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Effect of Different Reaction Parameters on the Synthesis of Biodiesel from Soybean Oil Using Acid Ionic Liquid as Catalyst

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Response surface methodology (RSM) was successfully applied to optimize transesterification of biodiesel from soybean oil catalyzed by ionic liquid. The effects of various reaction conditions, including reaction time, methanol/oil molar ratio and the amount of ionic liquid were investigated. A central composite design (CCD) was employed to search for the optimal yield of biodiesel. The obtained optimum conditions were *n*(soybean oil):*n*(methanol) = 1:13, amount of catalyst of 4 wt. % to soybean oil and reaction time 8.5 h at 120 °C. Under the optimized conditions, the yield of biodiesel reached 94.7 %, in close agreement with values predicted by the mathematical model. The [HSO_3-pmim]HSO_4 ionic liquid showed the best catalytic activity, highly stability on the transesterification of soybean oil and could be reused six times without noticeable drop in activity.

Keywords: Ionic liquid, Transesterification, Biodiesel, Response surface methodology.

INTRODUCTION

Fatty acid methyl ester (FAME), which is defined as biodiesel fuel, is produced by the transesterification between animal fats or vegetable oils and methanol in the presence of a catalyst. It has become new sanitary fuel that could be seemed as diesel substitutes for engines. It is worth noting that FAME was useful in other applications and as intermediate compounds for other higher-value products. Some may be more practical for application of the proposed conversion process. The traditional synthesis routes are usually harmful, which may cause corrosiveness, environmental pollution, non-renewable and easily saponification of products. To overcome these disadvantages, some efforts have been made to research and develop the using of heterogeneous catalysts systems. Solid acid or base catalyst[1,2], resins[3,4], zeolites[5,6] by different groups and heteropoly acids[7,8] have been carried out on the preparation of biodiesel. However, all these catalysts and courses still had one or more problems related to reaction activity, product selectivity, catalyst recyclability and environmental safety. Therefore, it is necessary to develop an environmentally benign method for the synthesis biodiesel on a large scale.

Recently, ionic liquids (ILs) were receiving a widespread attention as an environmentally acceptable reaction medium due to their advantageous properties[9,10], such as excellent chemical and thermal stability, potential recycle ability[11,12]. These properties made them be widely used in catalytic and non-catalytic reactions[9,13]. Ionic liquids had been used as catalyst for the transesterification of vegetable oils or animal fats to the biodiesel. Liang *et al.*[14] used chloroaluminate ionic liquid as catalyst for the synthesis of biodiesel from soybean oil. They reported that this catalyst was efficient for transesterification. Brønsted acidic ionic liquid containing an alkanesulfonic acid group was also reported to produce biodiesel from waste oils[15]. The yield of fatty acid methyl esters was 93.5 % under the optimized reaction conditions and the catalyst was recovered by distillation.

Response surface methodology is a collection of statistical and mathematical technique for optimizing multifactor experiments, building models, evaluating the effects of several factors for desirable responses, which was originally described by Box and Wilson 1951. This methodology has been widely used to optimize different analytical chemistry processes and synthesis processes extensively[16]. In order to minimize the wastage of the laboratory prepared catalyst by rigorous experimental procedures, response surface methodology was used for parameter optimization. Hence, the present work was taken up to establish the optimum conditions for the transesterification of soybean oil with methanol in a laboratory prepared Brønsted acid functionalized ionic liquid catalyst using response surface methodology.

EXPERIMENTAL

Catalyst preparation and characterization: SO_3H-functionalized Brønsted acidic ionic liquids were prepared and characterized by IR, NMR, TG and UV-visible spectrophotometer in the laboratory following the procedure outlined in literature[17,18]. All the chemicals were research grade and were used without further purification unless otherwise stated.

General procedure for the synthesis of biodiesel: A typical transesterification procedure was conducted as follows: soybean oil, methanol and the catalyst were mixed together in 100 mL stainless steel autoclave equipped with a magnetic stirrer at a constant speed and heated up by oil bath at a certain temperature. Upon completion, the reaction mixture was cooled to room temperature and the layers separated. The upper layer is biodiesel. The lower layer consisting of the ionic liquid was reused in a further run. Chemical analysis of the products was performed by gas chromatography Agilent 6890N GC, equipped with a FID detector and HP-5 capillary column. Reactants and products were identified by comparison with authentic samples. Methyl laurate was used as internal standard.

