

Research note

## Biodiesel Production from Soybean Oil Using Ionic Liquid as a Catalyst in a Microreactor

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### ARTICLE INFO

#### Article history:

Received: 2017-01-24

Accepted: 2017-05-30

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#### Keywords:

Biodiesel

Ionic Liquid

Transesterification

Microchannel

Soybean Oil

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### ABSTRACT

*In the present study, Choline hydroxide (ChOH) as an ionic liquid catalyst was used for transesterification of soybean oil into biodiesel in a microchannel reactor. The effects of three variables, i.e., reaction temperature, catalyst dosage, and total flow rate, on fatty acid methyl ester (FAME) content (wt %), were optimized using Box–Behnken experimental design. In order to predict the FAME content, a quadratic polynomial model was obtained. The optimal conditions from the model were reaction temperature of 53.53 °C, catalyst dosage of 2.6 wt %, and total flow rate of 11.82 mL/min. In these conditions, the predicted FAME content was 96.45 wt % and the experimental FAME content was obtained as 97.6 wt %. The proximity of the experimental results and predicted values showed that the regression model was significant. Using the ionic liquid catalyst in the studied microreactor for transesterification leads to diminishing the reaction time to the order of seconds compared to conventional batch systems. In addition, the reusability of ChOH catalyst was investigated. The results revealed that the catalyst had perfect utility after several runs without much loss in the activity.*

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### 1. Introduction

Due to the crisis of fossil fuel availability and increasing environmental pollution by their indiscriminate use, biodiesel is considered as an alternative for fuel resource and clean energy [1]. Biodiesel is mainly produced via transesterification or esterification of vegetable oils and animal fats with alcohol [2]. Transesterification can be catalyzed by different catalysts including homogeneous, heterogeneous or enzymatic catalysis. The homogeneous acids or bases are commonly

used [3]. An alkaline catalyst might react with the free fatty acids and form soap, and this undesirable reaction decreases the yield of the biodiesel and the soap inhibits the separation of the esters from the glycerol. The removal of the homogeneous catalysts after the reaction is technically difficult and a large amount of residual wastewater is produced. Furthermore, these catalysts are corrosive and difficult to remove after the reaction, and the process of separating the catalyst from

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product produces a large amount of wastewater [4].

Recently, ionic liquids that are environmentally-friendly catalysts have attracted considerable attention in biodiesel production. Furthermore, they act as catalysts and solvents simultaneously [5]. In the last decade, investigation of properties and applications of ionic liquids has increased significantly. Ionic liquids are considered as environmentally-friendly replacement for volatile organic solvents and more attractive due to their ability to act as catalysts [6].

For biodiesel production, ionic liquids present an excellent potential as green catalysts. The use of ionic liquids leads to a reduction of the amount of residual water generated in the treatment of biodiesel compared to the traditionally used catalysts, which produce alkaline wastewater. Moreover, high purity glycerol is produced using ionic liquids within 3 or 4 washing steps; however, several purification steps are required to achieve similar purity level using traditional alkaline catalysis. Another advantage of using ionic liquids is the solubility presented by glycerol in a mixture of ionic liquid with methanol. Thus, glycerol is removed from the transesterification equilibrium reaction, and the equilibrium is shifted to product formation, increasing the reaction yield [7-9].

Liang et al. used chlorometallate ionic liquids for the synthesis of biodiesel from soybean oil [10]. 98.5 % conversion of soybean oil was reported after 9 hours of reaction at 70 °C with a methanol-to-oil ratio of 12:1. The great features of the method include ease of operation, low cost of catalyst used, high yields, lack of saponification, and reusability.

Esterification of free fatty acids present in

crude palm oil using ionic liquids based on 1-n-butyl-3-methylimidazolium was studied by Elsheikh et al. [11]. During 3 hours of reaction, 98.4 % yield of biodiesel was obtained.

In a research done by Yassin et al. [12], imidazolium tetrachloroferrate was proved to be a selective catalyst for the transesterification process. After 8 h, the yield achieved 97 %, while 1:10 catalyst-to-oil ratio at 55 °C was used. High yields, no saponification, and reusability of the used catalyst (after 8 times usage) are the important features of this methodology. The ionic liquid was easily separated from the reaction products.

In another work, butyl-methyl imidazolium hydrogensulfate (BMIMHSO<sub>4</sub>) was found to be effective in conversion of waste palm cooking oil to biodiesel by a two-step process [13]. With 5 wt % BMIMHSO<sub>4</sub>, methanol-to-oil ratio of 15:1, 60 min reaction time at 160 °C, and agitation speed of 600 rpm, acid value of the waste cooking oil reduced to lower than 1.0 mg KOH/g. The second step of transesterification was catalyzed by KOH. At 60 °C, 1.0 wt % and 60 min of reaction time the yield was found 95.65 wt %.

