of methanol evaporation, which finally influenced the esterification reaction [16]. Taking into account the energy consumption of the process, 50 °C was selected as the optimum reaction temperature.

The oleic acid conversion effected by reaction time is shown in Figure 3d. It was found that the oleic acid conversion increased gradually was maintained during the reaction from 0.5 h min to 3 h. This result could be due to the reaction of methanolysis approaching equilibrium after 3 h. Over 90% of the oleic acid conversion was obtained within 1 h while the highest yield (97.02%) was achieved after 3 h. When the time was extended to 3 h and longer, the oleic acid conversion decreased, which indicated that the conversion to byproducts was probably more rapid than the generation of methyl oleate. Hence, 3 h could be the optimal reaction time for the reaction.

3.3 RSM Experiments and Studying

3.3.1 Regression equations and analysis of variance

The independent variables and their levels for BBD were given in Table 1. The experiments were required and the obtained response values shown in Table 2. Table 2 showed that there was no observable difference between actual values and predicted values. Based on data of Table 2 and the regression equation model Eq. (1), the relationship between the oleic acid conversion and the independent variables was given by Eq. (2):

$$\begin{aligned} Y(\%) = {} & -27.89+4.59X_1+1.98X_2+ \\ & 3.23X_3-2.28X_4+0.036X_1X_3+ \\ & 0.33X_1X_4+0.036X_2X_3+ \\ & 0.41X_2X_4+0.29X_3X_4-0.34X_1^2- \\ & 0.20X_2^2-0.047X_3^2-3.23X_4^2 \end{aligned} \tag{2}$$

where X_1, X_2, X_3 and X_4 were the coded values of the independent variables amount of catalyst, methanol/oleic acid molar ratio, reaction temperature and reaction time, respectively, whereas Y was the response of oleic acid conversion.

Statistical analysis based on the analysis of variance (ANOVA) shown in Table 3 was used to estimate whether the quadratic model and model terms were significant or not by *P*-value. Model terms with values less than 0.05 implied that they were significant to the model response.

Table 2. Results of the response surface tests.

Entry	Variable and level				Oleic acid conversion (%)	
	X_1- Amount of catalyst (wt %)	X_2- Methanol/ oleic acid molar ratio	X_3- Temperature (°C)	X_4-Time (h)	Experimental value	Predicted value
1	12	14	50	3	96.37	96.48
2	10	14	50	3.5	97.01	96.63
3	10	12	50	3	96.83	96.74
4	10	14	50	2.5	95.11	94.62
5	8	10	50	3	93.13	92.67
6	10	12	50	3	96.75	96.71
7	10	12	50	3	96.88	96.71
8	10	12	50	3	96.61	96.71
9	10	12	55	3.5	97.32	97.17
10	12	12	50	2.5	95.17	95.03
11	8	12	50	2.5	92.96	92.90
12	10	12	50	3	96.47	96.71
13	12	10	50	3	95.29	95.35
14	8	14	50	3	93.15	93.71
15	12	12	50	3.5	96.67	96.86
16	12	12	55	3	97.03	97.07
17	10	12	45	3.5	93.58	93.47
18	10	14	45	3	93.51	93.79
19	8	12	55	3	93.52	93.56
20	10	14	55	3	96.83	96.74
21	10	10	55	3	95.13	94.99
22	10	10	50	2.5	94.36	94.41
23	10	10	45	3	93.24	93.47
24	10	12	45	2.5	93.42	93.75
25	10	12	55	2.5	94.23	94.52
26	10	10	50	3.5	94.61	94.77
27	8	12	50	3.5	93.16	93.44
28	12	12	45	3	94.47	94.10
29	8	12	45	3	92.42	92.06

The model F-value of 42.49 demonstrated the fitted model with the output response was reliable. The coefficient of determination (R^2) of the model was 0.9736, which indicated that the quadratic model was well fitted to the actual data. The value of adjusted determination coefficient ($R^2_{adj} = 0.9506$) was high and found to be in reasonable agreement with each other.

The adequate precision, illustrating the signal to noise ratio, was 20.821, much greater than the minimum requirement of 4, which showed adequate model discrimination [24]. Accordingly, this model was extremely significant and the P value of 'the lack of fit' of 0.0535 was not significant, which implied that this model was reasonable.

Table 3. Variance analysis of the regression model.