Factorial experimental design and optimization of parameters: Applications of response surface methodology techniques with central composite design and optimize the chemical processes have been recently reported and their reliability to generate a model equation and calculate optimum conditions have been proven. In this paper, the three-dimensional response surface and two-dimensional contour plots were generated by the Design Expert (Version 8.0.6, Stat-Ease. Inc., USA). The central composite design was applied to design the experimental conditions involving three different factors, alcohol/oil molar ratio, amount of ionic liquid and reaction time. The maximum value of the yield was taken by the responses of the design experiment. Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). For this study, a set of 20 experiments including the 14 factorial points and 6 center points were carried out.

The coded values were designated by associated plus signs (+1) with high levels, zero (0) indicating center value and minus signs (-1) with low levels, plus signs (+α) with high axial and minus signs (-α) with low axial. Alpha (α) is defined as a distance from the centre point which can be either inside the range or outside, with the maximum value of $2^{n/4}$, where n is the number of factors. Hereby the value of alpha is set at 1.682. The actual design of this work was presented in Table-1a. The coded values of these factors were obtained according to eqn. 1 below:

$$x_i = \frac{X_i - X_0}{\Delta X_i} \quad (1)$$

where x_i was the coded value of the independent variable; X_i was the uncoded value of the real variable, X_0 was the average value of variables in high and low and ΔX_i was (variable at high level- variable at low level)/2. The methanol/oil molar ratio (x_1), amount of ionic liquid (x_2) and reaction time (x_3) were chosen as three independent factors in the experimental design.

After conducting the experiments, the response variable (FAME yield) was fitted a second-order model in order to correlate the response variable to the independent variable. The full quadratic model for yield was established by using the method of least squares and the equation is as follows:

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

where Y and x_i refer to the predicted response and the coded independent variables or factors, respectively. The term β_0 is the offset term, β_i are the linear terms, β_{ii} are the squared terms and β_{ij} are the interaction terms, which are all the regression coefficients. k is the total number of designed variables. ε is a random error.

The coefficient of determination (R^2) could be used to evaluate the accuracy and general ability of the second order multiple regression models. The fitted polynomial equation was expressed as response surface and contour plots in order to visualize the interaction between the response and experimental levels of each factor and to infer the optimum conditions.

RESULTS AND DISCUSSION

Effects of operating parameters

Acidities of the ionic liquids-catalytic activity relationships: Generally, sulfuric acid has been used as an acid catalyst for a variety of organic acid- catalyzed reactions. However, in the case of transesterification of soybean oil with MeOH, the sulfuric acid is undesirable though it is a strong acid. H_2SO_4 mainly distributed into the MeOH phase. The carbonyl oxygen of triglyceride in soybean oil cannot be activated to enable the reaction. The SO_3H-functionalized Brønsted acidic ionic liquids were prepared. These ionic liquids can distribute into the oil phase, so we used them as catalyst on the transesterification of soybean oil with MeOH. The results of the transesterification to biodiesel by various catalysts were listed in Table-2. From Table-2, we could find that ionic liquids with the same cations showed different catalytic activity on the transesterification of soybean oil with MeOH. Ionic liquid with HSO_4^- anion gave 94.3 % yield of biodiesel. Ionic liquid containing *p*-$CH_3C_6H_4SO_3^-$, $H_2PO_4^-$ and CF_3COO^- anions showed poor activity. The order of activity for the anions in

TABLE-1A
PARAMETER LEVELS AND CODED VALUES USED IN THE EXPERIMENTAL DESIGN

Factors	Symbol	Range and level				
		-1.682 (-α)	-1	0	+1	+ 1.682 (+ α)
Methanol/oil mole ratio	x_1	8.64	10	12	14	15.36
Amount of catalyst (wt.%)	x_2	2.32	3	4	5	5.68
Reaction time (h)	x_3	4.64	6	8	10	11.36

TABLE-2
RESULTS OF TRANSESTERIFICATION OF SOYBEAN OIL WITH METHANOL USING IONIC LIQUID AS CATALYST[a]