Maymandi et al. [14] used Choline hydroxide as an ionic liquid catalyst for producing biodiesel from lipid. At 60 °C, catalyst concentration of 4 wt %, molar ratio of methanol to lipid 6:1 and 2.5 h of reaction time, the yield of methyl ester was obtained as 79.48 %.

Transesterification of Jatropha oil to biodiesel in the presence of Choline hydroxide as a catalyst was performed by Reddy et al. [15]. The yield was obtained as 95 ± 1 % when the reaction was carried out with 9: 1 molar ratio of methanol to oil and 4 wt % catalysts at 60 °C for 4 h. A further

study showed that the catalyst exhibited almost constant activity in four successive experiments after being recycled.

Among the basic ionic liquid catalysts for transesterification of soybean oil to biodiesel, Choline hydroxide showed better catalytic performance, when methanol-to-oil molar ratio was 9:1 and catalyst dosage was 4 wt %. The suitable reaction temperature and the desirable reaction time were reported 60 °C and 2.5 h, respectively. The reusability test showed that catalyst had great performance [16].

As mentioned above, ionic liquids due to their significant environmental benefits and process improvements were interested in the esterification and transesterification process. They act as a solvent and catalyst simultaneously in the reaction [17].

Furthermore, there are some challenges that need to be investigated, such as decreasing reaction time, costs, and increasing the reusability of ionic liquids. Applying micro-structure devices could reduce the process cost by less energy consumption and low amount of fluids. Reduction of reaction time from some hours for the conventional batch system to seconds was conducted by microreactors. To build up a compact micro plant with higher capacities, microreactors of same dimensions are connected in parallel cascade. Therefore, a greater amount of products per reactor volume can be produced in a shorter period of time by these micro scale reactors [18].

However, microreactors have been recently applied in biodiesel production, almost all researchers have used homogenous catalysts, which are not so ecofriendly [19-25].

In the present work, choline hydroxide as a basic ionic liquid catalyst was selected for biodiesel production in a micro scale reactor.

The influences of reaction temperature, catalyst dosage and total flow rate on FAME content were studied and optimized. The box-Behnken experimental design was carried out for optimization of the variables. In addition, the reusability test was performed for the catalyst.

## **2. Materials and methods**

### **2.1. Materials**

In this study, soybean oil was supplied from Nazgol oil company (Kermanshah, Iran). saponification index, average molecular weight, specific gravity and composition of fatty acid are reported in Table 1. Methanol and n-butanol (purity > 99.5 %) were purchased from Merck Co. Ltd. Choline hydroxide (48-50 % W/W), reaction solvent and catalyst, and methyl laurate (methyl dodecanoate, 99.7 %), GC standard were supplied by Kimia-Exir Co. and Sigma-Aldrich, respectively. All materials were employed as received without any further processing.

**Table 1**

Properties and fatty acid composition for soybean oil in this study.

Characterization	
Saponification index (mg KOH/g oil)	191.88
Average molecular weight (g/mol)	863.47
Specific gravity (kg/m <sup>3</sup> )	910
Fatty Acid Composition (wt %)	
Myristic (C14:0)	0.07
Palmitic (C16:0)	10.9
Stearic (C18:0)	6.8
Oleic (C18:1)	22.1
Linoleic (C18:2)	54.2
Linolenic (C18:3)	6.7
Arachidic (C20:0)	0.55

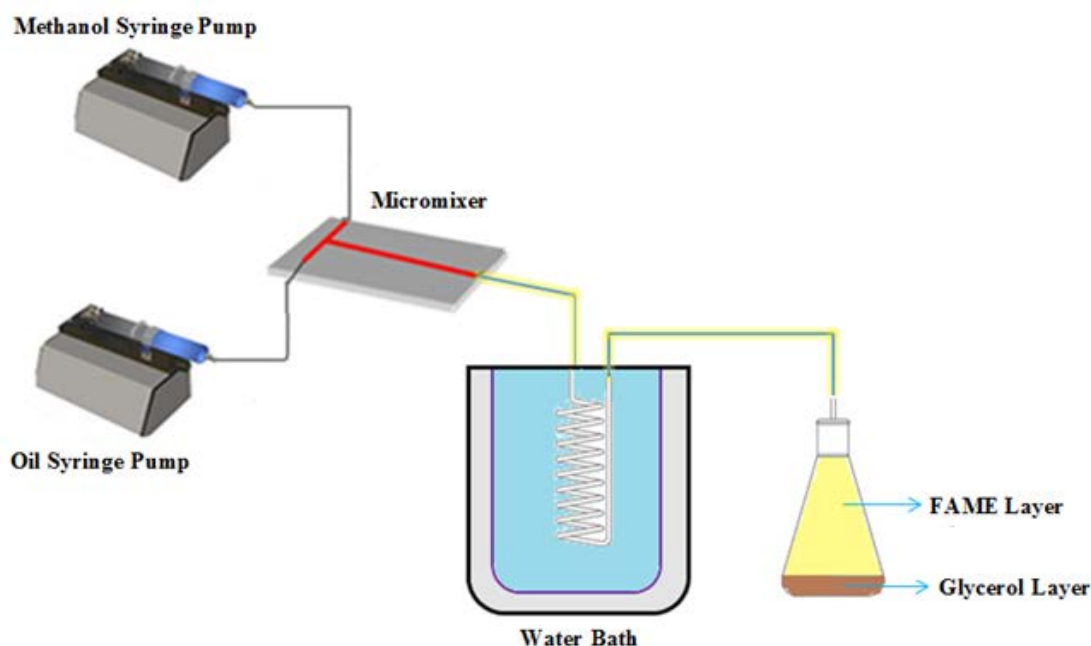
### **2.2. Methods and experimental procedure**

