



Investigating the Batch and Continuous Transesterification of Linseed Oil by Using an Alkaline Heterogeneous Catalyst in a Packed Bed Reactor

Mahdi Hashemzadeh Gargari, Seyed Mojtaba Sadrameli*, Mohammad Taherkhani

Department of Process Engineering, Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran.

PAPER INFO
Paper history:

Received 03 December 2017

Accepted in revised form 26 June 2018

Keywords:

 Transesterification
 Linseed Oil
 Continuous Biodiesel Production
 Batch Biodiesel Production
 Heterogeneous and Homogeneous Catalyst

A B S T R A C T

The continuous and batch transesterification of linseed oil were examined in order to maximize the fatty acid methyl esters (FAMES) yield. The continuous process was conducted in a packed bed reactor using calcium oxide as a heterogeneous catalyst. In addition, the impact of two variables, the molar ratio of methanol to oil and the flow rate (ml/min), on the FAME yield were studied. Also, the reaction was performed in the Continuous Stirred-Tank Reactor (CSTR) by using KOH as a homogeneous catalyst in the batch process. Moreover, the influence of the molar ratio of methanol to oil and the catalyst concentration (wt. %) were investigated on the FAME yield. In the both batch and continuous process, FAME yield was optimized by using the Design Expert (Ver. 7.0.0) software. The optimum conditions for the continuous method were reported as follows: the molar ratio of methanol to oil of 11.75:1, a flow rate of 1.07 ml/min and a temperature of 50 °C. Under the optimum conditions, the FAME yield was achieved to 94.94%. Under the optimum conditions, the FAME yield was reached to 95.0672% in the batch process. Also, the optimum conditions for the batch process were as follows: the molar ratio of methanol to oil of 9.12:1, a catalyst concentration of 1.52 wt. %, a temperature of 40 °C, an agitation rate of 650 rpm and a reaction time of 60 minutes.

1. INTRODUCTION

Although the largest energy consumption is now produced by fossil fuels, the increasing price, non-renewability and the environmental disadvantages of them have caused to seek the suitable alternative fuels [1-3]. According to the some advantages, such as renewability, lower greenhouse gas emission, more lubricating than fossil fuels and a high flash point, biodiesel is one of the most attractive alternative fuels. Moreover, biodiesel does not emit SO₂ or extra amounts of CO₂ during the combustion [4, 5]. In the presence of three moles of short-chain alcohol, triglyceride generally transforms into glycerol and biodiesel. Likewise, the production of fatty acid methyl ester (FAME) occurs in a continuous three steps reaction: (i) triglyceride is converted to diglyceride in the presence of one mole of short chain alcohol, (ii) diglyceride produces monoglyceride, and (iii) monoglyceride transforms to glyceride and three moles of methyl ester (see Fig. 1) [4, 6]. Biodiesel synthesis occurs as a result of either batch or continuous processing. In the batch method, the main purpose of investigating the influence of parameters on the FAME yield is optimizing the

reactions conditions. However, in continuous biodiesel production, the effects of parameters on the FAME yield are investigated with the aim of scaling up the process [7]. Different continuous reactors are exploited to produce biodiesel, such as a fixed bed reactor, a packed bed reactor and a rotary fixed bed reactor.

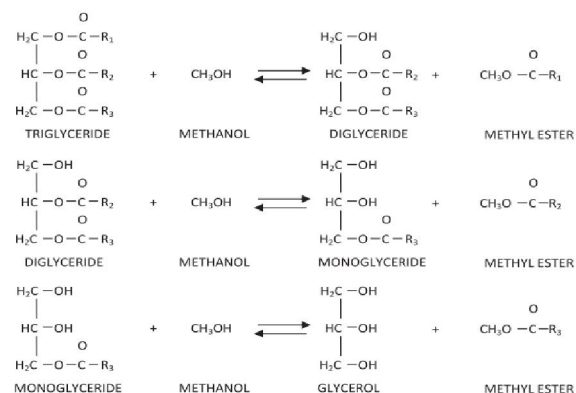


Figure 1. Stoichiometry of production of methyl ester from triglyceride [4]

The main sources of biodiesel production are vegetable oils, animal fats, algae, and waste oils. Non-edible crops, particularly linseed oil, castor oil and Jatropha oil have a good likelihood of being used as a feedstock due

*Corresponding Author's Email: sadrameli@modarcs.ac.ir (S. M. Sadrameli)

