Esterification of oleic acid to biodiesel using magnetic ionic liquid: Multi-objective optimization and kinetic study

Ahmad Hafiidz Mohammad Fauzi, Nor Aishah Saidina Amin *, Ramli Mat

Chemical Reaction Engineering Group (CREG), Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

HIGHLIGHTS

- Esterification of oleic acid using magnetic ionic liquid.
- Multi-objective optimization was performed for two responses.
- Both predicted yield and conversion were 83.4% at optimum conditions.
- Recycled ionic liquid can be used repeatedly without significant activity loss.
- Low activation energy and pre-exponential factor for esterification of oleic acid.

ARTICLE INFO

ABSTRACT

The esterification of oleic acid in the presence of magnetic ionic liquid, 1-butyl-3-methylimidazolium tetrachloroferrate ([BMIM][FeCl$_4$]) at reaction temperature of 65 °C has been investigated. Artificial neural network-genetic algorithm (ANN-GA) was used to simultaneously optimized methyl oleate yield and oleic acid conversion for the reaction. It was found that optimum responses for both yield and conversion were 83.4%, which can be achieved using molar ratio methanol–oleic acid of 22:1, catalyst loading of 0.003 mol and reaction time at 3.6 h. Esterification of oleic acid at optimum condition using recycled [BMIM][FeCl$_4$] registered not much loss in catalytic activity after six successive runs. Kinetic study indicated that the reaction followed a pseudo-first order reaction, with activation energy and pre-activation energy of 17.97 kJ/mol and 181.62 min^{-1}, respectively. These values were relatively low compared to homogeneous or heterogeneous catalysts for esterification of oleic acid. Thus, [BMIM][FeCl$_4$] is a promising new type of catalyst for conversion of high free fatty acid (FFA) feeds to biodiesel.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

In the wake of today's environmental concerns and limited fossil fuel resources, biodiesel has stepped up to be a viable solution to both problems. Biodiesel can be obtained via transesterification of triglycerides or esterification of free fatty acids (FFAs), where these reactions require the presence of alcohol to produce fatty acid alkyl esters (FAAEs) [1]. Triglycerides occur naturally in vegetable oils and animal fats, thus reducing the dependency on fossil fuel for energy. Some biodiesel properties are even superior to petroleum diesel. Its higher flashpoint ensures safety of biodiesel during transportation or distribution, while higher cetane number indicates that biodiesel has a higher combustion efficiency [2]. Generally, carbon monoxide, carbon dioxide, oxides of nitrogen and sulfur oxides are reduced for exhaust emissions from biodiesel combustion [3]. The reductions are beneficial for the environment, especially carbon dioxide as it is one of the main greenhouse gases that contributes to global warming phenomena.

Different range of materials can be used for biodiesel synthesis. These include vegetable oils such as soybean, rapeseed, canola, and palm [1]. In order to avoid competition with food sector, non-edible sources are utilized. Examples of these types of feedstock are waste cooking oil (WCO), and *Jatropha curcas*. However, they usually have higher FFAs content, which is not preferable for alkali-catalyzed process. A significant amount of FFAs in the feedstock can reduce the efficiency of the alkaline catalyst, where FFAs react with the catalyst and leads to the formation of soap and water through the saponification process [2]. This reaction is undesirable as it complicates the separation of products further downstream, and also consumes alkali catalysts. Consequently, a longer production process is required due to the loss of catalyst activity, and further resulted in higher operating cost.

Acid catalysts are preferable for conversion of FFAs to alkyl esters. The catalysts are able to tolerate high FFAs content in the feedstock. Sulfuric acid (H$_2$SO$_4$) is usually used as the conventional

---

* Corresponding author. Tel.: +60 7 553 5579; fax: +60 7 558 8166.
E-mail address: noraishah@cheme.utm.my (N.A.S. Amin).

catalyst in esterification of FFAs. Aranda et al. [4] explained that the higher H_2SO_4 catalytic activity in the esterification of palm fatty acids was due to its ability to protonate the carboxylic moiety of the fatty acid and also accelerate the formation of the tetrahedral intermediate. Although the catalyst effectively converts FFAs to biodiesel, there are some concerns regarding its utilization, which includes corrosion to the equipments and also its effluent is hazardous to the environment [5]. Since then, different types of catalysts have been developed and studied in order to obtain higher biodiesel yield. Heterogeneous catalysts allows easier separation from products after reaction and can be further recycled, thus eliminating dangerous acidic wastewater. Sulfated zirconia [6], tungsten oxide zirconia [7], and heteropoly acid [8] are heterogeneous catalyst that have been previously used for biodiesel synthesis.

In recent years, there have been growing interests in using ionic liquids (ILs) as catalysts in biodiesel synthesis. Among attractive characteristics offered by ILs are virtually negligible vapor pressure, high thermal stability, excellent solubility and miscibility with reactants, and also the acidity and basicity of ILs that can be tuned or controlled [9]. Ionic liquids with acidity nature are preferred for biodiesel production. Most ionic liquids involved in biodiesel synthesis can be categorized as Brønsted acidic ILs [5,10,11], while Lewis acid IL [12] and basic IL catalyst [13] have also been applied for the synthesis. The use of ionic liquid to catalyze transesterification and esterification reactions for biodiesel production has been reviewed recently [9,14].

In the pursuit of searching for an ionic liquid catalyst that can improve biodiesel synthesis, the magnetic property can facilitate the separation of IL from the homogeneous reactants. Hayashi and Hamaguchi [15] discovered a new type of IL that response to an externally applied magnetic field, and demonstrated that the IL showed a strong response towards a magnet placed nearby. The magnetic ionic liquid, 1-butyl-3-methylimidazolium tetrachloroferrate ([BMIM][FeCl4]) contains tetrachloroferrate anion ([FeCl4]−), which is said to exhibit paramagnetic properties, thus displays magnetic behavior under the influence of magnetic field. This property is potentially beneficial for the recovery of the catalyst and eliminates the generation of wastewater for removing the catalyst from the biodiesel product. The same type of IL has been employed as catalysts in several reactions. The IL was employed for catalyzing the synthesis of 3,4-dihydropyrimidin-2(1H)-ones via Bignelli condensation, where high product yields were obtained even for low catalyst loading (i.e. 0.5–1 mmol of [BMIM][FeCl4]) [16]. In another process, Wang et al. [17] successfully utilized the Lewis acidic [BMIM][FeCl4] to catalyze acetylation of alcohols and phenols and also conversion of aldehydes, with the recycled IL can be reused in six successive runs without significant drop in the product yield. With similar characteristics suitable for catalyzing esterification reaction, the catalyst, which has not been used in any prior studies concerning biodiesel production, is tested in this work.

In this study, artificial neural network coupled with genetic algorithm was employed to simultaneously optimize two responses for oleic acid esterification. It is essential to understand that the single- and multi-objective optimization processes are theoretically different. Baños et al. [18] explained that single response optimization provides only a single solution with a single optimized solution as the outcome, while multiple responses optimization gives a set of optimal solutions, particularly Pareto-based optimization method that is based on the Pareto-dominance relationships containing non-dominated solutions. A set of non-dominated solutions is known as Pareto front, where it is not possible to improve one objective without worsening any other objective for any of the solution [19]. Multi-objective optimization have been successfully applied in chemical reaction processes involving simultaneous responses, including oxidative coupling of methane for hydrocarbons production [20], alkali-catalyzed transesterification of waste cooking oil for biodiesel production [21], and non-catalytic combined reforming for synthesis gas formation [22].