The transesterification reaction was performed in a stainless steel T-junction

micromixer with an inner diameter of 500  $\mu\text{m}$  followed by a tube with an inner diameter of 1.58 mm and length of 1m. The scheme of experimental setup is shown in Fig.1. In order to control and set the reaction temperature, the stainless steel tube was immersed in a temperature-controlled water bath. Catalyst concentrations of 2, 3, and 4 wt % based on the weight of reactants (methanol/oil mixture) were used. Two syringe pumps were applied to inject solution of Choline hydroxide in methanol and the soybean oil at different flow rates. The total flow rate was the sum of the flow rates of the methanol phase and the oil phase, which was adjusted to 10, 20, and 30 mL/min in different experiments. For more description, the volume of reactants was

specified for each experiment according to a basis for methanol to oil molar ratio. Then, the pumps were calibrated for each test in a way that the specified volume of reactants was discharged with total flow rate of 10, 20, and 30 mL/min.

It should be noted that the residence time was controlled by adjusting the total flow rate of reactants (residence time is obtained by dividing the volume of microchannel reactor by total flow rate). Accordingly, the residence times were obtained 11.76, 5.88, and 3.92 s corresponded to the total flow rates of 10, 20, and 30 mL/min, respectively. In all experiments, the molar ratio of methanol to oil was kept constant at 9:1.



**Figure 1.** A scheme of the experimental setup.

Products of the reaction were collected in an erlen meyer flask and, then, transferred into a funnel at ambient temperature. After 15 min, the reaction mixture became biphasic, the upper phase was mainly the desired biodiesel, and the lower phase including ionic liquid, excess methanol, and glycerol.

Then, biodiesel layer was washed with

distilled water and dried at 100 °C for an hour. Afterwards, pure biodiesel was mixed with methyl laurate (internal standard) and subjected to gas chromatograph analysis.

The lower phase was first distilled for removing excess methanol. For separating ionic liquid from glycerol, n-butanol and water were added to the mixture, and then it

was stirred fully. After stirring, two phases were formed. The bottom phase included glycerol and water. The upper phase contained ionic liquid and n-butanol. Finally, n-butanol was removed by distillation and the favorable ionic liquid was reused as a catalyst. The separation procedure was the same after each use. At the end of the reaction, the catalyst was recycled again and repeated several times.

### 2.3. Biodiesel characterization

Characterization of fatty acid methyl esters in biodiesel samples was analyzed by gas chromatography (Agilent, model 6890N) with

a flame ionization detector (FID). The capillary column was a BPX-70 high polar column. The length, film thickness, and internal diameter of the column were 120 m, 0.25  $\mu\text{m}$ , and 0.25 mm, respectively. Nitrogen was used as the carrier gas and also as auxiliary gas for FID. One microliter of the sample was injected using a 6890 gilent series injector with a splitless mode. The inlet temperature of sample was 50  $^{\circ}\text{C}$ , which was heated up to 230  $^{\circ}\text{C}$  at a heating rate 5  $^{\circ}\text{C}/\text{min}$ . Methyl laurate (C12:0) as an internal standard GC reference was added into the samples. Fig. 2 shows the graph of GC analysis.