to their low prices [8]. In addition, the cost of biodiesel production depends on the type of feedstock available [9]. Although low-priced feedstock contains a higher amount of free fatty acids, this causes problems during the transesterification process. Free fatty acids react with the base catalysts and lead to soap formation, whereas acid catalysts can transform free fatty acids into FAME, such catalysts are more suitable for those feedstocks with a higher content of free fatty acids [10, 11]. The rate of biodiesel production can be increased through the use of various types of catalysts. Catalysts can be either homogeneous or heterogeneous [12]. Although homogeneous catalysts are more active than the heterogeneous ones, they require a complicated process to separate [13]. However, heterogeneous catalysts doesn't need not undergo a complex separation process and they can be reused after regeneration [14]. In continuous biodiesel production, most reactors are packed with exchange resin catalysts and base or acid heterogeneous catalysts either. Sun Peiyong et al. [15] were able to produce biodiesel from oils with the high content of acid in the presence of H_2SO_4 as a homogeneous acid catalyst. A the FAME yield of 99.5% was achieved under the optimum conditions of a 20:1 molar ration of methanol to oil, a temperature of 120 °C and a reaction time of five minutes. Continuous biodiesel production from soybean oil in the presence of a homogeneous base catalyst was investigated in the tubular reactors with static mixers by E. Santacesaria et al. [16]. Furthermore, under the optimum conditions (i.e., a 6:1 molar ratio of methanol to oil, a 2% w/w oil KOH concentration, and a temperature of 60 °C), a FAME yield of 98.2% was obtained. The influence of WO_3/ZrO_2 as a heterogeneous catalyst on biodiesel yield was investigated in a packed bed reactor by Park YM et al. [17]. Biodiesel reached the FAME yield of 70% under the following conditions: a 19.4:1 molar ratio of methanol to oil, a temperature of 70 °C and an operating time of 140 hours. Furthermore, the impact of $Ca(C_3H_7O_3)_2/CaCO_3$ as a syntheses heterogeneous catalyst on the FAME yield was studied in a packed bed reactor by Hsieh LS et al. [18], and a FAME yield of 97% was reported under the following conditions: a 30:1 molar ratio of methanol to oil, a temperature of 60 °C and a residence time of 168 minutes. Applying Mg/Al hydrotalcite as a heterogeneous catalyst in the packed bed reactor seems very beneficial to reaching the conversion rate of 85% for transformation of methyl ester from soybean oil under the optimal conditions (i.e., a 27:1 molar ratio of methanol to oil, a 27.4 g load of catalyst, a temperature of 220 °C, a 5 MPa of pressure and a residence time of 6 minutes) [19].

In the most of the previous works, the opportunity of conventional continuous biodiesel production from various heterogeneous and raw materials has been investigated. An investigation of the literature proves

that no research has been conducted on the optimization of continuous biodiesel production from linseed oil by using calcium oxide as a heterogeneous packed catalyst in the reactor. As long as refluxing occurs in the process, the biodiesel can be utilized as a co-solvent to increase the reaction rate. The influence of the main parameters, including the molar ratio of methanol to oil and a residence time at 50 °C, on the FAME yield was investigated in the continuous process. Also, the effect of the molar ratio of methanol to oil and the homogeneous catalyst concentration (wt. %) were studied on the FAME yield in the batch process. Finally, the optimal conditions were reported for the new reaction system.

2. MATERIALS AND METHODS

2.1. Materials

Linseed oil was provided from a local market in Tehran, Iran. The fatty acid profile of linseed oil by the gas chromatography is presented in Table 1. Potassium hydroxide (99% purity) and methanol (99.99% purity) were purchased from Dr. Mojalali Co. in Tehran. Calcium hydroxide was supplied by Merck.

TABLE 1. Fatty acid profile of linseed oil

Chemical Formula	Fatty acid Composition (wt. %)
C12:0	0.08
C14:0	0.08
C15:0	1.36
C16:0	5.61
C16:1	0.06
C17:0	0.05
C18:0	4.04
C18:1	19.34
C18:2	17.15
C19:0	0.07
C18:3	48.79
C20:0	0.17
C20:1	0.10
Others	3.10

Table 1 shows that linseed oil was an appropriate choice to produce biodiesel due to the high amount of C18:3.

2.2. Procedure of the batch biodiesel production

The reactions were conducted in a 250 mL spherical reactor which was contained two necks and equipped with the magnetic stirring, a thermostat and the condensation systems. Linseed oil of 40 gram of was used for all experiments. First, the linseed oil was filled into the reactor and heated to 40 °C. A solution that was obtained by dissolving a certain amount of catalyst in methanol was prepared. After mixing the linseed oil with the solvent mixture, the reaction was developed

over 90 minutes at 40 °C. The final mixture was placed in a fennel separator to separate the glycerol from biodiesel. Then, the biodiesel was washed with deionized water to remove any catalysts remnant. Finally, water and methanol were removed by heating the mixture at 100 °C for 5 hours.

2.3. The procedure of the continuous biodiesel production

The continuous biodiesel production was carried out in a packed bed reactor. The schematic diagram of the packed bed reactor is shown in Fig. 2. The height and the internal diameter of the reactor were 40 and 3 centimeters, respectively. First, the reactor was packed with calcium oxide (the catalyst) and loaded with 160 grams of catalyst. Second, methanol was poured in the reactor to calculate the volume of the packed bed reactor. Then, the porosity of the reactor was determined by dividing the volume of the packed bed reactor to the overall volume of the reactor (without packing) and it was 18%. Then, linseed oil and methanol were pumped into the reactor by two peristaltic pumps. The reactor was isolated to avoid the heat transfer and the transesterification reaction process progressed at 50 °C over 120 minutes. Finally, the main product was collected in the fennels by separating the biodiesel from glycerol. Subsequently, after washing the biodiesel and eliminating methanol from it, the pure biodiesel was stored for analysis.