Kinetic studies for esterification reaction have been conducted using both homogeneous and heterogeneous catalysts [23–27]. Activation energy (E_a) is often reported to determine the minimum amount of energy required for the esterification reaction to occur. Esterification of free fatty acids in sunflower oil was catalyzed by H_2SO_4, followed by the development of kinetic model [23]. In the report, they determined that the higher H_2SO_4 concentration employed resulted in higher activation energy, plus the activation energy for the forward reaction was larger than for the reversed reaction in the equilibrium system. Song and co-workers [24] determined the kinetic parameters for esterification of oleic acid in subcritical methanol and zinc acetate ($Zn(CH_3COO)_2$) as the catalyst. They found that the reaction order was 2.2, while E_a was 32.6 kJ/mol. The presence of methanol in subcritical form resulted in reasonably low activation energy compared to other reaction using heterogeneous catalyst. Esterification of oleic acid was carried out in the presence of 12-tungstophosphoric ($H_3PW_{12}O_{40}$) acid with methanol [25]. The process followed first order reaction, and the activation energy was determined to be 51.0 kJ/mol. Although biodiesel synthesis via esterification reaction have been conducted using ionic liquids as catalysts [5,10], however the kinetic study of the reaction has been scarce.

In this paper, magnetic ionic liquid (MIL), 1-butyl-3-methylimidazolium tetrachloroferrite ([BMIM][FeCl4]) was utilized to catalyze the esterification of oleic acid to biodiesel. Oleic acid was chosen as the model compound for feeds with high free fatty acid contents such as microalgae, *J. curcas*, and waste cooking oil. Table 1 lists feedstocks and their respective free fatty acid contents [28–32]. Multi-objective optimization was conducted to simultaneously determine the optimal value of two responses: methyl oleate yield and oleic acid conversion. Next, the performance of the recycled MIL in the process was observed and evaluated. Finally, kinetic study of oleic acid esterification using MIL was performed to determine the kinetic parameters, including the reaction rate constants at different temperatures, the activation energy of the reaction, as well as the pre-exponential factor.

2. Methods

2.1. Materials

All chemicals were commercially available and used without further purification. Oleic acid of high purity was purchased from QReC, New Zealand while methanol was obtained from Merck, Germany. Ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) and ferric chloride hexahydrate ($FeCl_3·6H_2O$) were also acquired from Merck (Germany) and were used for the preparation of magnetic ionic liquid.

2.2. Catalyst preparation

The catalyst, 1-butyl-3-methylimidazolium tetrachloroferrite ([BMIM][FeCl4]) was prepared following the method suggested

Table 1
Free fatty acids content in biodiesel feedstocks.

Feedstocks	FFAs content (%)	References
Chlorella oil	5.1	[28]
Waste cooking oil	8.7	[29]
Coconut oil	12.8	[30]
Animal fats	4.9–13.5	[31]
Jatropha curcas oil	14.0	[32]
Karanja oil	18.0	[32]

by Wang et al. [33]. [BMIM][Cl] (0.15 mol) was mixed with $FeCl_3 \cdot 6H_2O$ (0.15 mol) under vigorous stirring, and the mixture was stirred for 24 h. Upon completion, two distinct layers were formed, where the darker layer containing [BMIM][FeCl$_4$] was separated from the light layer containing mostly water after being centrifuged at 4500 rpm for 10 min. The catalyst layer was then heated in the oven at 105 °C for 24 h to evaporate water.

2.3. Design of experiment

Central composite design (CCD) was used for designing the experiment in order to gather enough information that will be used in the optimization part later. Three independent variables were chosen for the experiment, namely methanol to oleic acid molar ratio (X_1), catalyst loading (X_2) and reaction time (X_3). Table 2 tabulates the levels of independent variables and experimental plan based on CCD. A total of 16 experiments were generated based on CCD, including 8 factorial points, 6 axial points and 2 centre points.

2.4. Esterification of oleic acid

The process was conducted in a 100 ml three-necked flask attached to a reflux condenser, and a thermometer was used to monitor the reaction temperature. In brief, 0.05 mol (15.8 ml) oleic acid, 30.34–50.57 ml methanol (corresponding to 15:1–25:1 M ratio of methanol to oleic acid), and 5–15 mmol IL were charged into the flask. Experiments were carried out for 4–6 h, with constant stirring rate and reaction temperature (65 °C) for all the runs. After every reaction, the reaction mixture was poured into a separating funnel and allowed to settle overnight after which two distinct layers were observed in the funnel. The upper layer consisted of methyl oleate or biodiesel, while IL and water can be found in the lower layer, which was then isolated by decantation. Distilled water was used to wash the upper layer to remove any impurities present. It was later subjected to removal of water traces and unreacted methanol by putting the sample in the convection oven at 105 °C for 24 h.

2.5. Analysis of methyl oleate

Methyl oleate is the product formed by esterification of oleic acid in the presence of methanol. It is one of the component with high content in fatty acid methyl ester (FAME) or biodiesel, depending on type of feedstocks used for biodiesel synthesis. For the analysis of the product, firstly methyl oleate content in the final product was determined by using a gas chromatograph (GC) equipped with a flame ionization (FID) detector (Perkin Elmer, USA). The analysis was conducted using a DB-Wax column (30 m × 0.53 mm, 0.5 μm), where 1 μl of sample was injected into the GC for each run. The injector temperature was set to 250 °C, while the detector temperature was kept at 270 °C. The oven temperature was maintained at 60 °C for 1 min, and then increased to 220 °C in 10 min as the final oven temperature. Nitrogen was used as the carrier gas for the GC.

Methyl oleate yield (Y_1) and oleic acid conversion (Y_2) were the responses in this study. Methyl oleate content (C) was expressed as a relative percentage of the total peak area, and the methyl ester was identified by comparing its retention time to the retention time of methyl oleate standard. Then, methyl oleate yield was calculated by multiplying C with the ratio of the weight of methyl oleate to the weight of oleic acid used in the feed, as in the following equation:

$$\text{Methyl oleate yield, } Y_1 \, (\%) = C \times \frac{\text{Weight of product (g)}}{\text{Weight of oleic acid in feed (g)}} \times 100\% \quad (1)$$

The conversion of oleic acid to methyl oleate was determined by titration with a 0.1 M potassium hydroxide (KOH) standard solution, according to Eq. (2) [11].

$$\text{Oleic acid conversion, } Y_2(\%) = \left(\frac{AV_i - AV_t}{AV_i}\right) \times 100\% \quad (2)$$

where AV_i is the initial acid value (i.e. acid value of oleic acid), while AV_t is the final acidic value of methyl oleate produced.