Catalyst	Molar ratio (methanol/ soybean oil)	Amount of inoic liquid (wt.%)	Temperature (°C)	Time (h)	Yield of biodiesel (%)
$[HSO_3\text{-pmim}]HSO_4$	12:1	4	120	8	94.3
$[HSO_3\text{-pmim}]$PTSA	12:1	4	120	8	75.5
$[HSO_3\text{-pmim}]H_2PO_4$	12:1	4	120	8	67.5
$[HSO_3\text{-pmim}]COOCF_3$	12:1	4	120	8	61.5
$[HSO_3\text{-pmim}]HSO_4$	6:1	4	120	8	82.3
$[HSO_3\text{-pmim}]HSO_4$	8:1	4	120	8	84.3
$[HSO_3\text{-pmim}]HSO_4$	10:1	4	120	8	87.1
$[HSO_3\text{-pmim}]HSO_4$	14:1	4	120	8	92.5
$[HSO_3\text{-pmim}]HSO_4$	12:1	2	120	8	83.6
$[HSO_3\text{-pmim}]HSO_4$	12:1	3	120	8	92.8
$[HSO_3\text{-pmim}]HSO_4$	12:1	5	120	8	91.7
$[HSO_3\text{-pmim}]HSO_4$	12:1	6	120	8	89.9
$[HSO_3\text{-pmim}]HSO_4$	12:1	4	80	8	54.7
$[HSO_3\text{-pmim}]HSO_4$	12:1	4	100	8	82.5
$[HSO_3\text{-pmim}]HSO_4$	12:1	4	140	8	92.5
$[HSO_3\text{-pmim}]HSO_4$	12:1	4	120	4	84.6
$[HSO_3\text{-pmim}]HSO_4$	12:1	4	120	6	92.3
$[HSO_3\text{-pmim}]HSO_4$	12:1	4	120	10	92.6
$[HSO_3\text{-pmim}]HSO_4$	12:1	4	120	12	89.1

[a]Reaction conditions: molar ratio of methanol/oil 12:1; catalyst amount of 4 % (oil mass basis); temperature of 120 °C; reaction time of 8 h. Yield of biodiesel was obtained by GC

the ionic liquids was $[HSO_4^-] > [p\text{-}CH_3C_6H_4SO_3] > [H_2PO_4^-] > [CF_3COO^-]$. Based on previous results, we found that the activity of the acidic ionic liquids was in excellent agreement with their acidity order. Detailed investigations to optimize various reaction parameters were conducted using $[HSO_3\text{-pmim}]HSO_4$ as catalyst since it was also less toxic and cost effective besides showing high product selectivity.

Optimization of reaction conditions: In order to optimize the reaction conditions of the transesterification of soybean oil with methanol, the influence of molar ratio of the reactants, the reaction time, the amount of catalyst and reaction temperature were studied and the results were shown in Table-2.

The transesterification is a reversible reaction. To improve the yield of biodiesel, excessive methanol was usually added to the reaction system. The yield was enhanced while increasing the amount of methanol, because it provided more opportunity for reactant molecules to collide, which was favorable for moving the equilibrium toward biodiesel. Moreover, the increase of amount of methanol could result in a better dispersion of the ionic liquid catalyst in reaction system. However, excessive methanol would dilute the concentration of the catalyst and triglyceride, which may increase the amount of recycling methanol and reduce the reaction rate. As the amount of ionic liquids increased, the yield of biodiesel increased. The main reason was that the number of available acid sites increased clearly. However, when the amount of catalyst was beyond 4 %, the conversion rate dropped. It was probably due to the solubility of ionic liquid. Generally, high temperature could contribute to the enhancement of reaction rate and conversion efficiency. We found that the yield of biodiesel increased with an increase in reaction temperature. When the temperature was higher than 120 °C, the conversion rate declined for the steam press of methanol ascended rapidly. With the experiment continuing, the reaction reached the equilibrium after 8 h and the yield of biodiesel did not increase when the reaction time was prolonged.