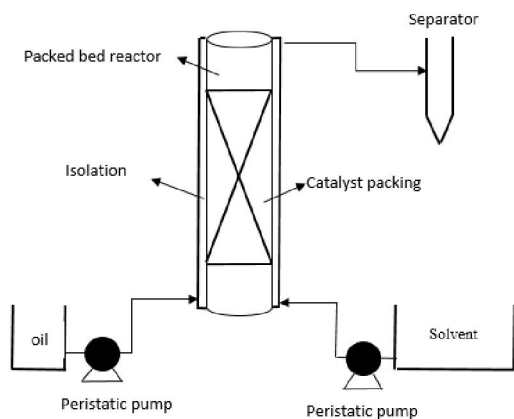


Figure 2. Schematic of the continuous biodiesel production

2.4. Analytical method

The methyl ester content was determined by using gas chromatography. An ACME 6100 gas chromatograph equipped with a FID detector and a 60 m silica capillary column (CN 100) was employed to perform the analysis. Helium was applied as a carrier gas. Almost, 0.2 of the sample were injected with a split ratio of 1:100. The injector temperature was 220 °C and the detector temperature was 280 °C. The oven was maintained at 180 °C for 20 minutes. The internal standard method was handled with methyl

nonadecanoate as the standard with heptane as the solvent. The FAME yield was computed using by Equations (1) and (2) [20]:

$$W_{FAME} = \frac{(\sum A) - AIS}{AIS} \times \frac{CIS \times VIS \times M}{m} \quad (1)$$

$$\%Yield = \frac{W_{FAME} \times MW_{OIL}}{W_{OIL} \times 3MW_{FAME}} \times 100 \quad (2)$$

Where ΣA , AIS, CIS, VIS, m, M, MW_{OIL} , W_{OIL} and MW_{FAME} are total peak area of FAME, peak area of methyl nonadecanoate, concentration of the internal standard (mg/ml), volume of the internal standard (ml), the mass of the sample (mg), molecular weight of nonadecanoate, molecular weight of oil, weight of oil sample (mg) and molecular weight of methyl ester, respectively.

The properties, such as pour point, cloud point, flash point and viscosity of the product were determined by the ASTM standard (Table 2). The result of the gas chromatography for the biodiesel in the optimum condition is shown in the Fig. 3.

The result of the Gas Chromatography for the biodiesel in the optimum condition is showing in the Fig. 2.

TABLE 2. Physico-chemical properties of methyl ester of linseed oil

Properties	Measurement	Standard number
Flash point	141 °C	D92
Viscosity at 40 °C	4.38 (centiStokes)	D445
Pour point	-2 °C	D97
Cloud point	-6 °C	D2500

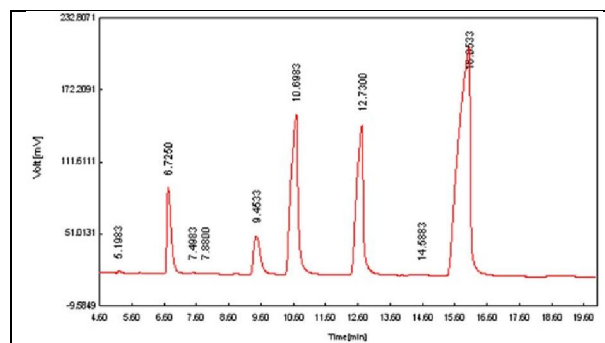


Figure 3. Results of biodiesel characterization by gas chromatography

The residence time of feedstock in the packed bed was calculated using Equation (3) [21]:

$$t = \frac{V_0}{v} = \frac{\alpha V}{v} = \frac{\pi \alpha}{4} \times \frac{hd^2}{v} \quad (3)$$

Where V , t , V_0 , v , α , d and h are the reactor volume, the residence time, the void volume (ml), the flow rate (ml/min), the bed porosity, the inner diameter of the reactor (cm) and the height of the packed bed in the reactor (cm), respectively.

2.5. Design of experiments

In this study, a statistical central composite design (CCD) was employed to maximize the FAME yield. In the continuous process, the CCD method was considered for two independent variables, each at five levels with five center points. The ranges and levels of variables are presented in Table 3. The impact of the two independent variables (i.e., the molar ratio of methanol to oil (X_1) and residence time (X_2)) and their interaction was studied. The other operating parameters were: a reaction temperature of 50 °C, a catalyst loading of 160 grams and a reaction time of 120 minutes.

TABLE 3. Ranges and levels of the independent variables in the continuous process

Variable	Symbol	Ranges and levels				
		-2	-1	0	1	2
Molar ratio of methanol to oil	X_1	3	4.32	7.5	10.68	12
Flow rate (ml/min)	X_2	0.5	0.8	1.25	1.7	2

According to the design, 13 runs were required to optimize the process. The results of the experimental designs and their performance under all conditions are depicted in Table 4.

TABLE 4. The central composite design arrangement and the experimental results in the continuous process

Run number	X_1	X_2	Temperature (°C)	Yield (%)
1	7.5	2	50	89.65
2	10.68	1.85	50	88.15
3	7.5	1.5	50	82.09
4	4.32	1.85	50	82.85
5	10.68	1.15	50	81.64
6	12	1.5	50	84.04
7	3	1.5	50	78.27
8	7.5	1	50	80.34
9	4.32	1.15	50	78.83
10	7.5	1.5	50	82.18
11	7.5	1.5	50	82.48
12	7.5	1.5	50	81.89
13	7.5	1.5	50	82.58

In the batch process, two independent variables, each at five levels with six center points, were evaluated. The range and levels for variables are presented in Table 5. The effect of two independent variables (i.e., the molar ratio of methanol to oil (X_3) and the catalyst concentration (X_4)) and their interaction was investigated. The other operating parameters were: a reaction temperature of 40 °C, an agitation rate of 650 rpm, and a reaction time of 90 minutes.

TABLE 5. Ranges and levels of the independent variables in the batch process

Variable	Symbol	Ranges and levels				
		-2	-1	0	1	2
Molar ratio of methanol to oil	X_3	10.83	1	8	4	5.17
Catalyst concentration (wt. %)	X_4	0.3	0.7	1.65	2.6	3

According to the design, 14 runs were required to optimize the process. The results of the experimental designs and their performance under all condition are shown in Table 6.