2.6. Kinetics measurements and analysis

Esterification of oleic acid in this part was performed using a set of variables obtained from the multi-objective optimization part. Methanol-oleic acid molar ratio was set to 22:1 (44.5 ml), with catalyst loading of 3 mmol, and the reaction was conducted for 3.6 h. Different reaction temperatures were used for this part of the study in order to collect sufficient data for kinetic profile analysis (i.e. $T = 40, 50, 60, 65$ and 70 °C). The sampling was done every 36 min to observe the change in oleic acid conversion during the reaction. The conversion was determined by titration with a 0.1 M potassium hydroxide (KOH) standard solution as mentioned previously. Reaction rate constant (k'), activation energy (E_a) and pre-exponential factor (A) for the esterification reaction was then calculated. An important equation that relates reaction rate constant with activation energy is the Arrhenius equation in the following equation.

$$\ln K' = \frac{E_a}{-RT} + \ln A \quad (3)$$

where R is the gas constant (J/K mol) and T is the temperature (Kelvin). Change in reaction temperature leads to change in value of k', which then can be used to determine the activation energy and pre-exponential factor of the reaction using Eq. (3) by plotting the relationship between the reaction rate constant with temperature.

3. Results and discussion

3.1. Experimental results and ANOVA analysis

The experimental results for esterification of oleic acid catalyzed by [BMIM][FeCl$_4$] are tabulated in Table 3. The methyl oleate yield differed from 58.6% to 73.2%, while the conversion varied between 77.1% and 89.2%, depending on the conditions of the experiments. It can be seen that the chosen process variables resulted in higher conversion than yield for all runs, thus multi-objective optimization was utilized to increase the yield, but at the same time maintaining high conversion.

The conformity between the experimental and predicted responses was evaluated based on their respective coefficient of regression (R^2). For methyl oleate yield, the value of R^2 was 0.966, while the value of R^2 for oleic acid conversion of 0.920. Ideally, when the value of R^2 is 1, this represents a complete agreement between the predicted and experimental responses. Based on R^2 obtained, it can be concluded that the networks used for

Table 2
Experimental range and level of independent variables.

Factors	Symbol	Range and levels		
		−1	0	+1
Methanol: oleic acid molar ratio	X_1	15:1	20:1	25:1
Catalyst loading (mol)	X_2	0.005	0.010	0.015
Reaction time (h)	X_3	4	5	6

Table 3
Experimental and predicted responses for esterification of oleic acid.

No.	Process variables			Yield, Y_1 (%)		Conversion, Y_2 (%)	
	X_1	X_2 (mol)	X_3 (h)	Experimental	Predicted	Experimental	Predicted
1	25:1	0.015	4	58.6	58.6	80.8	80.8
2	25:1	0.005	4	72.5	72.7	80.0	80.1
3	15:1	0.005	4	66.5	65.6	81.3	81.3
4	15:1	0.005	6	59.8	58.3	85.3	85.3
5	20:1	0.010	5	57.2	59.0	79.8	83.2
6	20:1	0.010	3	69.4	69.4	77.1	77.1
7	11.6:1	0.010	5	59.1	59.0	84.3	84.3
8	28.4:1	0.010	5	67.8	65.8	85.2	85.2
9	20:1	0.010	7	64.2	64.2	85.5	85.5
10	15:1	0.015	6	69.8	69.7	83.4	84.5
11	25:1	0.005	6	73.2	73.2	88.1	88.1
12	15:1	0.015	4	71.6	71.6	81.6	81.6
13	20:1	0.010	5	60.8	59.0	83.4	83.2
14	20:1	0.002	5	67.9	68.2	86.7	86.7
15	20:1	0.018	5	65.2	64.4	83.9	83.9
16	25:1	0.015	6	70.5	70.5	89.2	89.2

the prediction of the responses were able to cover more than 90% of the variability in the experiments.

The analysis of variance for both responses in oleic acid esterification is given in Table 4. None of the variables was significant to the methyl oleate yield, as shown by low F-values and high P-values (Prob > F). On the other hand, reaction time (X_3) was the only variable that was significant at 95% confidence level in oleic acid conversion, with F-value of 6.9 and p-value of 0.032. Mazaheri et al. [34] explained that for a factor to have large effect on the response, the corresponding F-value must be high, while p-value must be low (<0.05) for analysis at 95% confidence level.

3.2. Development and training of the network

The number of neurons in hidden layer is an important parameter for a feed forward backpropagation (FFBP) network. Too many neurons can cause overfitting of the data, where the network fails to relate the relationship between patterns, while insufficient neurons leads to underfitting of the data due to inability to detect the signals in the data set [35]. The lowest mean square error (MSE) recorded for respective number of neurons was then further used to train the network with the experimental data. The plots of mean square error for different number of neurons in hidden layer (e.g. 1–20) for both yield and conversion as responses are graphically presented in Fig. 1. By closer observation, lowest MSE were observed with 10 neurons for methyl oleate yield and 18 neurons for oleic acid conversion. Therefore, the structure of the networks used for further training was 4-10-1 for the first response and 4-18-1 for the second response, which represents 4 inputs in first layer, followed by respective number of neurons in the hidden layer and 1 output in the last layer.

Table 4
Analysis of variance (ANOVA) for oleic acid esterification.

Source	Sum Sq.	d.f	Mean Sq.	F	Prob > F
Response: methyl oleate yield					
X_1	63.95	3	21.32	0.47	0.714
X_2	60.93	3	20.31	0.45	0.728
X_3	76.46	3	25.49	0.57	0.668
Error	225.105	5	45.021		
Total	427.744	15			
Response: oleic acid conversion					
X_1	15.61	3	5.20	1.1	0.429
X_2	17.62	3	5.87	1.25	0.386
X_3	97.53	3	32.51	6.9	0.032
Error	23.555	5	4.71		
Total	157.47	15			

From there, the networks were trained and those with lowest MSE were then used to determine the optimum process parameters for responses. 70% of the data was used to train the network, while the remaining data were used for validating and testing the networks. Levenberg–Marquardt method was selected for training purpose, which involved nonlinear least-squares algorithm for learning the multilayer perceptrons [36]. The learning rate and maximum epochs were set at 0.5 and 100, respectively.

3.3. Interaction between independent variables and methyl oleate yield

Response surface plots facilitated the interaction study of the process variables with methyl oleate yield for esterification of oleic acid using [BMIM][FeCl$_4$] as the catalyst (Fig. 2a–c). The relationship between methanol–oleic acid molar ratio and catalyst loading towards the yield is depicted in Fig. 2a. Methyl oleate yield above 65% was achieved at both lowest (15:1) and highest (25:1) molar ratios provided that the catalyst loading exceeded 0.01 mol. The same trend was observed by Lucena et al. [37], who reported higher yields were obtained when the catalyst loading (H$_2$SO$_4$) increased from 0.5% w/w to 1.0% w/w.

Fig. 2b relates the molar ratio of methanol–oleic acid and reaction time with methyl oleate yield. High yield was achieved in shorter reaction time (4 h) and low methanol–oleic acid molar ratio (15:1), and also longer reaction time (6 h) and higher methanol–oleic acid molar ratio (25:1). Excess methanol used in the reaction lowered the yield, as Zhang et al. [5] explained that the reactants was too dilute and possibly had reduced the esterification rate. In addition, insufficient reaction time also led to low yield as well.

The interaction between catalyst loading and reaction time on methyl oleate yield is shown in Fig. 2c. It is clearly seen that the highest response was achieved (75%) using the combination of lowest catalyst loading (0.005 mol) and shortest reaction time (4 h), with increasing any of these two variables only resulted in lower methyl oleate yield.

