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Ultrasound-Assisted Biodiesel Production in Microreactors

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ABSTRACT

The ultrasound-assisted (UA) soybean oil methanolysis using KOH as a catalyst was studied at different reaction conditions in a microreactor. Box–Behnken experimental design, with three variables, was performed and the effects of three reaction variables, i.e., reaction temperature, catalyst concentration and the methanol-to-oil molar ratio on fatty acid methyl ester (FAME) yield were evaluated by method of analysis of variance (ANOVA) and multiple regression. A quadratic polynomial model was obtained to predict the methyl ester yield. A yield of 97.1% for methyl ester was obtained at the deduced optimal conditions: reaction temperature of 47°C, KOH catalyst concentration of 1.29 (w/w%) and methanol-to-oil molar ratio of 6:1. Validation experiments confirmed the validity of the predicted model.

At the optimal operation condition for the ultrasonic process, a higher yield of methyl esters was obtained in comparison with that of the non-ultrasonic layout. The results show that UA transesterification in microreactor minimizes the reaction time and temperature, alcohol-to-oil molar ratio as well as energy consumption.

1. Introduction

Due to the depletion of the world's petroleum reserves and the increasing environmental concerns, there is great demand for alternative sources of petroleum-based fuel, including diesel and gasoline fuels [1,2].

Biodiesel, with a chemical structure of fatty acid alkyl esters (usually fatty acid methyl esters, FAMEs), is a clean burning fuel produced from renewable domestic sources such as vegetable oils and animal oils. It is biodegradable, non-inflammable, nontoxic and has a favorable combustion–emission profile, producing much less carbon monoxide, sulfur dioxide and unburned hydrocarbons compared to petroleum-based diesel. These properties make biodiesel a good alternative fuel to petroleum-based diesel oil [3].

The general transesterification reaction consisting primarily of triglycerides in reaction with alcohols to form alkyl esters is shown in Fig. 1. Excess alcohol with

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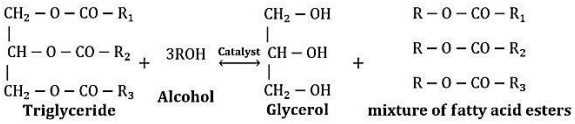

Figure 1. Transesterification reaction scheme

adequate catalyst generally forces the reaction equilibrium toward the products of biodiesel esters and glycerol [4,5]. Based on the stoichiometric relationship three moles of alcohol per mole of triglyceride (3:1) is required but excess amounts of alcohols usually used range from 6:1 up to 20:1, depending on the reaction chemistry for base-catalyzed transesterification, and as high as 50:1 for acid transesterification [4].

Examination of the literature data highlights that transesterification is limited by mass transfer rate between reactants [6]. Indeed, the reaction rate is limited by the immiscibility of triglycerides and methanol at the beginning of the reaction. Consequently, as the reaction proceeds, some loss in catalyst happens in glycerol phase separation [7].

Microreactors are of particular interest for performing immiscible liquid–liquid reactions because they offer a potentially very high interfacial area between phases, thereby improving the rate of mass transfer [8]. The typical advantage of microreactors over batch reactors is that a smaller emulsion droplet size is achieved in a shorter processing time, which means that higher conversion in a shorter time can be achieved in microreactors [9].

Ultrasound wave is defined as sound waves with a frequency beyond that which humans hear. Like any sound wave, ultrasound alternately compresses and stretches the molecular spacing of the medium through which it passes, causing a series of compression and rarefaction cycles. If a large negative pressure gradient is applied to the liquid so that the distance between the molecules exceeds the critical molecular distance necessary to hold the liquid intact, the liquid will break down and voids (cavities) will be created, i.e., cavitation bubbles will form. At high ultrasonic intensities, a small cavity may grow rapidly through inertial effects. As a result, some bubbles undergo sudden expansion to an unstable size and collapse violently, generating energy for chemical and mechanical effects. The collapse of the cavitation bubbles disrupts the phase boundary and causes emulsification by ultrasonic jets that impinge one liquid to another.

A low frequency ultrasonic irradiation could be useful for transesterification of triglyceride with alcohol. Ultrasonication provides the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction [10].