TABLE 6. The central composite design arrangement and the experimental results in the batch process

Run	X_3	X_4	Temperature (°C)	Agitation rate (rpm)	Yield (%)
1	8	0.3	40	650	92.37
2	10.83	0.7	40	650	94.98
3	8	1.65	40	650	93.29
4	8	1.65	40	650	92.71
5	8	1.65	40	650	92.84
6	4	1.65	40	650	85.68
7	5.17	2.6	40	650	86.26
8	10.83	2.6	40	650	93.39
9	12	1.65	40	650	95.76
10	8	1.65	40	650	92.35
11	5.17	0.7	40	650	87.27
12	8	3	40	650	77.74
13	8	1.65	40	650	92.24
14	8	1.65	40	650	91.86

3. RESULTS AND DISCUSSION

An analysis of variance (ANOVA) and a regression analysis was performed and Design Expert software (Ver. 7.0.0) was used to generate response surface plots. The regression coefficients of the second-order multiple regression models (expressed as Equation 4) were determined using the gained data from the CCD. The optimum values of the selected variables were obtained

by solving the regression equation and analyzing the response surface contour plots: [22]:

$$\%Yield = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \alpha_{1,1} X_1^2 + \alpha_{2,2} X_2^2 + \alpha_{1,2} X_1 X_2 + \varepsilon \quad (4)$$

Where α_0 to $\alpha_{1,2}$ are constant coefficients to be estimated from the regression, and ε is random error.

3.1. Response surface methodology analysis

The full regression coefficients of the quadratic model and their statistical significance were evaluated using the Design Expert software. A regression analysis was employed to fit the empirical model with the generated response variable data. Equation 5 represents the second-degree polynomial model as a function of the variables and their interaction in the continuous process. Furthermore, Equation 6 indicates the second-degree polynomial model in the batch process. Positive terms indicate a synergistic effect on the FAME yield, whereas negative terms indicate an antagonistic effect [23]:

$$\%Yield = +86.439 + (1.97989 \times X_1) - (19.26543 \times X_2) - (1.52444 \times X_1 X_2) + (0.099111 \times X_1^2) + (8.428 \times X_2^2) \quad (5)$$

$$\%Yield = +66.42998 + (5.74723 \times X_{3,3}) + (2.23521 \times X_{4,4}) + (0.22407 \times X_{3,3} X_{4,4}) - (0.32747 \times X_{3,3}^2) - (1.31939 \times X_{4,4}^2) \quad (6)$$

The ANOVA was conducted to study the significance and fitness of the quadratic model and the effect of the significant individual terms and their interactions on the selected response [24].

TABLE 7. Analysis of variance (ANOVA) of response surface quadratic model in the continuous process

Source	SOS*	DOF**	MS***	F-value	P-value
Model	166.88	5	33.38	35.21	0.0001
X ₁	29.32	1	29.32	30.93	0.0008
X ₂	112.76	1	112.76	118.95	0.0001
X ₁ X ₂	11.76	1	11.76	12.41	0.0097
X ₁ ²	7.72	1	7.72	8.14	0.0246
X ₂ ²	7.01	1	7.01	7.39	0.0298
Residual	6.64	7	0.95		
Lack of Fit	5.26	3	1.75	5.08	0.0752
Pure Error	1.38	4	0.35		
Total	173.51	12			

* Sum of Squares ** Degree of Freedom *** Mean Square
C.V. = 1.2%, R²=0.9618, =0.9344, predicted R²=0.7722

Table 7 demonstrates the results of the conducted ANOVA in the continuous process. Table 8 shows the results of the ANOVA in the batch process. P-values>0.1 indicate that the model parameters are not significant, whereas 0.05≤P-values≤0 indicate possibly

significant parameters that require extra analysis to determine the significance level. However, P-values>0.05 indicate the significant parameters [25]. Note: In statistical hypothesis testing, the p-value or probability value or asymptotic significance is the probability for a given statistical model that, when the null hypothesis is true, the statistical summary would be the same as or of greater magnitude than the actual observed results.

Table 8. Analysis of variance (ANOVA) of response surface quadratic model in the batch process

Source	SOS*	DOF**	MS***	F-value	P-value
Model	109.63	5	21.93	336.66	0.0001
X ₃	49.27	1	49.27	756.46	0.0001
X ₄	0.78	1	0.78	11.91	0.0087
X ₃ X ₄	1.46	1	1.46	22.48	0.0015
X ₃ ²	50.68	1	50.68	778.22	0.0001
X ₄ ²	10.67	1	10.67	163.90	0.0001
Residual	0.52	8	0.065		
Lack of Fit	0.082	3	0.027	0.31	0.8175
Pure Error	0.44	5	0.088		
Total	110.15	13			

* Sum of Squares ** Degree of Freedom *** Mean Square
C.V. = 0.28%, R²=0.9953, =0.9923, predicted R²=0.9890

An F-test and P-value were used to evaluate the statistical significance of the equation. In the continuous process, the highly significant mode was occurred in the F-value of 35.21 and the P-value of 0.0001. Also, the F-value of 336.66 and the P-value of 0.0001 indicated that the model was efficiently adjusted in the batch method [23, 24]. The outcome of the ANOVA indicated that all the linear terms (X₁, X₂, X₃ and X₄) and all the quadratic terms significantly affected the FAME yield due to their low P-values and high F-values.