3.4. Interaction between independent variables and oleic acid conversion

The graphical representation of interaction between process variables and oleic acid conversion in oleic acid esterification are portrayed in Fig. 3a–c. The relationship between methanol to oleic acid molar ratio and catalyst loading on the conversion is presented in Fig. 3a. Low conversion was observed at higher catalyst loading and medium molar ratio. There was not much difference in the conversion when 0.01 mol catalyst was employed for the whole range of methanol–oleic acid molar ratio. This was in good agreement with the conversion reported by Zhang et al. [5] facilitated by a Brønns acidic ionic liquid, where the conversion remain unchanged after the ratio of ethanol to oleic acid reached 2:1.

Fig. 3b illustrates the response surface plot for interaction of methanol–oleic acid molar ratio and reaction time on the conversion. It was obvious here that reaction time was more significant than molar ratio, as discussed earlier from analysis of variance for oleic acid conversion. Increasing molar ratio did not enhance the conversion for shorter reaction time, but the conversion exceeded 85% for reaction time of 5 h even at low molar ratio. Guo et al. [38] pointed out that reaction with longer reaction time resulted in higher oleic acid conversion in a single-step biodiesel production, as nearly complete conversion was achieved after 5 h.

According to Fig. 3c, maximum oleic acid conversion occurred at catalyst loading of 0.005 mol and reaction time of 6 h. Too much catalyst used in the reaction reduced the conversion. Elsheikh et al. [11] reported that the conversion of FFA decreased for
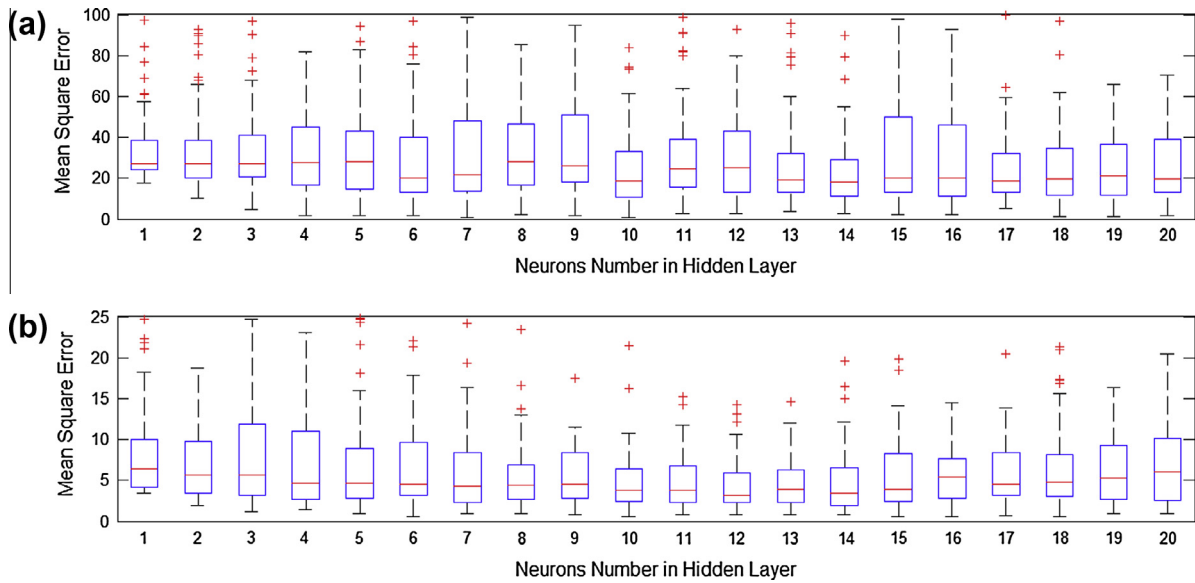
Fig. 1. Mean square error (MSE) for different number of neurons in hidden layer for (a) methyl oleate yield and (b) oleic acid conversion.
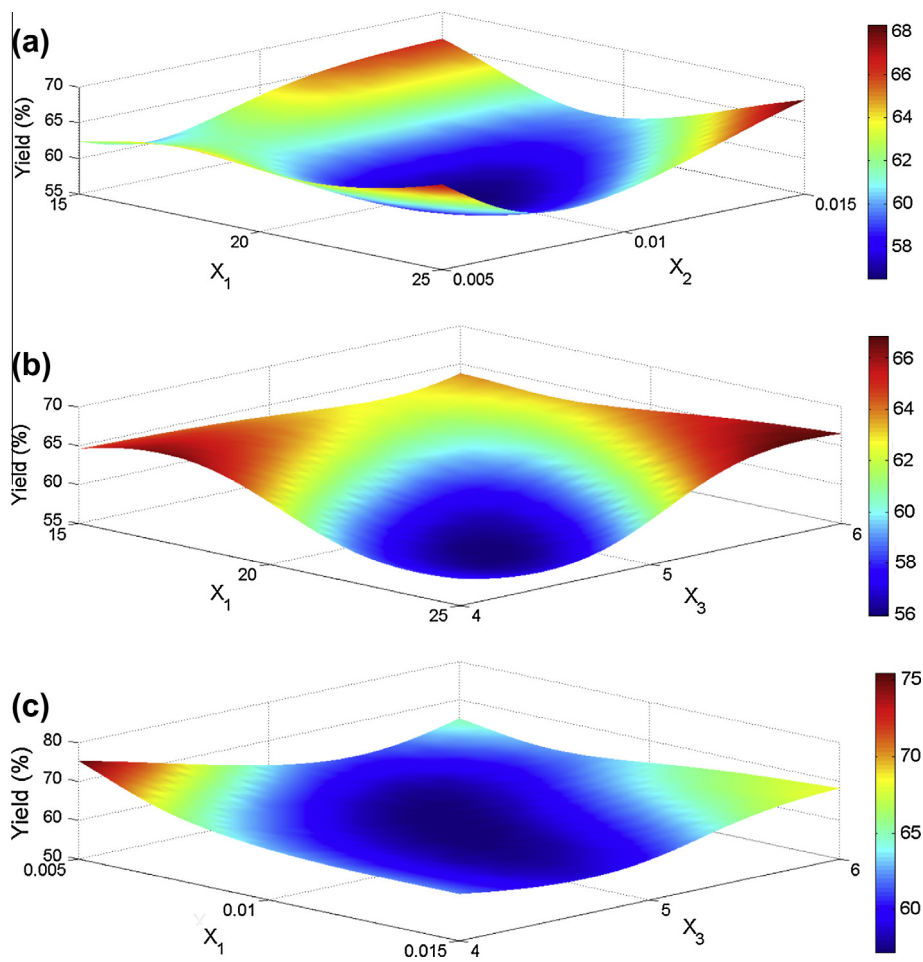

Fig. 2. Response surface plots of methyl oleate yield based on FFBP network as a function of (a) methanol–oleic acid molar ratio (X_1) and catalyst loading (X_2), (b) methanol–oleic acid molar ratio (X_1) and reaction time (X_3), and (c) catalyst loading (X_2) and reaction time (X_3).