Statistical analysis: The analysis of variance (ANOVA) method has become a attractive mean in the evaluation of the effects of the parameters and reaction parameters optimization. The coded and uncoded (actual) levels of the independent variables were given in Table-1a. In order to minimize the wastage of the laboratory prepared catalyst by rigorous experimental procedure, a three-factor-five-level multifactorial analysis was adopted to evaluate the effects of the aforementioned factors on yield of biodiesel. Results have been summarized in Table-1b. By applying multiple regression analysis on the Table-1b, a quadratic polynomial equation eqn. 3 was generated to fit the experimental data.

$$Y = +94.25 + 2.30x_1 + 1.80x_2 + 1.28x_3 - 0.90x_1x_2 + 0.45x_1x_3 + 0.23x_2x_3 - 2.31x_1^2 - 2.91x_2^2 - 2.63x_3^2 \quad (3)$$

where x_1, x_2 and x_3 are the coded values of the test variables methanol/oil molar ratio, amount of ionic liquid and reaction time, respectively; Y is the response of yield of biodiesel. It shows that the yield of biodiesel has a linear and quadratic effect on the three process variables. The significance of each coefficient in eqn. (3) was determined by t-test and P-values. The positive sign in front of the terms indicates synergistic effect while negative sign indicates antagonistic effect.

The results of the second-order response surface model fitting in the form of ANOVA are given in Table-1c. Based on 95 % confidence level, the model was found significant as the Fisher's F-tests ($F_{model} = 41.52$) with very low probability value ($p < 0.0001$). The high significance of the fitted model indicates the reliability of the regression model for predicting the yield of biodiesel. In this case, the R^2 values (0.9739, sum of squares attributed to the regression/total sum of squares), which means that 97.39 % of the response variability could be explained by the previously discussed model and only 2.61 % of the total

TABLE-1B
EXPERIMENTAL DESIGN AND RESPONSE VALUE

Experimental no.	Variable and level			Yield of biodiesel (%)
	Methanol/oil mole ratio	Amount of catalyst (wt. %)	Reaction time (h)	
1	+1	+1	+1	91.83
2	−1	+1	+1	87.28
3	+1	−1	+1	88.38
4	−1	−1	+1	82.00
5	+1	+1	−1	86.57
6	−1	+1	−1	85.60
7	+1	−1	−1	85.80
8	−1	−1	−1	79.44
9	+α	0	0	92.34
10	−α	0	0	84.56
11	0	+α	0	89.42
12	0	−α	0	84.08
13	0	0	+α	89.17
14	0	0	−α	85.95
15	0	0	0	94.05
16	0	0	0	93.11
17	0	0	0	94.41
18	0	0	0	95.05
19	0	0	0	94.29
20	0	0	0	94.31

TABLE-1C
ESTIMATED REGRESSION COEFFICIENTS AND CORRESPONDING STATISTICAL *t*- AND *P*-VALUES FOR YIELD OF BIODIESEL

Source	Sum of squares	Degrees of freedom (DF)	Mean square	F value	Prob > F	Significance
Model	397.56	9	44.17	41.52	<0.0001	**
x_1	71.94	1	71.94	67.62	<0.0001	**
x_2	44.46	1	44.46	41.79	<0.0001	**
x_3	22.41	1	22.41	21.07	0.0010	*
x_1^2	77.12	1	77.12	72.49	<0.0001	**
x_2^2	122.40	1	122.40	115.05	<0.0001	**
x_3^2	99.52	1	99.52	93.55	<0.0001	**
$x_1 x_2$	6.52	1	6.52	6.12	0.0328	*
$x_1 x_3$	1.62	1	1.62	1.52	0.2454	-
$x_2 x_3$	0.41	1	0.41	0.38	0.5510	-
Residual	10.64	10	1.06	-	-	-
Lack of fit	8.64	5	1.73	4.33	0.0669	-
Pure error	2.00	5	0.40	-	-	-
Cor total	408.20	19	-	-	-	-