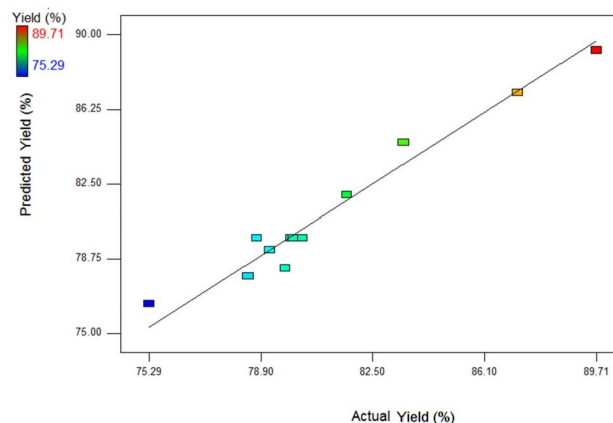


Figure 4. The experimental fatty acid methyl ester yield versus the predicted one in the continuous process

The model also illustrated the statistically non-significant lack of fit of the continuous method (P -values > 0.0752) and the batch method (P -values > 0.8175), indicating that the responses were appropriate for this model. Moreover, the results revealed an adequate fit between the experimental data and the statistical model (Figs. 4 and 5).

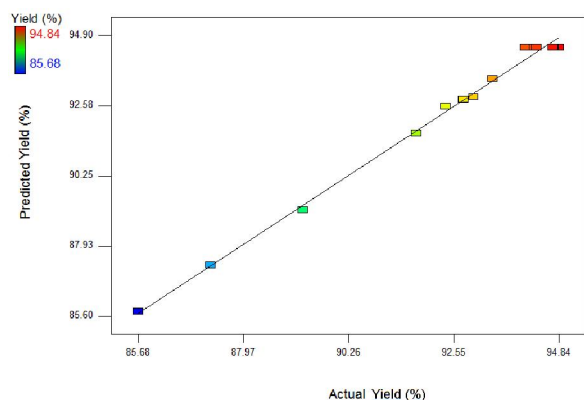


Figure 5. The experimental fatty acid methyl ester yield versus the predicted one in the continuous process

The efficiency of the fit of the regression equation was able to be adjudicated by the determination coefficient (R^2) and the adjusted determination coefficient (R^2_{Adj}). In the continuous process, the values of R^2 and R^2_{Adj} were 0.9618 and 0.9344, respectively and they were 0.9953 and 0.9923, respectively, in the batch process.

3.2. The molar ratio of methanol to oil

The molar ratio of methanol to the oil is one of the main factors of biodiesel production that has a strong effect on the FAME yield. According to the stoichiometry of biodiesel production, three moles of methanol are sufficient for the reaction progress. An extra volume of methanol results to a high yield of FAME, due to the reversibility of the reaction. Although an additional volume of methanol can boost the FAME yield, it increases the cost of biodiesel production [26-28].

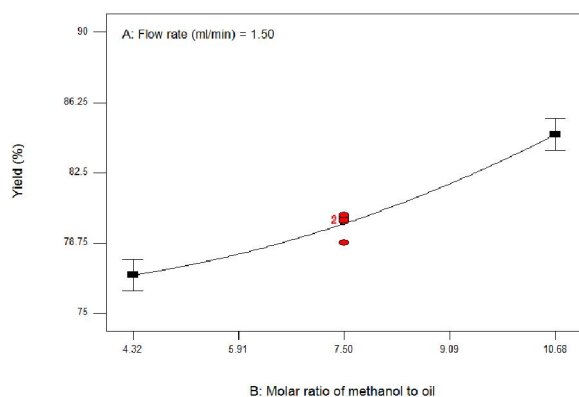


Figure 6. The effect of the molar ratio of methanol to oil on the yield in the continuous process

Hence, the amount of used methanol must be optimized. Fig. 6 indicates the FAME yield in the continuous biodiesel production, which closely depends on the molar ratio of methanol to oil. Therefore, the increasing of molar ratio causes a rise in the yield, due to the reversibility process of transesterification. Also, Fig. 7 reveals that a high volume of methanol results to the low yield of FAME in the batch biodiesel production, due to the diluting of the catalyst concentration in the methanol. Therefore, as long as the catalyst concentration remains constant in methanol, the FAME yield may be increased by adding methanol.

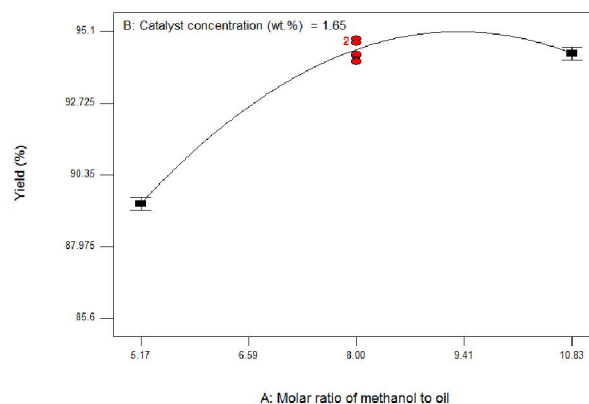


Figure 7. The effect of the molar ratio of methanol to oil on the yield in the batch process

3.3. Flow rate

Residence time is one of the most effective variables in the continuous biodiesel production. Adjusting the residence time mostly depends on the flow rate. Furthermore, Equation 3 shows that flow rate and the residence time are inversely related to each other [21, 29].