catalyst concentration of higher than 4.4 wt% using 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO$_4$]) as the catalyst. Although better conversion can be achieved with more catalyst loading, the high viscosity of ionic liquid may caused mass transfer limitation in the reaction mixture, thus lowering the conversion [39].
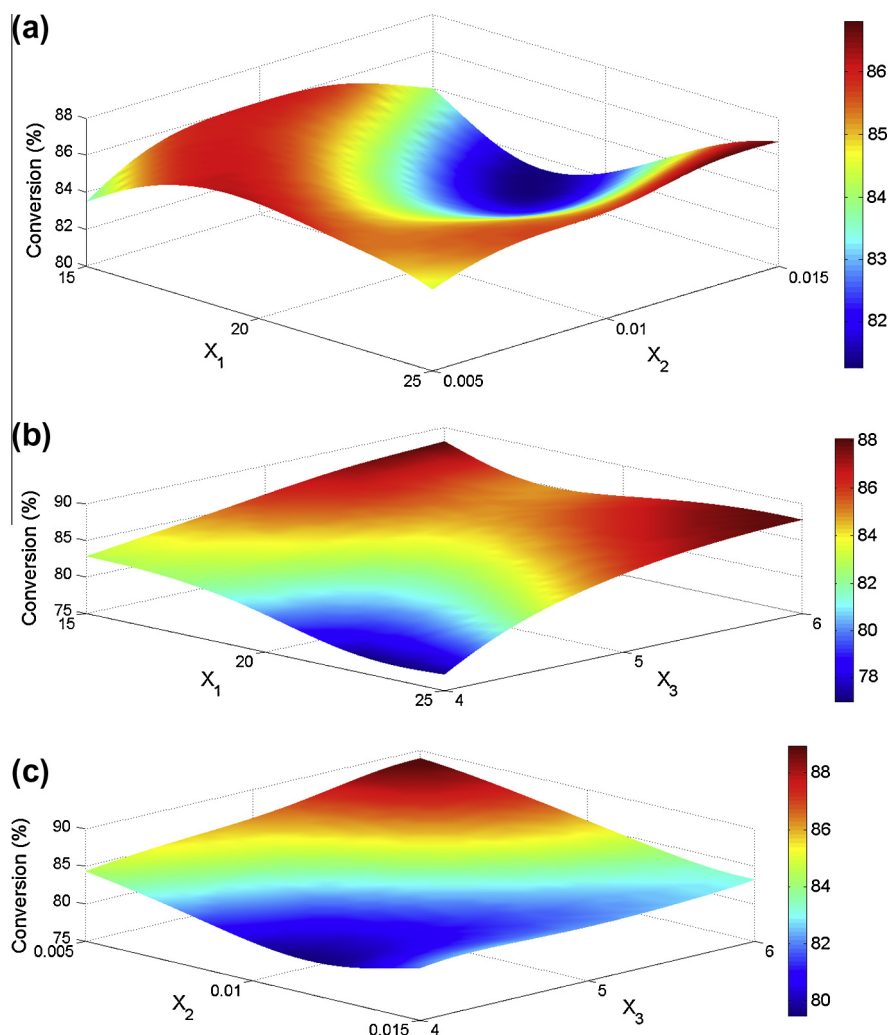
Fig. 3. Response surface plots of oleic acid conversion based on FFBP network as a function of (a) methanol–oleic acid molar ratio (X_1) and catalyst loading (X_2), (b) methanol–oleic acid molar ratio (X_1) and reaction time (X_3), and (c) catalyst loading (X_2) and reaction time (X_3).

3.5. Multi-objective optimization of methyl oleate yield and oleic acid conversion

Prior to the optimization part, the experimental data was used for training of the network, where Levenberg–Marquardt algorithm was applied. After obtaining the best network, the genetic algorithm tool (gatool) available from MATLAB software was launched, and the solver option for multi-objective optimization was selected (gamultiobj). At the end of the run, MATLAB produced several optimal conditions for optimum responses of oleic acid esterification, which are then arranged in Table 5. In addition, the Pareto-optimal solutions for simultaneous optimization corresponding to methyl oleate yield and oleic acid conversion are depicted in Fig. 4. The choice of the final solution (optimal point) was based on the conditions that have same values or almost identical for both responses. From there, a solution on the Pareto front that fulfilled this requirement was identified, where both methyl oleate yield and oleic acid conversion were 83.4%, at the following conditions: methanol to oleic acid molar ratio, 22:1; catalyst loading, 0.003 mol; and reaction time, 3.6 h.

3.6. Comparison between single- and multi-objective optimization

The performance of ANN-GA in predicting optimum conditions for single and multiple responses for oleic acid esterification was studied and the results are shown in Table 6. At optimum conditions, 83.4% methyl oleate yield and 83.4% oleic acid conversion were achieved, which corresponds to process parameters of 22:1 M ratio of methanol to oleic acid, 0.003 mol catalyst loading, and 3.6 h reaction time for simultaneous responses optimization. A lower methyl oleate yield was predicted (82.4%) for single-objective optimization, which can be obtained using 28:1 M ratio of methanol to oleic acid, [BMIM][FeCl$_4$] loading of 0.006 mol, with reaction time of 3.9 h. Although the optimal yield for the single-response is close to the multi-responses optimization, however the latter requires higher catalyst loading and can be uneconomical for the process when considering the cost of the IL catalyst that is several times higher than conventional catalyst used in the process [40].

As for the single-objective optimization for oleic acid, higher optimum conversion was predicted. 90.0% conversion was attainable for the following reaction conditions: molar ratio methanol–oleic, 27:1; catalyst loading, 0.004 mol; and reaction time, 6.7 h. The amount of catalyst used in the reaction was quite similar to the one used in the multi-objective optimization (0.003 mol). It is clearly observed that longer reaction time resulted in higher oleic acid conversion. However, longer reaction needed to reach the optimum conversion can affect the methyl oleate yield as extended reaction time favoured the backward reaction in esterification process (i.e. hydrolysis of esters), especially as water was formed during the reaction, thus lowering yield of methyl esters [41].

Table 5
Multi-objective optimization using ANN-GA for esterification of oleic acid.

No.	Process variables			Predicted responses	
	X_1	X_2 (mol)	X_3 (h)	Yield, Y_1 (%)	Conversion, Y_2 (%)
1	21.9	0.003	3.3	85.6	80.3
2	26.7	0.014	6.5	69.3	90.7
3	22.5	0.002	4.0	79.6	85.6
4	22.3	0.003	3.9	81.0	85.0
5	22.1	0.002	4.2	77.6	86.2
6	22.0	0.004	6.0	70.9	88.2
7	22.0	0.003	3.6	83.4	83.4
8	23.3	0.004	6.1	74.2	87.1
9	22.0	0.003	4.4	74.8	86.3
10	22.1	0.002	3.5	84.4	82.5
11	22.3	0.004	6.0	71.5	88.0
12	21.9	0.003	3.3	85.6	80.3
13	22.8	0.004	6.1	72.9	87.6
14	22.0	0.002	4.3	76.0	86.3
15	22.1	0.003	3.7	82.8	83.9
16	22.3	0.003	3.8	81.6	84.5

3.7. Recycling of [BMIM][FeCl₄]

A distinct feature of the IL that is different from other conventional homogeneous catalyst in biodiesel synthesis is that it can be recovered after each run and then reused in subsequent processes. After the separation of the upper layer containing methyl oleate from the bottom layer consisted of water and spent ionic liquid, the recovery of ionic liquid was carried out by placing the resultant bottom layer of the reaction mixture in the oven at 105 °C for 24 h to ensure complete removal of water and unreacted methanol. The reclaimed IL was then charged into the flask with new batch oleic acid and methanol for subsequent run of esterification reaction. The responses for oleic acid esterification utilizing recycled [BMIM][FeCl₄] are demonstrated in Fig. 5.