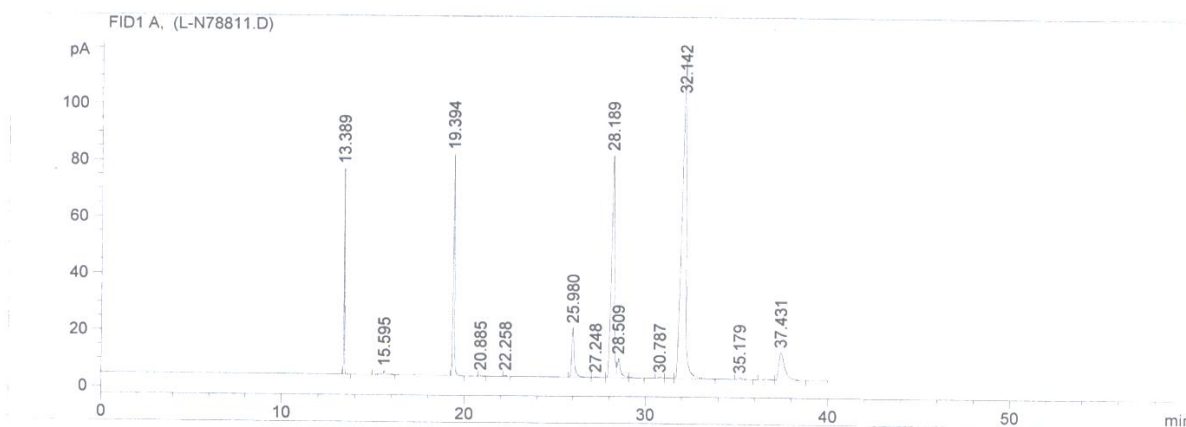


Figure. 2. The graph of GC analysis for biodiesel.

The Fatty acid methyl ester weight percent was calculated using Eq. (1) as follows [26]:

$$\text{FAME (wt \%)} = \frac{(\sum A)}{A_s} \times \frac{W_s}{W} \times 100 \quad (1)$$

where  $\sum A$  is the sum of all areas under the curve from C12 to C24,  $A_s$  is the area under the curve of C12:0,  $W_s$  is the Weight of C12:0 (g), and  $W$  is the Weight of product (g).

### 2.4. Experimental design

Response Surface Methodology (RSM) is a powerful tool for the optimization of chemical reactions and/or industrial processes. It is a

useful statistical technique for complicated processes. It makes use of multiple regression and correlation analyses as tools to assess the effects of independent factors on the dependent variables. In this study, Box-Behnken experimental design technique was applied to investigate the effect of the independent variables on the FAME content as the response and determination of the optimum combination of variables. Independent variables chosen for optimization were the reaction temperature ( $^{\circ}\text{C}$ ) (A), catalyst dosage (wt %) (B), and total flow rate

(mL/min), respectively. The experimental range and levels of the independent variables used for the transesterification reaction are listed in Table 2.

**Table 2**

Experimental range and levels of the independent variables.

Variable	Symbol coded	Range and levels		
		-1	0	1
Reaction temperature (°C)	A	40	50	60
Catalyst dosage (wt %)	B	2	3	4
Total flow rate (ml/min)	C	10	20	30

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). The coefficient of the polynomial model of the response variable was fitted. The general equation of the quadratic response surface model was used:

$$Y = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_{ij} X_i^2 + \sum_{i < j}^k \sum_j^k b_{ij} X_i X_j + e \quad (2)$$

where Y is the response factor (the FAME content), i and j indicate the linear and quadratic coefficients, respectively, b<sub>0</sub> is the regression coefficient, b<sub>i</sub> is the first-order model coefficient, k is the number of factors, and e is the random error.

### 3. Results and discussion

#### 3.1. Statistical analysis

The effect of three independent variables (reaction temperature, catalyst dosage, and total flow rate) on FAME content as response was studied. The total number of experiments was 17, whose replicate number of the central point was 5. Experimental results and predicted values of FAME content are listed in Table 3.

**Table 3**

The Box-Behnken design and the FAME content.

Run	A: reaction temperature (°C)	B: catalyst dosage (wt %)	C: total flow rate (ml/min)	FAME (wt %)	
				Experimental	predicted
1	40	3	30	70.2	70.03881
2	60	3	10	98.6	98.36381
3	40	3	10	74	73.91381
4	50	4	10	98	98.29868
5	50	2	30	89.3	89.24868
6	40	2	20	66.7	67.03618
7	50	4	30	95.5	96.02368
8	50	3	20	93.5	92.92105
9	50	2	10	91.5	91.52368
10	50	3	20	93.4	92.92105
11	50	3	20	92.7	92.92105
12	50	3	20	91.9	92.92105
13	60	4	20	99.8	99.86118
14	60	2	20	94	94.48618
15	40	4	20	75.3	75.21118
16	60	3	30	98	97.68881
17	50	3	20	93.9	92.92105

Based on the experimental design, a quadratic polynomial model (Eq. 2) was obtained for

$$\text{FAME (wt \%)} = 92.9211 + 13.025 * A + 3.3875 * B - 1.1375 * C - 0.7 * AB + 0.8 * AC - 8.7724 * A^2 + 0.8526 * C^2 \quad (3)$$

where A is the reaction temperature (°C), B is the catalyst dosage (wt %), and C is total flow rate. In order to determine the significance of

predicting the FAME content as the response:

the model, analysis of variance (ANOVA) was performed. Results of ANOVA are presented in Table 4.