*Represents it is significant; **Represents it is highly significant

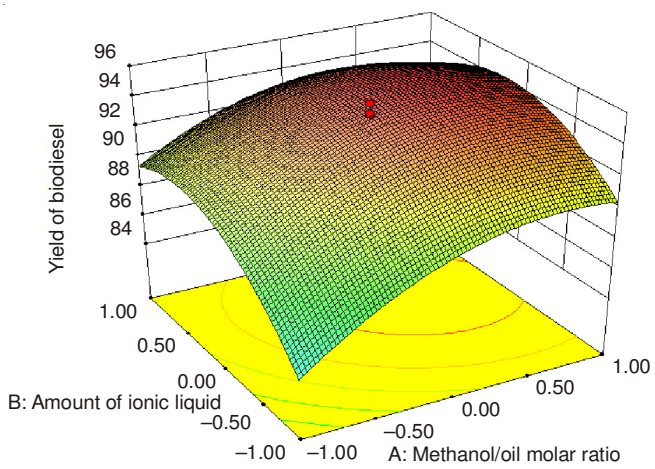
variations can not be explained by the model. Moreover, the value of the adjusted determination coefficient (Adj. R^2 = 0.9505) was also high enough to advocate for a high significance of the model. Adequate precision is a measure of signal to noise ratio (S/N) and as requirement of the model. In this model, the ratio of 18.46 for biodiesel yield is much greater than 4 so that it indicates adequate model discrimination. At the same time, a relatively lower value of the coefficient of variation (CV = 1.16 %) indicates that the experiment was precision and reliability. Apart from that, Lack of Fit is the weighted sum of squared deviations between the corresponding fitted value and the mean response at each factor level. In this model, the 'Lack of Fit F-value' of 4.33 was not significant implies that model is fitted to all data. From these statistical tests, it was found that the model was adequate for predicting the biodiesel yield within the range of the variables studied.

The regression coefficients with the corresponding *P*-values were showed in Table-1c. The *P*-values were used as a tool to check whether the term was significance or not by each coefficient. The smaller *P*-value is, the more significant parameter is. From Table-1c, analysis of these parameters with the *P*-value indicated that x_1, x_2, x_3, $x_1 x_2$, x_1^2, x_2^2 and x_3^2 terms had significant effect on the conversion of biodiesel.

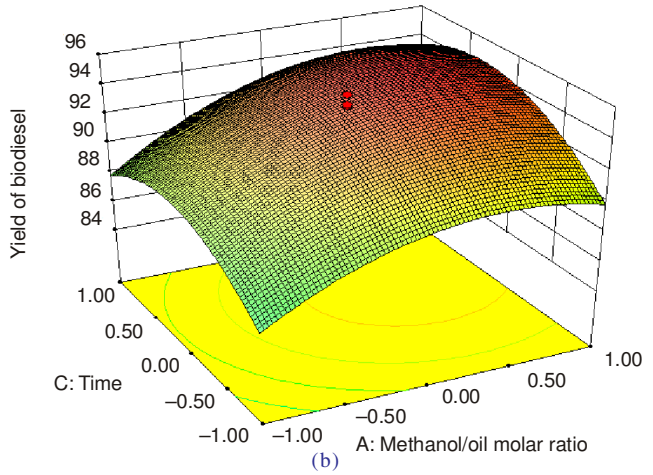
Figs.1 and 2 showed the three dimensional response plots and contour plots for methanol/oil molar ratio, amount of ionic liquid and reaction time, respectively.

The variation of yield of biodiesel with methanol/oil molar ratio and amount of ionic liquid, methanol/oil molar ratio and reaction time was given in Figs.1a and 2a, Figs. 1b and 2b, respectively. As it can be seen, the two functions on yield of biodiesel were very similar. It was noticed that for a low methanol/oil molar ratio, the biodiesel yield increased with time and the amount of ionic liquid but after 8 h and 4 % ionic liquid, it reached a plateau. With increasing the amount of ionic liquid and reaction time, opposite trend was appeared due to mass transfer limitation between immiscible liquid phase

and the reactant and more by-products. The two-dimensional contour lines showed an unsymmetrical mound shape with the maximum response occurring in the central contour. It demonstrated that the interactive effect of two sets above on yield of biodiesel was significant.



(a)