Source	Sum of squares	Degree of freedom	Mean square	F Valve	P Valve	Significant
Model	69.1	13	5.32	42.49	< 0.0001	**
X_1	23.13	1	23.13	184.89	< 0.0001	**
X_2	3.22	1	3.22	25.77	0.0001	**
X_3	15.01	1	15.01	119.97	< 0.0001	**
X_4	4.2	1	4.2	33.58	< 0.0001	**
X_1X_3	0.53	1	0.53	4.26	0.0568	
X_1X_4	0.42	1	0.42	3.38	0.086	
X_2X_3	0.51	1	0.51	4.09	0.0614	
X_2X_4	0.68	1	0.68	5.44	0.034	*
X_3X_4	2.15	1	2.15	17.16	0.0009	**
X_1^2	11.65	1	11.65	93.14	< 0.0001	**
X_2^2	4.05	1	4.05	32.38	< 0.0001	**
X_3^2	8.88	1	8.88	71.01	< 0.0001	**
X_4^2	4.23	1	4.23	33.83	< 0.0001	**
Residual	1.88	15	0.13			
Lack of fit	1.76	11	0.16	5.7	0.0535	
Pure Error	0.11	4	0.028			
Cor Total	70.98	28				

3.3.2 Analysis of the response surface

The response surface corresponding to the quadratic equation is depicted in Figure 4. The three dimensional (3-D) response plots and contour plots of $[H_{NMP}]CH_3SO_3$ dosage, molar ratio, reaction temperature and reaction time were presented in Figures 4 and 5, respectively.

The variations of oleic acid conversion with dosage of catalyst and reaction temperature were depicted in Figures 4a and 5a. The oleic acid conversion first increased gradually to the maximum value and then decreased with increasing methanol/oleic acid molar ratio because the excess methanol, which diluted the concentration of $[H_{NMP}]CH_3SO_3$, resulted in decreased catalytic efficiency. The oleic acid conversion increased quickly and then changed smoothly with increased reaction temperature. It was evident that both $[H_{NMP}]CH_3SO_3$ dosage and reaction temperature exerted significant influence on the oleic acid conversion. The contour line with a symmetrical mound shape indicated that the combined effect of the amount of catalyst and reaction temperature was not further significant.

The interactive effect of dosage of catalyst and reaction time is depicted in Figures 4b and 5b. With time prolonging, more by-products produced and the rate of conversion was decreased. At a certain period of time, the conversion changing fractionally means that the effect of time on the response was less than amount of catalyst. The result was in good accordance with the values of Table 3. The effect of interaction of the two variables was not significant with a symmetrical mound shape and the P-values (0.086) of the interaction term.

Figures 4c and 5c showed the relationship between methanol/acid molar ratio and reaction temperature. The trend resembled to the effect of amount of catalyst and reaction temperature. The rate of oleic acid conversion first increased