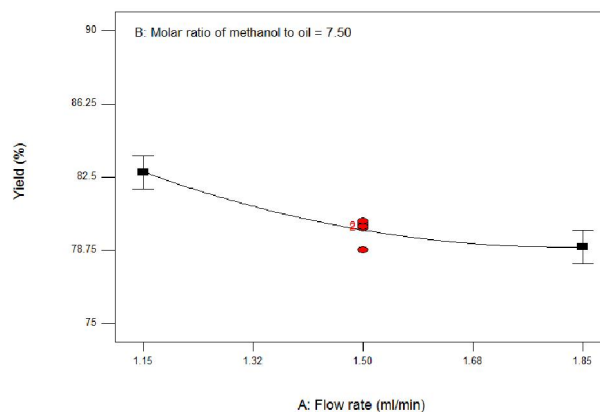


Figure 8. The impact of the flow rate on FAME yield in the continuous process

The impact of flow rate on the FAME yield at 50 °C and the various ranges of molar ratio of methanol to oil was investigated. It was found that a diminished flow rate

increased the residence time of linseed oil next to the catalyst. Moreover, the reaction was able to progress rapidly in the presence of the catalyst. Therefore, as shown in Fig. 8, a decrease in flow rate results to the high yield of FAME. The optimum flow rate was 1.03 ml/min and according to the Equation 3, the optimum residence time was calculated to be 37.05 minutes.

3.4. Catalyst concentration

Catalyst concentration is considered an important variable in the batch biodiesel production, due to most catalysts are homogeneous in this process. In the absence of an appropriate catalyst, biodiesel production reaction rate is very low. Therefore, catalysts play a significant role in increasing the reaction rate. Base catalysts cause to form soap from free fatty acids, which results to the decreasing of the FAME yield. It is suggested using the feedstock with the low free fatty acids (5 wt. % free fatty acid) for preventing a saponification reaction. Moreover, a high catalyst concentration causes emulsions, which requires a complex separation process [4, 22]. Fig. 9 illustrates that a high catalyst concentration is not suitable for increasing the FAME yield. According to the Fig. 9, the FAME yield is increased at first. Then, the extra amount of the catalyst is caused a reduction in the FAME yield, due to the soap formation during the reaction. Therefore, this important variable was optimized in 1.41 wt. % of the oil.

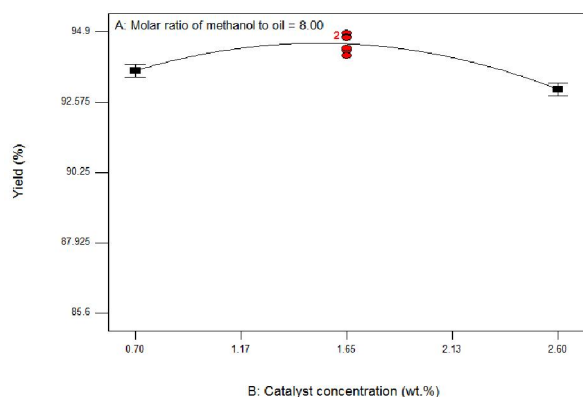


Figure 9. The influence of the catalyst concentration on the yield in the batch process

3.5. Interaction between variables

Fig. 10 depicts the interaction effect of the flow rate (ml/min) and the molar ratio of methanol to oil. According to Fig. 10, there is a slight interaction between these variables, which means flow rate (ml/min) and the molar ratio independently affect the FAME yield and they have no influence on the each other.

Fig. 11 depicts the interaction effect of the molar ratio of methanol to oil molar and the catalyst concentration (wt. %). The 3D interaction figure shows a strong

interaction between the two parameters.

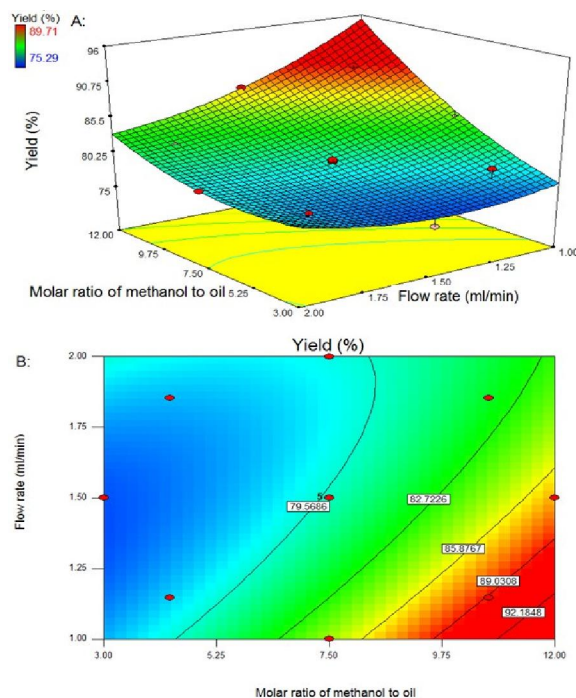


Figure 10. (A) Response surface 3D plot and contour plot of FAME conversion in the continuous process (the molar ratio of methanol to oil vs. the flow rate (ml/min)), and (B) Response surface 2D plot and contour plot of FAME conversion in the continuous process