**Table 4**  
ANOVA for the fitted quadratic polynomial model.

Source	Sum of squares	df	Mean square	F value	p-value
Model	1789.361	7	255.6231	652.0948	< 0.0001
A-reaction temperature	1357.205	1	1357.205	3462.232	< 0.0001
B-catalyst dosage	91.80125	1	91.80125	234.1851	< 0.0001
C-total flow rate	10.35125	1	10.35125	26.40605	0.0006
AB	1.96	1	1.96	4.999963	0.0522
AC	2.56	1	2.56	6.530564	0.0309
A <sup>2</sup>	324.9188	1	324.9188	828.8683	< 0.0001
C <sup>2</sup>	3.069474	1	3.069474	7.830232	0.0208
Residual	3.528026	9	0.392003		
Lack of fit	1.040026	5	0.208005	0.334414	0.8696
Pure error	2.488	4	0.622		
Correlation total	1792.889	16			

The significance level for the value of probability (p-value) is 0.05 (or 95 % confidence limit). The proposed p-value of this study is lower than 0.0001, indicating the significance of the model. From basic analysis of variance, a larger value of regression coefficient  $R^2$  is desired. The value of  $R^2$  for the model is 0.998, implying the desirable fitness. The value of the adjusted coefficient of determination ( $R^2_{Adj}$ ) is 0.9965. Closeness of the values of  $R^2$  and  $R^2_{Adj}$  indicates the significance of the model.

According to p-values of A, B, C, AB, AC, A<sup>2</sup>, and C<sup>2</sup>, they are significant model terms in this work.

Regarding Eq. (2), reaction temperature with higher coefficient value has the maximum effect on the FAME content

followed by catalyst dosage and total flow rate.

Fig. 3 illustrates the predicted versus the experimental values of FAME content. It shows that the results of the model are quite close to the actual data.

### 3.2. Effect of process parameters on FAME content

The effect of operating parameters, reaction temperature, catalyst dosage, and total flow rate with coded units on FAME content is shown in Fig. 4.

This figure shows that FAME content is more influenced by reaction temperature. The FAME content is sharply increased when temperature raises from 40 to 50 °C; afterwards, the increment of FAME is slight

and inconsiderable. At high temperature, viscosity of oil decreases; therefore, reaction rate improves due to more efficient mass transfer between alcohol and oil [27]. Furthermore, increasing temperature of reaction enhances the activity of ionic liquid.

The desirable reaction temperature for Choline hydroxide activity in transesterification was obtained, about 60 °C. Evaporation of methanol at higher temperature causes a decrease of biodiesel production [15, 16].

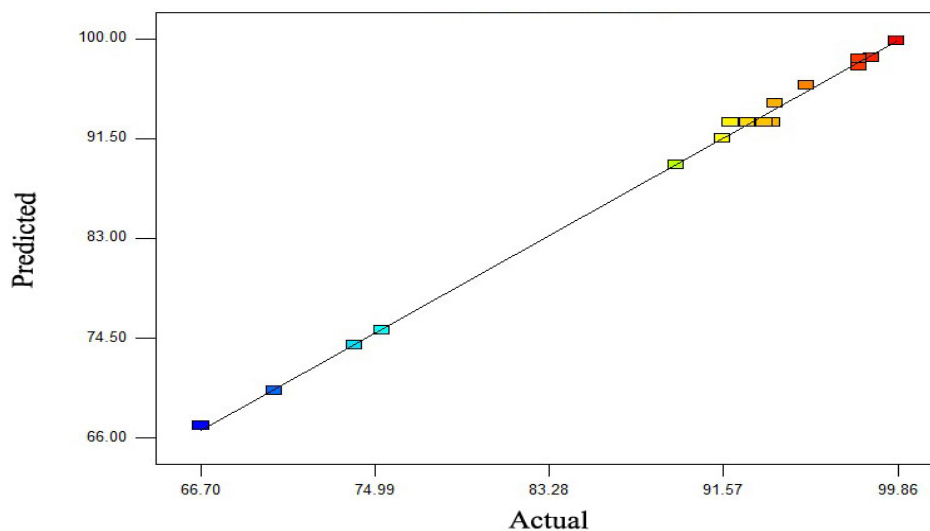


Figure 3. Predicted versus actual FAME content values.