Ultrasonic irradiation can enhance mass transfer rate between the reactants which are immiscible liquids. Many researches have reported that physical effect of ultrasound on the formation of the fine emulsion between immiscible fluids is responsible for accelerating the transesterification reaction. Collapse of cavitation bubbles generates microturbulence, disrupts the phase boundary and causes emulsification of alcohol into the oil phase by ultrasonic jets that impinge on one liquid to another [11,12]. Furthermore, once the emulsion is formed, the surface area available for the reaction between the two phases significantly increases, thus accelerating

the reaction [11].

Intensified reaction causes shorter reaction time, efficient molar ratio of methanol to triglyceride, better product yield and less energy consumption than the conventional mechanical stirring method [13].

Vitthal *et al.* [14] expressed the advantages offered due to the use of sonochemical reactors, as revealed by optimization studies in batch reactors related to the various operating parameters such as molar ratio, catalyst concentration, and reaction temperature. These advantages include a reduced reaction temperature (savings in the energy required for heating of the process streams), a lower reaction time (energy savings in reactor processing), and the requirement of a smaller amount of excess methanol for equivalent levels of equilibrium conversion (considerable energy savings in the methanol separation units).

Ultrasonic transducers have been applied in batch reactors for promoting homogeneous base-catalyzed transesterification [11]. Although ultrasonic wave has been excessively employed in batch systems, it has not been used for biodiesel production in micro scale devices.

It seems that the combination of microreactor technology and ultrasonic irradiation for the transesterification reaction is a viable choice to overcome mass transfer limitation of the reaction completely as well as saving energy in an efficient way. Thus the aim of the current study was to produce biodiesel in a microtube reactor in the presence of ultrasonic waves for promoting the reaction yield.

Response surface methodology (RSM) is a powerful tool for the optimization of chemical reactions and/or industrial processes. It is a useful statistical technique that has been applied in research into complex variable processes. It makes use of multiple regression and correlation analyses as tools to assess the effects of independent factors on the dependent variables. Its principal advantage is that it reduces the number of experiment runs required to generate sufficient information for a statistically acceptable result [15,16]. The present work investigates the UA transesterification in microreactors using RSM. The effect of three important variables, i.e., reaction temperature (30-50°C), catalyst concentration (0.5-1.5 wt%), and methanol-to-oil molar ratio (3:1-9:1) have been studied and optimized.

2. Materials and methods

2.1. Materials

The soybean oil used in this study was supplied from Nazgol Oil Company (Kermanshah, Iran). Saponification index, average molecular weight, specific gravity and fatty acid composition of soybean oil were measured and reported in Table 1.

Methanol (purity > 99.5%), potassium hydroxide (purities > 85%, pellets) were purchased from Merck Co. Ltd. Methyl laurate (methyl dodecanoate, 99.7%) as standard for GC analysis was supplied by Sigma–Aldrich. All materials were used as received without any further processing.

2.2. Methods and experimental procedure

The soybean oil and methanol were aggregated through a Y shape micromixer.

Table 1
Obtained properties and fatty acid composition for soybean oil used in current study.

Characterization	
Saponification index (mg KOH/g oil)	191.88
Average molecular weight (g/mol)	863.47
Specific gravity (kg/m^3)	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

The outlet of the micromixer was connected to the inlet of a microchannel reactor. The micro-channel reactor was immersed in a water bath to ensure the accuracy of reaction temperature.

The residence time was controlled by adjusting the flow rates of pumps, while the molar ratio of methanol-to-oil was controlled by the flow rate ratio of two pumps. After dissolving the KOH catalyst in methanol, the mixed solution was injected through the methanol pump. The residence time was kept constant at 30 s in all experiments.

Ultrasonic waves were applied to promote the transesterification reaction of soybean oil and methanol. Low-frequency high-intensity ultrasound under atmospheric pressure and specified temperature was used. The low frequency ultrasonic transducer (Fig. 2) (25 KHz, 100 W, Type BJC-25100T- 68HS PZT-4, Beijing Ultrasonic, China) was installed at the bottom of the water bath.

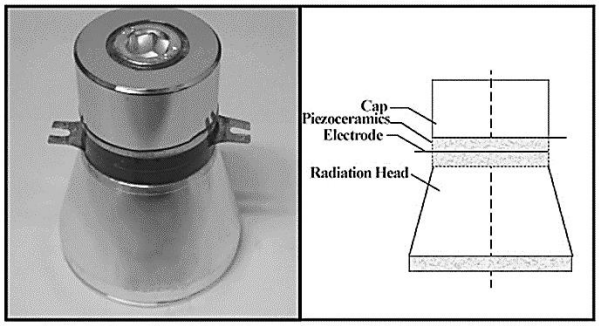

Figure 2. 25 KHz 100W Ultrasonic Transducer (A) real (B) schematic.