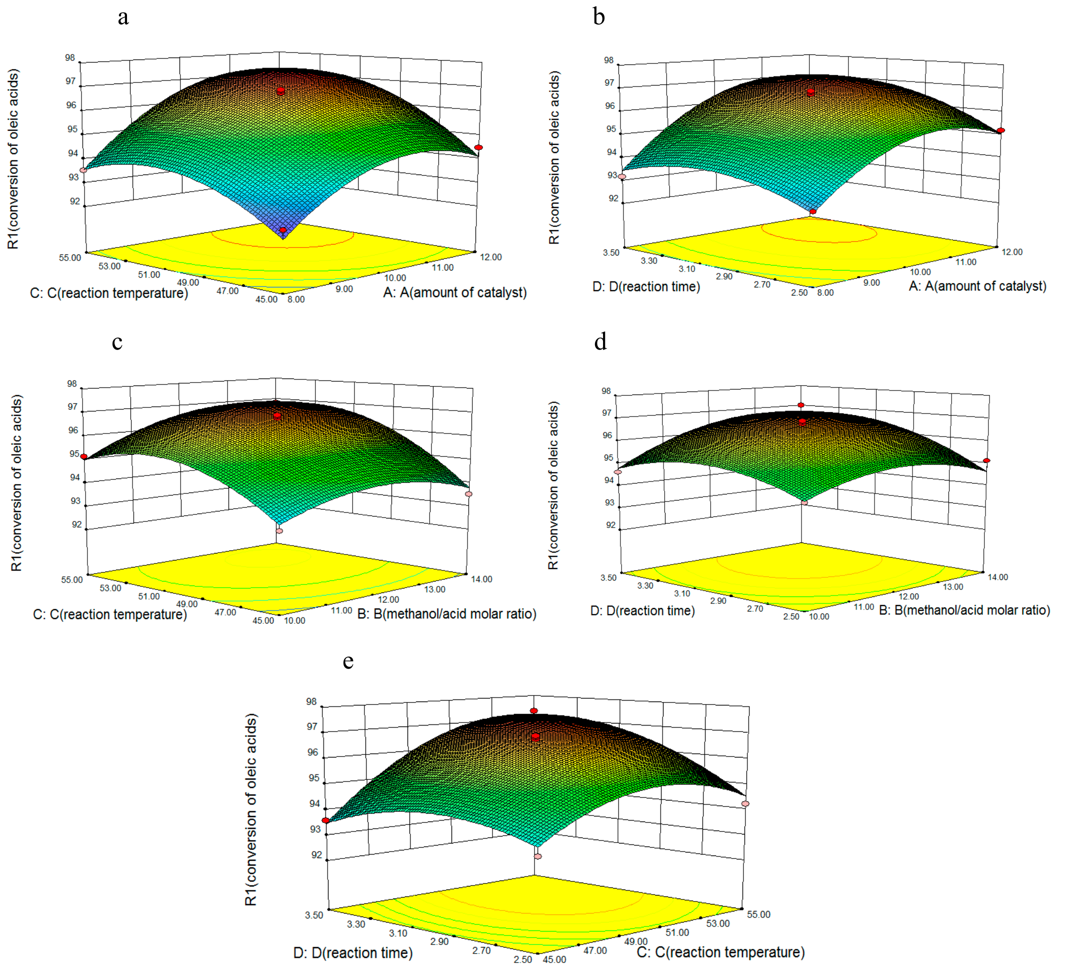


Figure 4. Response surface plots showing the predicted values of the oleic acid conversion. (a) effect of amount of catalyst and reaction temperature, (b) amount of catalyst and reaction time, (c)methanol/acid molar ratio and reaction temperature, (d)methanol/acid molar ratio and reaction time, (e) reaction temperature and reaction time, and other variables are held at constant level.

and then decreased with temperature rise according to methanol/acid molar ratio. The effect of interaction of them was also not significant with a symmetrical mound shape. The oleic acid conversion was good at low reaction temperature and moderate methanol/acid molar ratio.

Figure 4d and 5d represented the relationship between methanol/acid molar ratio and reaction time. The trend was also similar to the effect of reaction time and dosage of catalyst. The oleic acid conversion first increased and then decreased with time prolong according to methanol/acid molar ratio. The effect of interaction of them was also not significant with a symmetrical mound shape.

It was found that reaction temperature and time affected oleic acid conversion in a similar fashion as that affected by amount of catalyst and reaction temperature (Figures 4e and 5e). The oleic acid conversion first increased and then decreased with time prolong according