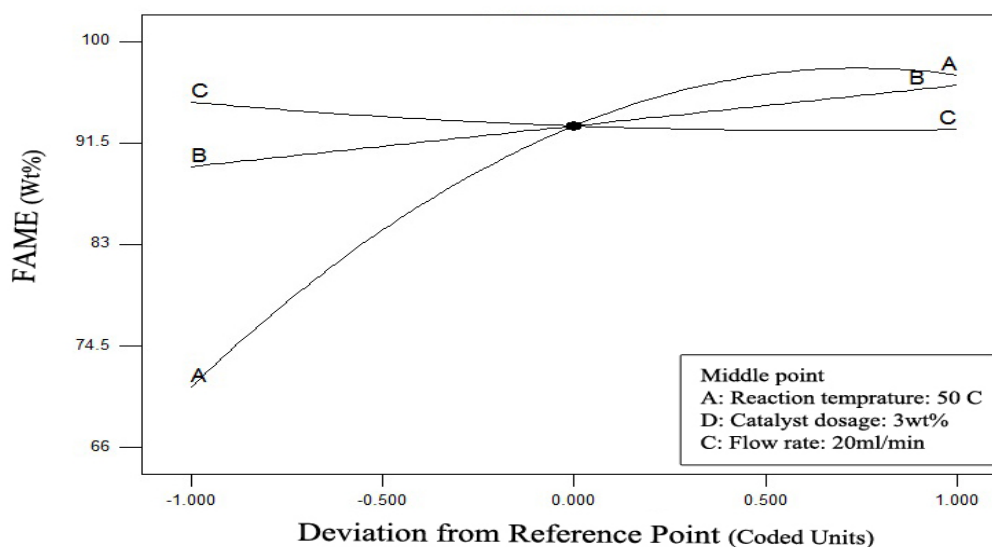


Figure 4. Effect of reaction temperature, catalyst dosage, and total flow rate on FAME content.

From results presented in Fig. 4, it can be seen that the FAME content is increased moderately from 89.53 to 96.31 wt %, when catalyst dosage increases from 2 to 4 wt %. Rising catalyst dosage higher than 4 wt % did

not have a significant impact on increasing the biodiesel yield [16]. In this study, an optimum catalyst dosage was obtained 2.6 wt % which is lower than the proposed amount (4 wt %) in the similar works [15, 16].

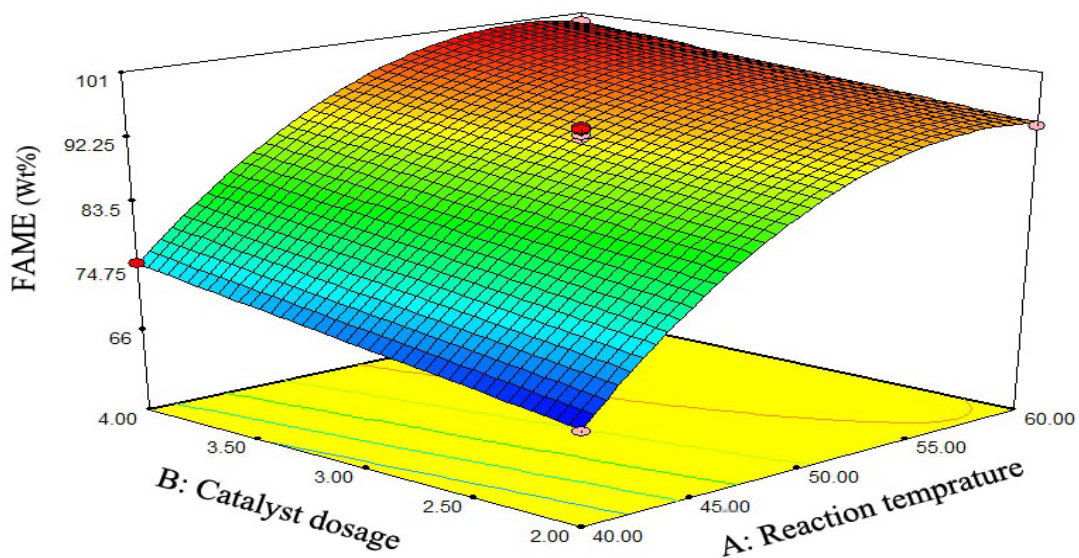


The FAME content is affected by total flow rate of reactants (Fig. 4). Increasing total flow rate from 10 to 30 mL/min causes a slight decline of FAME content from 94.91 to 92.64 wt %. Since large total flow rates are equal to small residence times, the FAME content is reduced by decreasing residence time from 11.76 to 3.92 s. It is obvious that all residence times (3.92-11.76 s) are small enough. By increasing residence time in the microreactor, mass transfer steeply increases between