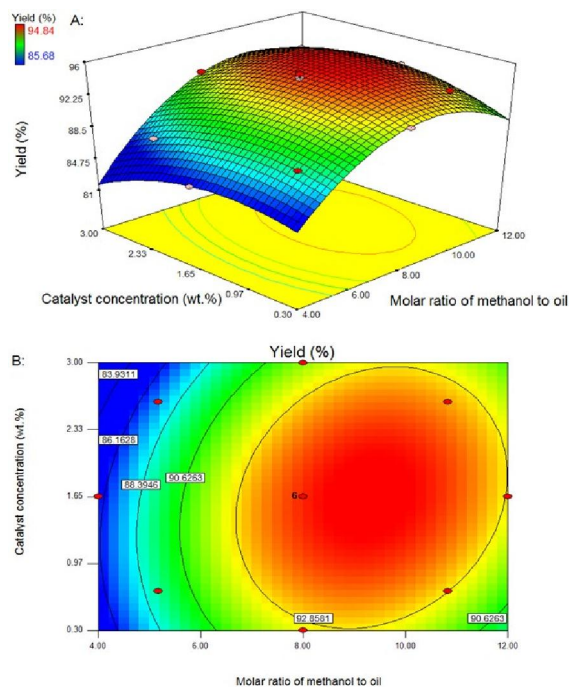


Figure 11. (A) Response surface 3D plot and contour plot of FAME conversion in the batch method (the molar ratio of methanol to oil vs. the catalyst concentration (wt. %)), and (B) Response surface 2D plot and contour plot of FAME conversion in the batch method

Fig. 11 illustrates that whereas the molar ratio of methanol to oil between 8 and 10 increases FAME yield but, increasing the amount of methanol leads to a reduction in the biodiesel yield due to the diluting of the catalyst concentration. However, a high catalyst concentration is not suitable for the transesterification reaction because it increases the rate of saponification. The optimum range of catalyst concentration was reported in the range of 0.98-1.65 wt. %.

3.6. Optimization

The optimization of variables in the continuous and batch transesterification of linseed oil was carried out in order to achieve the possible maximum FAME yield based on the fitted model (Eq. 4). The range of the variables for the continuous process is presented in Table 9. A maximum yield of 94.2423% was obtained under the following optimal conditions in the continuous process: the molar ratio of methanol to oil of 11.75:1 and a flow rate of 1.07 ml/min. Also, the range of the variables for batch process is shown in Table 10. The FAME yield of 95.0612 was obtained under the optimum conditions (i.e., the molar ratio of methanol to oil of 9.12:1 and a catalyst concentration of 1.52 wt. %).

Table 9. Ranges and symbol of independent variables in the continuous process

Variable	Symbol	Ranges
Molar ratio of methanol to oil	X_1	3-12
Flow rate (ml/min)	X_2	1-2
Yield (%)		Maximum

Table 10. Ranges and symbol of independent variables in the batch process

Variable	Symbol	Ranges
Molar ratio of methanol to oil	X_3	4-12
Catalyst concentration (wt. %)	X_4	0.3-3
Yield (%)		Maximum

4. CONCLUSION

In this study, we produced biodiesel was produced by a the continuous and batch process processes as well as a batch process. For In the continuous biodiesel production, the influence of two variables (i.e., the number of moles molar ratio of methanol to oil (3-12) and the flow rate (1-2 ml/min)) on the FAME yield was investigated. The continuous transesterification of linseed oil revealed that calcium oxide as a heterogeneous catalyst in a fixed bed reactor can could increase the FAME yield up to 94.2423% under the optimal conditions (i.e., a number of moles the molar ratio of methanol to oil of 11.75:1 and a flow rate of 1.07 ml/min). In the batch process, the impact of two

variables (i.e., the number of moles molar ratio of methanol to oil (4-12) and the catalyst concentration (0.3-3 wt. %)) on the FAME was studied. A maximum FAME yield of 95.0612% was obtained under the optimum conditions (i.e., a number of moles the molar ratio of methanol to oil of 9.12:1 and a catalyst concentration of 1.52 wt. %). According to the results, the FAME yield is was roughly the same equal in the both processes. the continuous and batch methods. The batch method is was a suitable technique that may might be used to optimize the reaction conditions, and the continuous process is was an appropriate way to increase the scale of the pilot plan.

5. ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support from the research department of Tarbiat Modares University.

REFERENCES

- Wang, Y.T., Fang, Z. and Yang, X.X., "Biodiesel production from high acid value oils with a highly active and stable bifunctional magnetic acid", *Applied Energy*, Vol. V, (2017), 702-714.
- Dixit, S. and Rehman, A., "Linseed oil as a potential resource for bio-diesel: a review. Renewable and Sustainable", *Energy Reviews*, Vol. 16, No. 7, (2012), 4415-4421.
- Wu, L., Huang, K., Wei, T., Lin, Z., Zou, Y. and Tong, Z., "Process intensification of NaOH-catalyzed transesterification for biodiesel production by the use of bentonite and co-solvent (diethyl ether)", *Fuel*, Vol. 186, (2016), 597-604.
- Issariyakul, T. and Dalai, A.K., "Biodiesel from vegetable oils", *Renewable and Sustainable Energy Reviews*, Vol. 31, (2014), 446-471.
- Lam, M.K. and Lee, K.T., "Accelerating transesterification reaction with biodiesel as co-solvent: A case study for solid acid sulfated tin oxide catalyst", *Fuel*, Vol. 89, No. 12, (2010), 3866-3870.
- Enweremadu, C.C. and Mbarawa, M., "Technical aspects of production and analysis of biodiesel from used cooking oil—a review", *Renewable and Sustainable Energy Reviews*, Vol. 13, No. 9, (2009), 2205-2224.
- Tran, D.T., Chang, J.S. and Lee, D.J., "Recent insights into continuous-flow biodiesel production via catalytic and non-catalytic transesterification processes", *Applied Energy*, Vol. 185, (2017), 376-409.
- Sajjadi, B., Raman, A.A.A. and Arandiyani, H., "A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: composition, specifications and prediction models", *Renewable and Sustainable Energy Reviews*, Vol. 63, (2016), 62-92.
- Alhassan, Y., Kumar, N., Bugaje, I.M., Pali, H.S. and Kathkar, P., "Co-solvents transesterification of cotton seed oil into biodiesel: effects of reaction conditions on quality of fatty acids methyl esters", *Energy Conversion and Management*, Vol. 84, (2014), 640-648.
- Chongkhong, S., Tongurai, C. and Chetpattananondh, P., "Continuous esterification for biodiesel production from palm fatty acid distillate using economical process", *Renewable Energy*, Vol. 34, No. 4, (2009), 1059-1063.