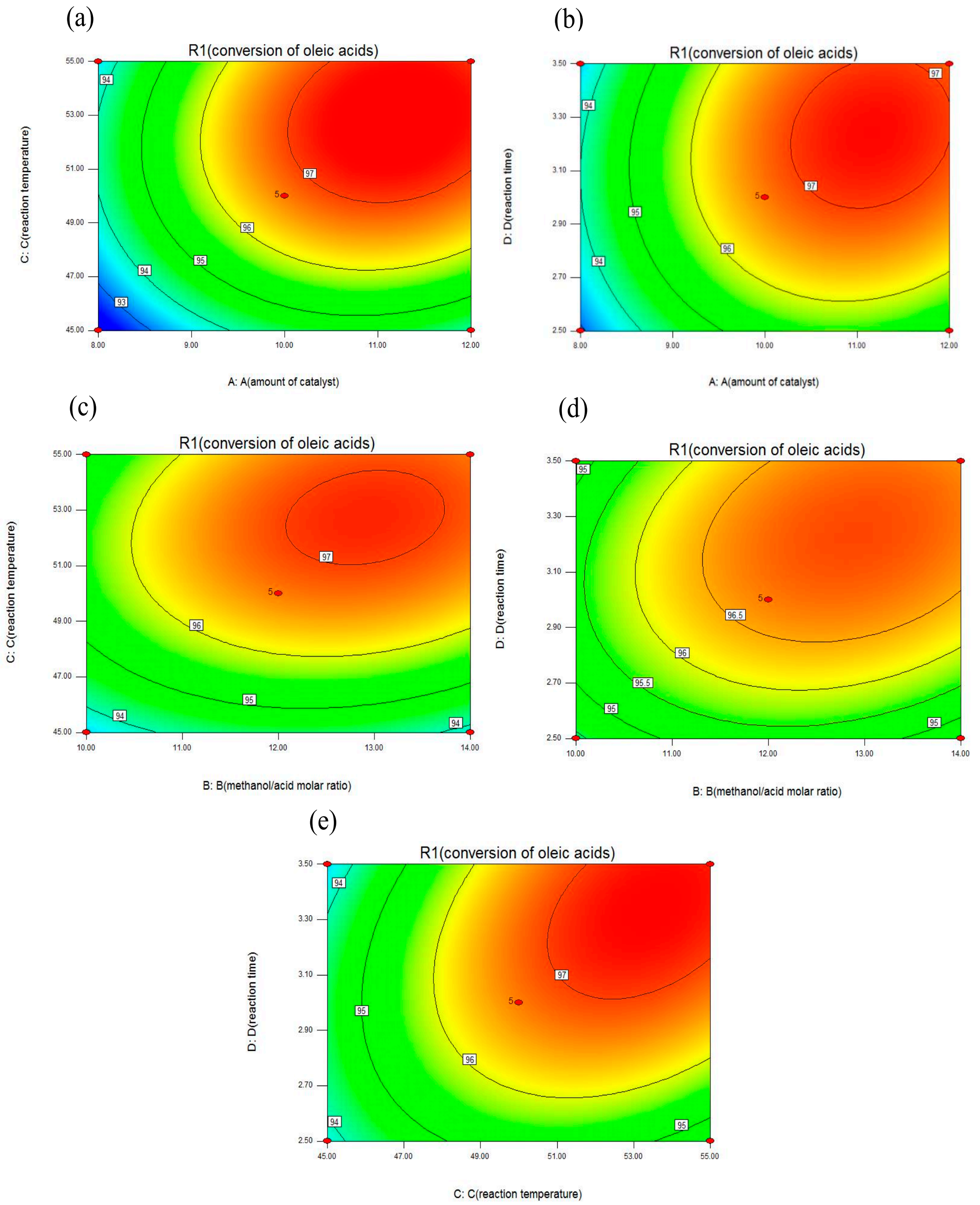


Figure 5. Contour plots showing the predicted values of the oleic acid conversion. (a) effect of amount of catalyst and reaction temperature, (b) amount of catalyst and reaction time, (c) methanol/acid molar ratio and reaction temperature, (d)methanol/acid molar ratio and reaction time, (e) reaction temperature and reaction time, and other variables are held at constant level.

to temperature. The effect of interaction of them was significant, which indicated that temperature and time could influence each other in the esterification reaction [22]. The oleic acid conversion was good at low reaction temperature and short reaction time. Reduction in oleic acid conversion was observed at longer reaction time once the optimum conversion was achieved, due to the reversible nature of the esterification reaction, where hydrolysis of ester may be hydrolyzed and conversion was reduced.

In view of the comprehensive analysis of the response surface, we found only the interaction effect of reaction temperature and time was the significant parameters affecting the rate of oleic acid conversion. According to the BBD, the optimal conditions were as follows: $[H_{NMP}]CH_3SO_3$ dosage 10.48%, methanol/oleic acid molar ratio 11.23:1, reaction temperature 52.86 °C and reaction time 2.81 h. The oleic acid conversion was predicted to 97.32% according to this model. The operations were tested and verified, the oleic acid conversion reached 97.35%, which confirmed that this model was reasonable.

3.4 Comparison of Catalytic Activity Over Various Catalysts for Esterification

Catalytic results of esterification over various acid catalysts were shown in Table 4. Previously, $[BHSO_3MIM][HSO_4]$ exhibited benign conversion for esterification reaction of oleic acid and methanol, but a high temperature was required [21]. $[MIM\text{-}PSH]_{2.0}HPW_{12}O_{40}$ presented good catalytic activity (92.3%) for production of biodiesel from palmitic acid, which expanded the application of heteropoly acid ILs [1]. What's more, imidazolium IL ($[BMIM][HSO_4]$) was used for the synthesis of biodiesel from oleic acid. It was found that the oleic acid conversion could only reach at 80.4% at a long reaction time of 5.2 h [14]. Despite the above 98% conversion obtained by using BD20-DES as catalyst at 85 °C, it was not easy to prepare the catalyst [25]. While $[H_{NMP}]CH_3SO_3$ based on cheap cation exhibited higher catalytic activity for production biodiesel from oleic acid under the condition of low reaction temperature and short reaction time.