The experimental setup is shown schematically in Fig. 3. The reactants were diverted into the 0.8 mm ID micromixer by two syringe pumps. The outlet of the mixer was connected to a stainless steel tube with an inner diameter of 1.5 mm. The microreactor was placed in a water bath. The low frequency piezoelectric transducer was placed in the beginning of the microtube at the bottom of the water bath and the stainless steel tube reactor was wrapped around it in a way that the reaction mixture was sonicated uniformly in every part of the tube. The outgoing product was captured in a container and centrifuged to separate FAMEs part. This part was washed three times with water and consequently dehydrated at 100°C in an oven for an hour. Finally, the product was analyzed by a gas chromatograph system.

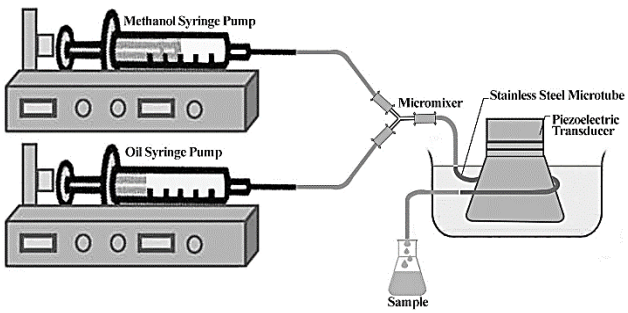

Figure 3. A schematic view of the experimental reaction setup.

2.3. Biodiesel characterization

Characterization of FAME in biodiesel samples was determined by a HP 6890 Gas Chromatograph with a flame ionization detector (FID). The capillary column was a BPX-70 high polar column with a length of 120 m, a film thickness of 0.25 µm and an internal diameter of 0.25 mm. Nitrogen was used as the carrier gas and also as an auxiliary gas for FID. One microliter of the sample was injected using a 6890 Agilent Series Injector with a splitless mode. The inlet temperature of sample into injector was 50°C, which was heated up to 230°C at a heating rate 5°*C/min*. Methyl laurate (C12:0) was added as a reference into the crude biodiesel, and the samples were analyzed by GC which was mentioned above.

The FAME yield was calculated using Eq. (1) as follows [17]:

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

Where ∑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

Box–Behnken is a spherical, revolving design. This design proposed three level designs for fitting response surfaces. These designs are formed by combining 2^k factorials with incomplete block designs. Box–Behnken design requires an experiment number according to $N=k^2+k+n_c$, where (k) is the factor number and (n_c) is the replicate number of the central point [18]. Findings indicate that the best overall design performance occurs with $2 \leq n_c \leq 5$ in Response Surface Designs [19].

Box–Behnken experimental design technique with three variables was used to study the response pattern and to determine the optimum combination of variables. Seventeen experiments were conducted separately for obtaining the experimental response of yield and the replicate number of the central point was 5. The reaction temperature (°C) (A), catalyst amount (wt%) (B) and methanol-to-oil molar ratio (C) were the independent variables selected for optimization. The coded and uncoded levels of the independent variables used for the transesterification reaction are listed in Table 2.

Statistical analysis of the model was performed to evaluate the ANOVA. The coefficient of the polynomial model of the response variable was fitted in order to correlate the response variable to the independent variable. The general equation of the quadratic response surface model was used:

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

where Y is the response factor (the yield of biodiesel), i and j represent the linear and

Table 2
Experimental range and levels of the independent variables.

Variable	Symbol Coded	Range and levels		
		-1	0	1
Reaction temperature (°C)	A	30	40	50
Catalyst amount (wt%)	B	0.5	1	1.5
Methanol to oil molar ratio	C	3	6	9

quadratic coefficients, respectively, b_0 is the intercept, b_i 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

In this work, the relationship between response (biodiesel yield) and three independent factors (reaction temperature, catalyst amount, methanol-to-oil molar ratio) were studied. In order to minimize the effects of the uncontrolled factors, the sequence of the experiments was performed randomly. Experimental and predicted values of yield responses at the design points and all the three variables in uncoded form are given in Table 3. The summary of ANOVA is also provided in Table 4.