11. Gargari, M.H. and Sadrameli, S. "Investigating continuous biodiesel production from linseed oil in the presence of a co-solvent and a heterogeneous based catalyst in a packed bed reactor", *Energy*, Vol. 148, (2018), 888-895.
12. Di Serio, M., Tesser, R., Pengmei, L. and Santacesaria, E., "Heterogeneous catalysts for biodiesel production", *Energy & Fuels*, Vol. 22, No. 1, (2007), 207-217.
13. Jiang, B., Wang, Y., Zhang, L., Sun, Y., Yang, H., Wang, B. and Yang, N., "Biodiesel production via transesterification of soybean oil catalyzed by superhydrophobic porous poly (ionic liquid) solid base", *Energy & Fuels*, Vol. 31, No. 5, (2017), 5203-5214.
14. Tan, Y.H., Abdullah, M.O., Nolasco-Hipolito, C. and Taufiq-Yap, Y.H., "Waste ostrich-and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance", *Applied Energy*, Vol. 160, (2015), 58-70.
15. Sun, P., Sun, J., Yao, J., Zhang, L. and Xu, N., "Continuous production of biodiesel from high acid value oils in microstructured reactor by acid-catalyzed reactions" *Chemical Engineering Journal*, (2010), 364-370.
16. Santacesaria, E., Turco, R., Tortorelli, M., Russo, V., Di Serio, M. and Tesser, R., "Biodiesel process intensification by using static mixers tubular reactors", *Industrial & Engineering Chemistry Research*, Vol. 51, No. 26, (2011), 8777-8787.
17. Park, Y.M., Lee, D.W., Kim, D.K., Lee, J.S. and Lee, K.Y., "The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel", *Catalysis Today*, Vol. 131, No. 1, (2008), 238-243.
18. Hsieh, L.S., Kumar, U. and Wu, J.C., "Continuous production of biodiesel in a packed-bed reactor using shell-core structural $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2/\text{CaCO}_3$ catalyst", *Chemical Engineering Journal*, Vol. 158, No. 2, (2010), 250-256.
19. Di Serio, M., Mallardo, S., Carotenuto, G., Tesser, R. and Santacesaria, E., "Mg/Al hydrotalcite catalyst for biodiesel production in continuous packed bed reactors", *Catalysis today*, Vol. 195, No. 1, (2012), 54-58.
20. Koutsouki, A., Tegou, E., Kontakos, S., Kontominas, M.G., Pomonis, P.J. and Manos, G., "In situ transesterification of *Cynara cardunculus* L. seed oil via direct ultrasonication for the production of biodiesel", *Fuel Processing Technology*, Vol. 134, (2015), 122-129.
21. He, B., Shao, Y., Ren, Y., Li, J. and Cheng, Y., "Continuous biodiesel production from acidic oil using a combination of cation-and anion-exchange resins", *Fuel Processing Technology*, Vol. 130, (2015), 1-6.
22. Mcher, L., Sagar, D.V. and Naik, S., "Technical aspects of biodiesel production by transesterification—a review", *Renewable and Sustainable Energy Reviews*, Vol. 10, No. 3, (2006), 248-268.
23. Lee, H., Yunus, R., Juan, J.C. and Taufiq-Yap, Y.H., "Process optimization design for jatropha-based biodiesel production using response surface methodology", *Fuel Processing Technology*, Vol. 92, No. 12, (2011), 2420-2428.
24. Eevera, T., Rajendran, K. and Saradha, S., "Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions", *Renewable Energy*, Vol. 34, No. 3, (2009), 762-765.
25. Chen, X., Du, W. and Liu, D., "Response surface optimization of biocatalytic biodiesel production with acid oil", *Biochemical Engineering Journal*, Vol. 40, No. 3, (2008), 423-429.
26. Darnoko, D. and Cheryan, M., "Kinetics of palm oil transesterification in a batch reactor", *Journal of the American Oil Chemists' Society*, Vol. 77, No. 12, (2000), 1263-1267.
27. Melero, J.A., Iglesias, J. and Morales, G., "Heterogeneous acid catalysts for biodiesel production: current status and future challenges", *Green Chemistry*, Vol. 11, No. 9, (2009), 1285-1308.
28. Leevijit, T., Tongurai, C., Prateepchaikul, G. and Wisutmethangoon, W., "Performance test of a 6-stage continuous reactor for palm methyl ester production", *Bioresource Technology*, Vol. 99, No. 1, (2008), 214-221.
29. Shibasaki-Kitakawa, N., Honda, H., Kuribayashi, H., Toda, T., Fukumura, T. and Yonemoto, T., "Biodiesel production using anionic ion-exchange resin as heterogeneous catalyst", *Bioresource Technology*, Vol. 98, No. 2, (2007), 416-421.