Table 4. Results of esterification of different catalysts.

Catalyst	Feedstock	Molar ratio	Tem. (°C)	Time (h)	Conversion (%)	Recycle times	Ref.
$[BHSO_3MIM]HSO_4$	Oleic acid	4:1	130	4	97.7	10	[21]
$[MIM\text{-}PSH]_{2.0}HPW_{12}O_{40}$	Palmitic acid	13:1	80	5	92.3	6	[1]
$[BMIM][HSO_4]$	Oleic acid	9:1	87	5.2	80.4	5	[14]
BD20-DES	Oleic acid	12:1	85	1.67	>98.0	4	[25]
$[H_{NMP}]CH_3SO_3$	Oleic acid	11.23:1	52.86	2.81	97.35	5	This work

3.5 Recycle Use of $[H_{NMP}]CH_3SO_3$

Reusability of catalyst technology plays a critical role in reducing the total cost of the production [25]. The reusability of the ionic liquid catalyst is remarkable from the standpoint of economy. In order to evaluate the reusability of the catalyst, we conducted the possibility of recycling of $[H_{NMP}]CH_3SO_3$, and the results were shown in Figure 6. The ionic liquid was separated from the mixture solution and washed by diethyl ether, then vacuum dried for 5 h at 80 °C. From Figure 6, $[H_{NMP}]CH_3SO_3$ was repeatedly reused for 5 cycles without major loss of catalytic activity, which indicated that $[H_{NMP}]CH_3SO_3$ as catalyst for the esterification could be reusable.

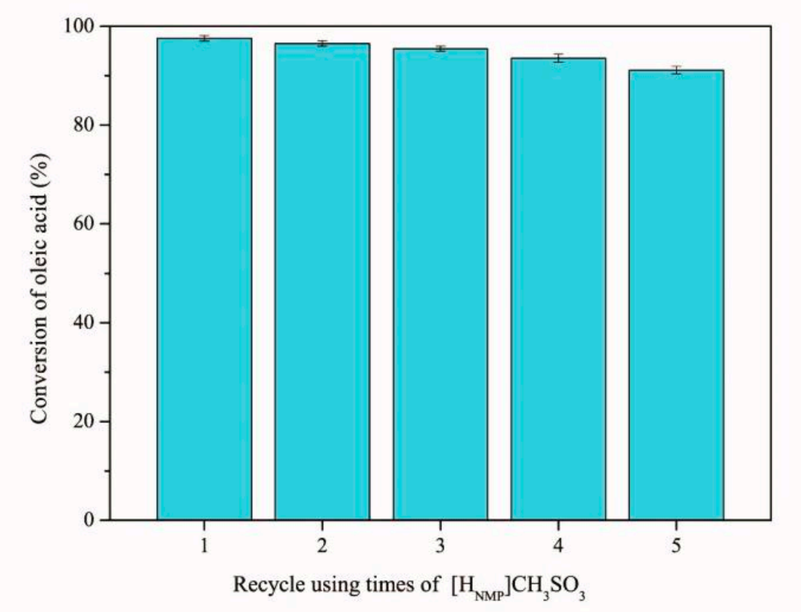


Figure 6. Effects of number of cycles of the catalyst on the oleic acid conversion.

4. CONCLUSIONS

In the present work, biodiesel production from the esterification of oleic acid with methanol catalyzed by ionic liquid $[H_{NMP}]CH_3SO_3$ was investigated. The reaction conditions were optimized using RSM. Comparison of the catalytic efficiencies of six catalysts confirmed that $[H_{NMP}]CH_3SO_3$ was the most proper catalyst. Moreover the catalyst was easily separated from the system. Response surface tests indicated that the optimal conditions were as follows: $[H_{NMP}]CH_3SO_3$ dosage 10.48%, methanol/oleic acid molar ratio 11.23:1, reaction time 2.81 h at 52.86 °C; under these conditions, the oleic acid conversion reached 97.35%. It is important that the catalytic activity of $[H_{NMP}]CH_3SO_3$ was still high after 5 cycles.

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