Both methyl oleate yield and oleic acid conversion remained unchanged for the first 3 cycles, and started to decline in the 4th cycle. There were not much differences in the yield and conversion for all runs involving recycled IL. Decreasing catalytic activity for recycled ionic liquid have been observed by other researchers [13,42], where the factors affecting the catalytic performance can be explained by the gradual loss of ionic liquid during the separation of upper and bottom layers from the separating funnel, and the presence of glycerine for the process involving transesterification of triglycerides.

3.8. Comparison of different catalysts for esterification of oleic acid

At optimum condition, the conversion of oleic acid for the esterification reaction catalyzed by [BMIM][FeCl₄] reached 83.4%. The obtained conversion was higher compared to the conversion achieved when conventional catalyst (H_2SO_4) was utilized for the reaction. Zhang et al. [5] reported that the conversion of oleic acid
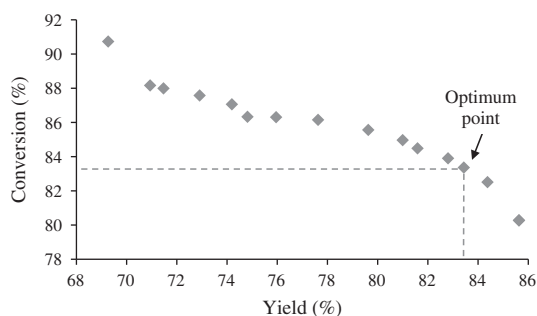
Fig. 4. Pareto front plot of multi-objective optimization responses in oleic acid esterification.

Table 6
Predictions of optimum responses for single- and multi-objective optimization.

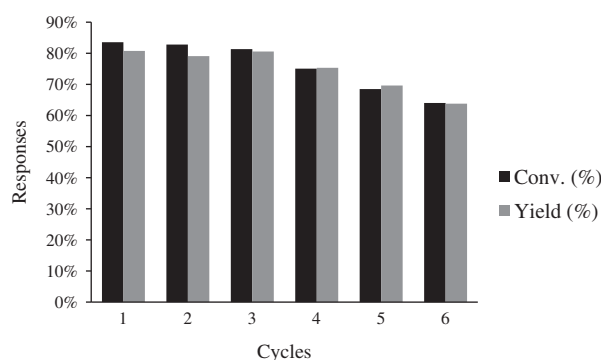| Optimization method	Independent variables			Optimum responses	
	X_1	X_2 (mol)	X_3 (h)	Yield (%)	Conversion (%)
Single-objective (Yield)	28:1	0.006	3.9	82.4	–
Single-objective (Conversion)	27:1	0.004	6.7	–	90.0
Multi-objective	22:1	0.003	3.6	83.4	83.4

Fig. 5. Catalytic performance of recycled [BMIM][FeCl₄].

was 66.9% in 8 h reaction time when H_2SO_4 was employed as the catalyst, but the optimum conversion can be obtained within 3.6 h when using [BMIM][FeCl₄]. Aside from high catalytic activity, the preparation of the catalyst was simple and it can be reused directly in the subsequent esterification processes without significant loss of activity.

We had previously conducted the esterification of oleic acid using a Brønsted acid ionic liquid, 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO₄]), and the predicted responses at optimum conditions for the catalyst and [BMIM][FeCl₄] is summarized in Table 7. The responses were simultaneously optimized using artificial neural network-genetic algorithm based on the experimental data. There was not much difference in the predicted responses for both catalysts. However, the reaction involving [BMIM][HSO₄] needed higher catalyst loading, longer reaction time and higher reaction temperature to achieve appreciable responses. In contrast, comparatively lower catalyst loading and reaction temperature near to methanol boiling point were the advantages of using [BMIM][FeCl₄] for the reaction.

The performance of [BMIM][FeCl₄] in esterification of oleic acid was also better than other ionic liquid employed previously. Zhao et al. [43] employed 1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate [(CH₂)₄SO₃HMIM][CF₃SO₃] for catalyzing the esterification reaction and obtained conversion of 80%, but the process required longer reaction time (6 h) and higher reaction temperature (80 °C). In another literature, Guo et al. [38] screened several ionic liquids for conversion of oleic acid, where a Brønsted acid IL, 1-butyl-3-methylimidazolium methanesulfonate ([BMIM][CH₃SO₃]) prevailed as the catalyst with the best catalytic activity as the conversion reached 93%. However, the reaction temperature was set to 140 °C for high response, while using lower temperature (i.e. 80 °C) only gave conversion slightly above 40%.

4. Kinetic study of esterification using [BMIM][FeCl₄]

Esterification of oleic acid in the presence of methanol is a reversible reaction, and the reaction produces methyl oleate as

Table 7
Performance of [BMIM][HSO₄] and [BMIM][FeCl₄] at optimum conditions.

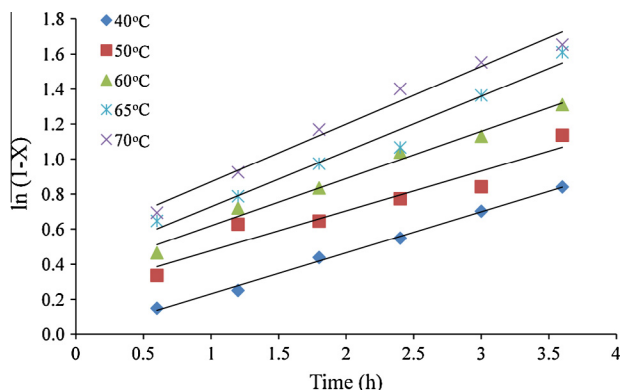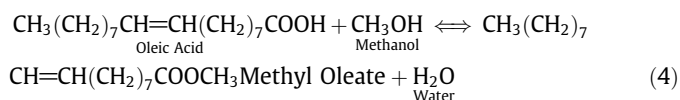| Catalyst	Molar ratio	Catalyst loading (mol)	Time (h)	Temperature (°C)	Yield (%)	Conversion (%)
[BMIM][HSO₄]	8:1	0.06	5.3	90	81.2	80.6
[BMIM][FeCl₄]	22:1	0.003	3.6	65	83.4	83.4

Fig. 6. Plot of ln (1 − X) versus time for determination of reaction rate constants.

the main product, and also generates water. The reaction can be described as in the following equation:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + CH_3OH \underset{\text{Methanol}}{\overset{\text{Oleic Acid}}{\Longleftrightarrow}} CH_3(CH_2)_7$$

$$CH{=}CH(CH_2)_7COOCH_3\underset{\text{Methyl Oleate}}{} + \underset{\text{Water}}{H_2O} \tag{4}$$

The reaction rate for oleic acid esterification can be expressed as in the following equation:

$$-\frac{dC_A}{dt} = kC_A^\alpha C_B^\beta - k'C_C^\gamma C_D^\lambda \tag{5}$$

where C_A, C_B, C_C and C_D are the concentrations of oleic acid, methanol, methyl oleate and water, respectively; α, β, γ and λ are their respective reaction order, and k is the kinetic constant for the forward reaction, while k' is the kinetic constant for the reverse reaction. In accordance with the subsequent steps previously reported by Song et al. [24] and Talebian-Kiakalaieh et al. [8], Eq. (5) can be simplified to the following equation:

$$\ln(1 - X) = k't \tag{6}$$

where X is oleic acid conversion at time t (min), and k' is the reaction rate constant. Two essential assumptions were made in arriving at Eq. (6). In this study, methanol to oleic acid molar ratio used was 22 to 1, which means that there was excess in methanol concentration compared to other components present (i.e. $C_B \gg C_A$, C_C, C_D). Thus, the expression for methanol (C_B^β) can be treated as a constant. Furthermore, excess methanol pushes the equilibrium esterification reaction towards the formation of methyl ester, therefore the kinetic constant for forward reaction outweighs the kinetic constant for reversed reaction (i.e. $k \gg k'$). This leads to another assumption, which is the reaction is predicted to be a pseudo-first order kinetic reaction, which was then justified from the experimental results.