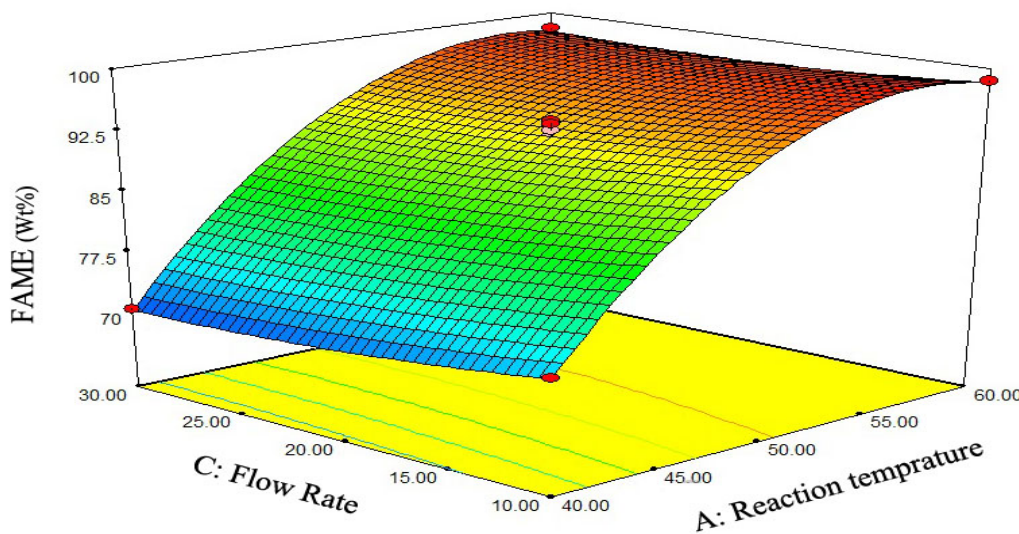
methanol and soybean oil; therefore, increasing the residence time up to 11.76 s is desirable [28].

Fig. 5 shows the interaction of reaction temperature with catalyst dosage on FAME content at constant total flow rate of 20 mL/min.

The effect of reaction temperature and the total flow rate on constant catalyst dosage of 3 wt % is observed in Fig. 6. These figures confirm the results discussed above.



**Figure 5.** Response surface of FAME content vs. reaction temperature and catalyst dosage.



**Figure 6.** Response surface of FAME content vs. reaction temperature and total flow rate.

#### 4. Optimization

The Box-Behnken experimental design was performed to analyze and optimize the operational parameters. In the process of optimization, the FAME content as the response was set maximum, and the process parameters reaction temperature, catalyst dosage and total flow rate were set in the range. A quadratic polynomial model was found to predict the response. By solving the regression equation using Design Expert software (Stat-Ease, trial version), the optimal values of variables were obtained. The optimal conditions of factors are as follows: 53.53 °C reaction temperature, 2.6 wt % catalyst dosage, and 11.82 mL/min total flow rate. The predicted FAME content under the optimal conditions was 96.45 wt %. Under the above conditions, the transesterification was performed three times and the mean of FAME content was obtained 97.6 wt %. The proximity of the experimental data to the predicted values confirms that the model is ideal and reliable.

#### 5. Comparison between the performances of ionic liquid in microreactor with batch reactor

Ionic liquids have been used as catalysts for producing biodiesel from vegetable oils in batch reactors by researchers [7-9]. Reaction times have been reported in the range of hours for high conversion of reactants in those conventional reactors. Fan et al. [16] reported reaction time of 2.5 h at reaction temperature of 60 °C, methanol-to-oil molar ratio of 9:1, and catalyst dosage of 4 wt % by using Choline hydroxide. While, in our study, in the same optimal conditions (reaction temperature of 53.53 °C, methanol-to-oil molar ratio of 9:1, and catalyst dosage of 2.6 wt %), the FAME content was found 97.6 wt

% just after 9.95 s. This significant difference of reaction time is the result of using microreactor. Reduction of reaction time and increment of the reaction rate in the microreactor are controlled by mass transfer effects. Microreactor provides high contact surface area between the immiscible two phases due to the formation of fine segments in the microchannel. Therefore, the rate of mass transfer can increase through segmentation by providing a large specific interfacial area and phase internal total flow [29]. The desirable reaction temperature for Choline hydroxide activity in a batch reactor is proposed 60 °C, while the present study's optimum temperature reaction is found 53.53 °C. In addition, Choline hydroxide dosage is diminished in this microreactor compared to a batch reactor [15, 16]. Comparison demonstrated that the process cost can relatively reduce in microreactors.