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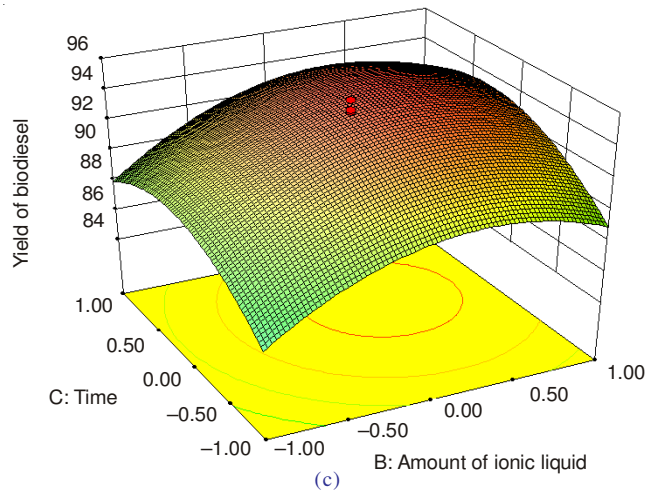
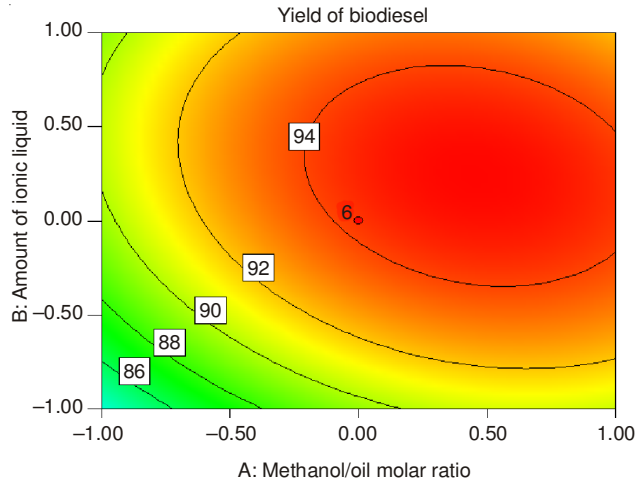
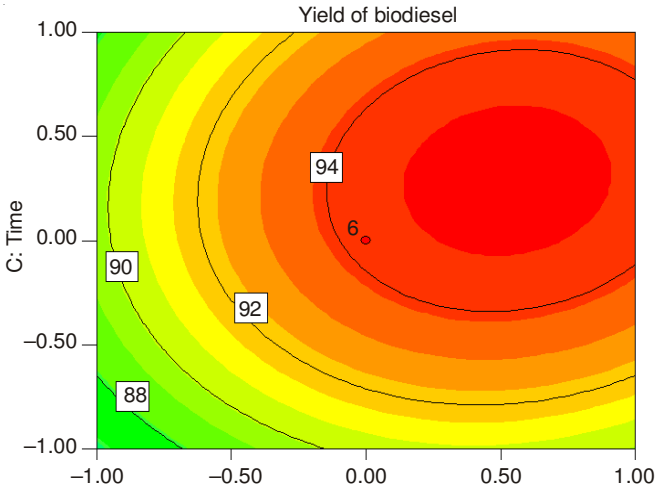


(c)

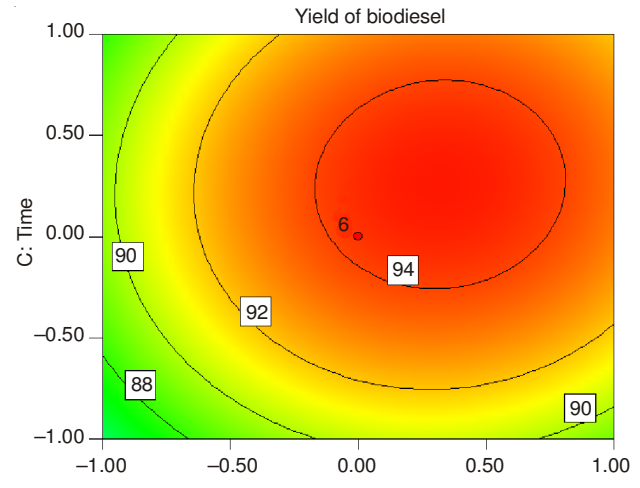
Fig. 1. Response surface plots showing the predicted values of yield of biodiesel: effect of methanol/oil mole ratio and amount of and amount of ionic liquid (a), methanol/oil mole ratio and reaction time (b), amount of ionic liquid and reaction time (c). Other variables are held at constant level



(a)



(b)



(c)

Fig. 2. Contour plots showing the predicted values of yield of biodiesel: effect of methanol/oil mole ratio and amount of and amount of ionic liquid (a), methanol/oil mole ratio and reaction time (b), amount of ionic liquid and reaction time (c). Other variables are held at constant level

3D-plot and contour plot of yield of biodiesel as a function of amount of ionic liquid and reaction time were presented in Figs. 1c and 2c, respectively. The trend was the similar to the effect of methanol/oil molar ratio and amount of ionic liquid, methanol/oil molar ratio and reaction time. This plot showed that optimal methanol/oil molar ratio was around 12:1 and optimal amount of ionic liquid was 4 wt. %. Under such con-dition, biodiesel was formed with a high yield.