Based on Eq. (6), reaction rate constant for respective temperatures can be determined by plotting graph of ln (1 − X) versus time after obtaining results for esterification of oleic acid at different temperatures. The corresponding plot is displayed in Fig. 6, while Table 8 tabulates the calculated reaction rate constants and their respective coefficients of determination (R^2). There was an increasing trend of reaction rate constants with increasing reaction

Table 8
Reaction rate constants for oleic acid esterification using [BMIM][FeCl₄].

Temperature (°C)	Reaction rate constant, k' (1/min)	Coefficient of determination (R^2)
40	0.2342	0.9961
50	0.2271	0.9235
60	0.2696	0.9848
65	0.3161	0.9744
70	0.3291	0.9797

temperature, with the lowest and highest reaction rate constants were observed at 40 °C and 70 °C, respectively. Furthermore, all reaction rate constants indicated high R^2; thus the assumption of the process having pseudo-first order reaction kinetic was verified. Berrios et al. [23] also found the same order of reaction for the forward reaction in esterification of free fatty acids in sunflower oil catalyzed by H₂SO₄ by making the same assumption of high methanol concentration employed in the reaction.

Values of k' were then used to find the activation energy and the pre-exponential factor for the reaction. The Arrhenius equation (Eq. (3)) was utilized to seek these parameters, where the constants from the linear equation of ln k versus 1/T (K) plot as shown in Fig. 7 were quantified for determination of E_a and A. By calculation, it was found that the activation energy and the pre-exponential factor were 17.97 kJ/mol and 181.62 min⁻¹, respectively. These values were compared with previous results focusing on kinetic study for oleic acid esterification, compiled in Table 9. Both activation energy and pre-exponential factor for this study were comparatively lower than those reported either by using homogeneous or heterogeneous catalysts.

There was a huge difference between the activation energy calculated from the experimental data with those obtained from esterification reaction using conventional catalyst such as sulfuric acid and also other heterogeneous catalysts. The activation energy for this reaction (17.97 kJ/mol) was comparable to the one obtained from esterification of acetic acid using a Brønsted acid ionic liquid, 2-methylpyridine hydrogen sulfate ([Hmpy][HSO₄]) as the catalyst (19.91 kJ/mol) [44]. The comparatively lower activation
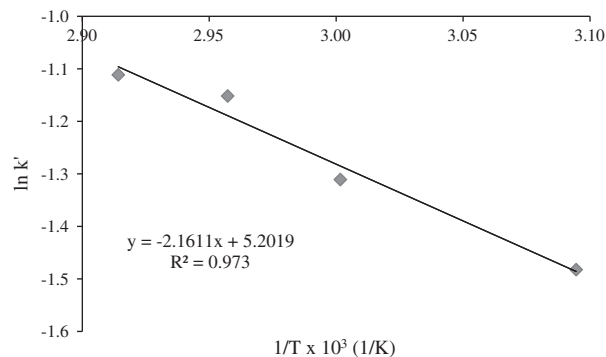

Fig. 7. Arrhenius plot for oleic acid conversion to methyl oleate.

Table 9
Activation energy and pre-exponential factor for oleic acid esterification.

Catalyst	Activation energy (kJ/mol)	Pre-exponential factor	References
H_2SO_4[a]	50.75	2.87×10^6	[23]
H_2SO_4[b]	44.56	3.91×10^5	[23]
$SnCl_2$	46.69	–	[26]
$Zn(CH_3COO)_2$	32.62	120.00	[24]
Tungstated zirconia	51.90	1.5×10^{10}	[27]
$H_3PW_{12}O_{40}$	51.00	–	[25]
[BMIM][FeCl$_4$]	17.97	181.62	This study

[a] 5% H_2SO_4 concentration.
[b] 10% H_2SO_4 concentration.

energy using ionic liquid highlights its feasibility for the esterification process, where the reaction can be conducted at lower energy needs. Thus, this demonstrates the potential of [BMIM][FeCl$_4$] as catalyst in esterification of free fatty acids for biodiesel synthesis at industrial scale.

5. Conclusions

The prepared magnetic ionic liquid [BMIM][FeCl$_4$] was successfully utilized as catalyst for esterification of oleic acid to produce biodiesel in a batch reactor process. By using ANN-GA to conduct multiple responses optimization for methyl oleate yield and oleic acid conversion, both responses were found to be 83.4% under optimal reaction conditions. There was no significant drop in the catalytic activity for the recycled catalyst in oleic acid esterification. The activation energy and pre-exponential factor obtained from the study showed promising result for the application of the catalyst at large-scale production. These values were relatively low compared to previous studies using either homogeneous or heterogeneous catalysts for esterification of oleic acid. Therefore, [BMIM][FeCl$_4$] can be a promising catalyst for esterification of free fatty acid for biodiesel synthesis.

Acknowledgements

References

[1] Leung DYC, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. Appl Energy 2010;87:1083–95.

[2] Meher LC, Vidya Sagar D, Naik SN. Technical aspects of biodiesel production by transesterification – a review. Renew Sust Energy Rev 2006;10:248–68.

[3] Basha SA, Gopal KR, Jebaraj S. A review on biodiesel production, combustion, emissions and performance. Renew Sust Energy Rev 2009;13:1628–34.

[4] Aranda D, Santos R, Tapanes N, Ramos A, Antunes O. Acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. Catal Lett 2008;122:20–5.

[5] Zhang L, Xian M, He Y, Li L, Yang J, Yu S, et al. A Brønsted acidic ionic liquid as an efficient and environmentally benign catalyst for biodiesel synthesis from free fatty acids and alcohols. Bioresour Technol 2009;100:4368–73.

[6] Misi SEE, Wan Omar WNN, Saidina Amin NA. Heterogeneous esterification of free fatty acid to biodiesel. J Inst Eng Mal 2010;71:35–45.

[7] Park Y-M, Lee JY, Chung S-H, Park IS, Lee S-Y, Kim D-K, et al. Esterification of used vegetable oils using the heterogeneous WO$_3$/ZrO$_2$ catalyst for production of biodiesel. Bioresour Technol 2010;101:S59–61.

[8] Talebian-Kiakalaieh A, Amin NAS, Zarei A, Noshadi I. Transesterification of waste cooking oil by heteropoly acid (HPA) catalyst: optimization and kinetic model. Appl Energy 2013;102:283–92.