#### 6. Reusability of catalyst

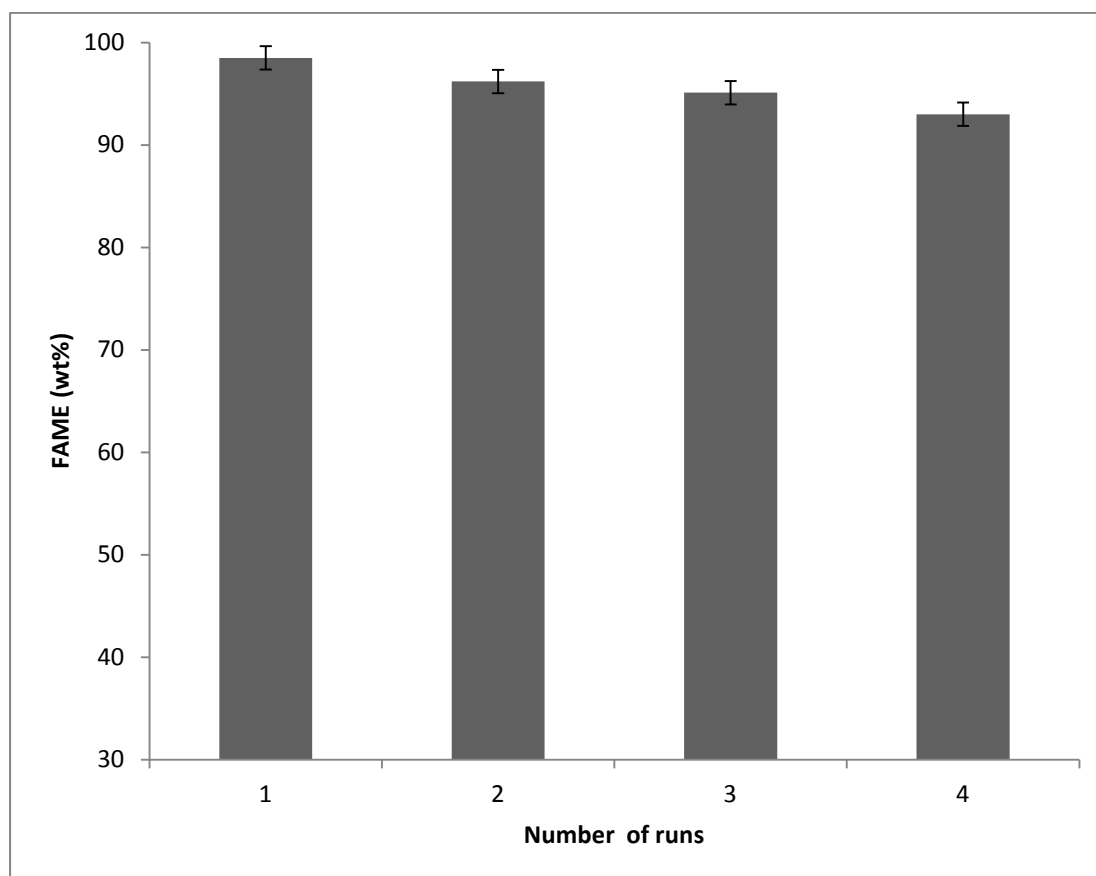
High price of the ionic liquid, compared to common catalysts, causes an increase of focus on the reduction of the process costs by increasing the catalyst reusability. In the present work, the reusability of Choline hydroxide (ChOH) as catalyst was examined.

Under the optimal conditions, 53.53 °C of reaction temperature, 2.6 wt % of catalyst dosage, and 11.82 mL/min of total flow rate, the reusability tests were done. The results of experiments are shown in Fig. 7.

From the Figure, the FAME content was 96.2 wt % for the second time, 95.1 wt % for the third time, and achieved to 93 wt % after four uses. The amount of FAME content was decreased slightly after four runs. Diminishing the activity of Choline hydroxide might be due to the deactivation of catalyst during the separation process. With this

explanation, glycerol accumulation in ionic liquid may decrease the Choline hydroxide

activity. The FAME content reached less than 90 wt % at the fifth usage.



**Figure 7.** Reusability of ChOH catalyst (reaction temperature: 53.53 °C, catalyst dosage 2.6 wt %: and flow rate: 11.82 ml/min).

In the similar work, Fan et al. reused the Choline hydroxide four times in a batch reactor [16]. The biodiesel yield after the fourth repeat was 82.5 %, while, in this work, it was 93 wt %. Therefore, it can be deduced from the microreactor technique in the presence of ionic liquid as the catalyst in transesterification reaction is desirable.

## 7. Conclusions

In this study, transesterification reaction was performed by Choline hydroxide (ChOH) as an ionic liquid catalyst in a microreactor. The Box-Behnken experimental design was used to investigate the effect of variables on the FAME content. Quadratic polynomial model was obtained for predicting the FAME

content. The FAME content was mostly influenced by reaction temperature followed by catalyst dosage and total flow rate. The optimal conditions were found 53.53 °C reaction temperature, 2.6 wt % catalyst dosage, and 11.82 mL/min total flow rate (or 9.95 s residence time). The experimental FAME content was obtained 97.6 wt % in these conditions. Using the ionic liquid catalyst in microreactor for transesterification reaction leads to a decrease in the reaction time to the order of seconds compared with conventional batch systems. The reusability of ChOH catalyst was investigated. The results revealed that the catalyst had perfect utility for repeated use without much loss in the activity. After the fourth reuse, the FAME

content reached 93 wt %. Therefore, the reduction of the reaction time to seconds in microreactor and reutilization of the catalyst for several cycles leads to a decrease in the process costs.

### Acknowledgment

The authors would like to thank the Mahidasht Vegetable Oil Company (NAZGOL) for their kind help in this study.

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