Determination of the optimum condition: Based on the response surface methodology from all the 20 experimental data, the optimal process condition was found to be: $x_1 = 12.96$ (methanol/oil molar ratio), $x_2 = 4.25$ wt. % (amount of ionic liquid) and $x_3 = 8.58$ h (reaction time), the yield of biodiesel predicted by the model is 95.21 %. The optimum parameters were converted as follows: $x_1 = 13$ (alcohol/acid molar ratio), $x_2 = 4$ wt. % (amount of ionic liquid), $x_3 = 8.5$ h (reaction time). In order to confirm the fit of predicted and actual data, four parallel experiments were preceded under the condition above and showed an average yield of 94.73 %, which was reasonably close to the predicted value and was regarded as satisfactory under the current constraints of experiments.

Analysis of biodiesel: The compounds of biodiesel produced from soybean oil under the optimized conditions were analyzed by GC-MS (Agilent 7890A-5975C, Agilent Technologies, Helium was used as the carrier gas and flow rates were regulator at 1 mL/min.). Based on the literature, the component of each peak was listed according to the retention time, respectively. We found that palmitic acid methyl ester (35 wt. %) and linoleic acid methyl ester (44.82 wt. %) were the main compounds in the biodiesel. It still contained a small quantity of oleic acid methyl ester, stearic acid methyl ester, gondoic acid methyl ester and erucic acid methyl ester. The total content of biodiesel obtained through area normalization method was 96.53 wt. %.

Recycling of ionic liquid [HSO_3-pmim]HSO_4: The main advantage of the ionic liquids catalysts is that it can be recyclable for further use. The stability of ionic liquid was investigated by performing several runs under the optimum reaction conditions. The results were shown in Fig. 3. After each run, the ionic liquid was separated and dried under vacuum for 5 h at 120 °C. The recyclability data of this catalyst showed that [HSO_3-pmim]HSO_4 owned highly stability except the third time during the reaction process. The yield remained unchanged even after the catalyst had been recycled for six times. At the third time, the ionic liquid phase without treating was used to the transesterification and the lower yield of biodiesel was obtained. Glycerin outgrowth in the mixture was responsible for lower yield of biodiesel. Based on above experiment results, we found that the Brønsted acid ionic liquids performed well as catalysts in the transesterification with high activity and stability and prospects for industrial applications.

Conclusion

It was demonstrated that [HSO_3-pmim]HSO_4 was an effective catalyst for transesterification in this study. The optimum reaction conditions were molar ratio methanol to oil of 13:1, catalyst amount of 4 %, temperature of 120 °C and duration of 8.5 h, in which a maximum yield of biodiesel 94.7 % was obtained. The ionic liquid [HSO_3-pmim]HSO_4 showed high activity for transesterification and without noticeable drop in activity after reusing five times. The biodiesel content of final products purified by molecular distillation was 96.53 wt. %. The strategy of using [HSO_3-pmim]HSO_4 as catalyst would be feasible for application of biodiesel industry.

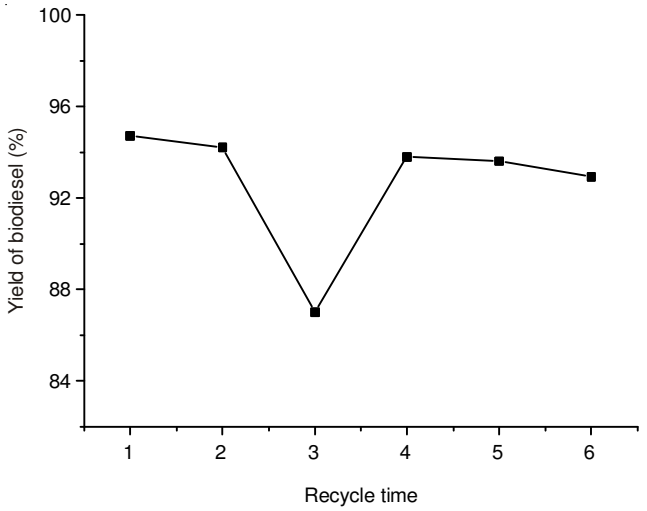


Fig. 3. Catalyst recycling of transesterification of soybean oil with methanol, Reaction conditions: molar ratio of methanol/oil 13:1; catalyst amount of 4 %; temperature of 120 °C; reaction time of 8.5 h

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