[9] Mohammad Fauzi AH, Amin NAS. An overview of ionic liquids as solvents in biodiesel synthesis. Renew Sust Energy Rev 2012;16:5770–86.

[10] Fang D, Yang J, Jiao C. Dicationic ionic liquids as environmentally benign catalysts for biodiesel synthesis. ACS Catal 2011;1:42–7.

[11] Elsheikh YA, Man Z, Bustam MA, Yusup S, Wilfred CD. Brønsted imidazolium ionic liquids: synthesis and comparison of their catalytic activities as pre-catalyst for biodiesel production through two stage process. Energy Convers Manage 2011;52:804–9.

[12] Long T, Deng Y, Gan S, Chen J. Application of choline chloride·xZnCl$_2$ ionic liquids for preparation of biodiesel. Chin J Chem Eng 2010;18:322–7.

[13] Zhou S, Liu L, Wang B, Xu F, Sun RC. Biodiesel preparation from transesterification of glycerol trioleate catalyzed by basic ionic liquids. Chin Chem Lett 2012;23:379–82.

[14] Liu C-Z, Wang F, Stiles AR, Guo C. Ionic liquids for biofuel production: opportunities and challenges. Appl Energy 2012;92:406–14.

[15] Hayashi S, Hamaguchi HO. Discovery of a magnetic ionic liquid [bmim]FeCl$_4$. Chem Lett 2004;33:1590–1.

[16] Chen X, Peng Y. Chloroferrate(III) ionic liquid: efficient and recyclable catalyst for solvent-free synthesis of 3,4-dihydropyrimidin-2(1H)-ones. Catal Lett 2008;122:310–3.

[17] Wang D-S, Li G-Y, Peng Y-Q. Chloroferrate(III) ionic liquid as recyclable catalyst for the acetylation of alcohols and phenols and for 1,1-diacylation of aldehydes. J Chin Chem Soc 2009;56:834–8.

[18] Baños R, Manzano-Agugliaro F, Montoya FG, Gil C, Alcayde A, Gómez J. Optimization methods applied to renewable and sustainable energy: a review. Renew Sust Energy Rev 2011;15:1753–66.

[19] Alarcon-Rodriguez A, Ault G, Galloway S. Multi-objective planning of distributed energy resources: a review of the state-of-the-art. Renew Sust Energy Rev 2010;14:1353–66.

[20] Istadi, Amin NAS. A hybrid numerical approach for multi-responses optimization of process parameters and catalyst compositions in CO$_2$ OCM process over CaO–MnO/CeO$_2$ catalyst. Chem Eng J 2005;106:213–27.

[21] Sharma S, Rangaiah GP. Multi-objective optimization of a bio-diesel production process. Fuel 2013;103:269–77.

[22] Ganesan T, Elamvazuthi I, Ku Shaari KZ, Vasant P. Swarm intelligence and gravitational search algorithm for multi-objective optimization of synthesis gas production. Appl Energy 2013;103:368–74.

[23] Berrios M, Siles J, Martín MA, Martín A. A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil. Fuel 2007;86:2383–8.

[24] Song C, Qi Y, Deng T, Hou X, Qin Z. Kinetic model for the esterification of oleic acid catalyzed by zinc acetate in subcritical methanol. Renew Energy 2010;35:625–8.

[25] Fernandes SA, Cardoso AL, da Silva MJ. A novel kinetic study of H$_3$PW$_{12}$O$_{40}$ – catalyzed oleic acid esterification with methanol via ^{1}H NMR spectroscopy. Fuel Process Technol 2012;96:98–103.

[26] Cardoso A, Neves S, Da Silva M. Esterification of oleic acid for biodiesel production catalyzed by SnCl$_2$: a kinetic investigation. Energies 2008;1:79–92.

[27] Zubir MI, Chin SY. Kinetics of modified zirconia-catalyzed heterogeneous esterification reaction for biodiesel production. J Appl Sci 2010;10:2584–9.

[28] Ehimen EA, Sun ZF, Carrington CG. Variables affecting the in situ transesterification of microalgae lipids. Fuel 2010;89:677–84.

[29] Patil P, Deng S, Isaac Rhodes J, Lammers PJ. Conversion of waste cooking oil to biodiesel using ferric sulfate and supercritical methanol processes. Fuel 2010;89:360–4.

[30] Nakpong P, Wootthikanokkhan S. High free fatty acid coconut oil as a potential feedstock for biodiesel production in Thailand. Renew Energy 2010;35:1682–7.

[31] Encinar JM, Sánchez N, Martínez G, García L. Study of biodiesel production from animal fats with high free fatty acid content. Bioresour Technol 2011;102:10907–14.

[32] Patil PD, Deng S. Optimization of biodiesel production from edible and non-edible vegetable oils. Fuel 2009;88:1302–6.

[33] Wang M, Li B, Zhao C, Qian X, Xu Y, Chen G. Recovery of [BMIM]FeCl$_4$ from homogeneous mixture using a simple chemical method. Korean J Chem Eng 2010;27:1275–7.

[34] Mazaheri H, Lee KT, Bhatia S, Mohamed AR. Subcritical water liquefaction of oil palm fruit press fiber in the presence of sodium hydroxide: an optimisation study using response surface methodology. Bioresour Technol 2010;101:9335–41.

[35] Majdi A, Rezaei M. Prediction of unconfined compressive strength of rock surrounding a roadway using artificial neural network. Neural Comput Appl 2012:1–9.

[36] Yuste AJ, Dorado MP. A neural network approach to simulate biodiesel production from waste olive oil. Energy Fuels 2005;20:399–402.

[37] Lucena IL, Silva GF, Fernandes FAN. Biodiesel production by esterification of oleic acid with methanol using a water adsorption apparatus. Ind Eng Chem Res 2008;47:6885–9.

[38] Guo F, Fang Z, Tian X-F, Long Y-D, Jiang L-Q. One-step production of biodiesel from Jatropha oil with high-acid value in ionic liquids. Bioresour Technol 2011;102:6469–72.

[39] Ha SH, Lan MN, Lee SH, Hwang SM, Koo Y-M. Lipase-catalyzed biodiesel production from soybean oil in ionic liquids. Enzyme Microb Technol 2007;41:480–3.

[40] Plechkova NV, Seddon KR. Applications of ionic liquids in the chemical industry. Chem Soc Rev 2008;37:123–50.

[41] Eevera T, Rajendran K, Saradha S. Biodiesel production process optimization and characterization to assess the suitability of the product for varied

environmental conditions. Renew Energy 2009;34:762–5.

[42] Li K-X, Chen L, Yan Z-C, Wang H-L. Application of pyridinium ionic liquid as a recyclable catalyst for acid-catalyzed transesterification of *Jatropha* oil. Catal Lett 2010;139:151–6.

[43] Zhao Y, Long J, Deng F, Liu X, Li Z, Xia C, et al. Catalytic amounts of Brønsted acidic ionic liquids promoted esterification: study of acidity–activity relationship. Catal Commun 2009;10:732–6.

[44] Tao D, Zhang X, Hu N, Li Z, Chen X. Kinetics study of the esterification of acetic acid with methanol using low-corrosive Brønsted acidic ionic liquids as catalysts. Int J Chem Reactor Eng 2012:10.