Table 3
The Box–Behnken design and the yield responses.

Run	A: reaction temperature	B: catalyst amount	C: methanol to oil molar ratio	Yield	
				Experimental	Predicted
1	50	1.5	6	98	95.67
2	40	1	6	83	84.42
3	40	1	6	85	84.42
4	30	1	3	83.22	81.58
5	30	1.5	6	93.3	93.39
6	40	1.5	9	95	95.97
7	50	0.5	6	61	59.36
8	40	1	6	85.7	84.42
9	40	1	6	84.5	84.42
10	40	0.5	9	43.82	44.1
11	30	1	9	86	86.76
12	40	0.5	3	45.87	46.44
13	50	1	3	89	91.90
14	40	1.5	3	82	83.27
15	50	1	9	96	97.08
16	40	1	6	87	84.42
17	30	0.5	6	40.22	41.00

Table 4
ANOVA for the fitted quadratic polynomial model.

Source	Sum of Squares	df	Mean Square	F Value	p-value
Model	5604.243	7	800.6062	204.761	< 0.0001
A-reaction temperature	212.7985	1	212.7985	54.4248	< 0.0001
B-catalyst amount	3933.402	1	3933.402	1005.997	< 0.0001
C-methanol to oil molar ratio	53.71661	1	53.71661	13.73843	0.0049
AB	64.6416	1	64.6416	16.53258	0.0028
BC	56.62563	1	56.62563	14.48243	0.0042
A^2	101.7407	1	101.7407	26.02094	0.0006
B^2	1216.447	1	1216.447	311.1156	< 0.0001
Residual	35.18958	9	3.909954		
Lack of Fit	26.45758	5	5.291516	2.423965	0.2058
Pure Error	8.732	4	2.183		
Correlation Total	5639.433	16			

The associated probability value (p-value**)** for the model is lower than 0.05 (i.e., α=0.05 or 95% confidence), implying the significance of the model. The value of regression coefficient R^2 for the model is 0.994, indicating the good fitness of the model. A high value of predicted R^2 (0.969) is an indication of precision of fitted model. The higher the value of R^2 toward unity, the better the model fits the experimental data. The value of the adjusted coefficient of determination (R^2Adj: 0.989) is also high, thus indicating the significance of the model [20]. In this case, *A* (reaction temperature), *B* (catalyst amount), *C* (methanol-to-oil molar ratio), interaction effect of *AB* (reaction temperature with catalyst amount), *BC* (catalyst amount with methanol-to-oil molar ratio), A^2 (quadratic effect of reaction temperature), B^2 (quadratic effect of catalyst amount) have significant effect on the yield. The regression Eq. (3) for the determination of predicted values of yield is given as follows:

$$\begin{aligned}\text{yield }(\%) = {} & 84.4205 + 5.1575 * \text{A} \\ & + 22.1737 * \text{B} \\ & + 2.5912 * \text{C} - 4.02 \\ & * \text{AB} + 3.7625 * \text{BC} \\ & + 4.9088 * A^2 \\ & - 16.9737 * B^2 \end{aligned} \quad (3)$$

Catalyst amount shows the maximum influence on the yield followed by reaction temperature and methanol-to-oil molar ratio according to the coded equation.

The relation between the predicted and actual yield, illustrated in Fig. 4, shows that the predicted values are quite close to the experimental values, thereby validating the reliability of the model developed for establishing a correlation between the process variables and the yield.

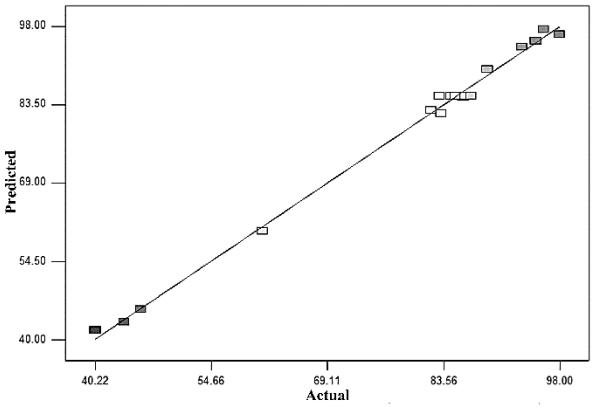

Figure 4. Predicted versus actual yield values.

3.2. Effect of process parameters on yield

Three-dimensional response surfaces were plotted on the basis of the model equation to investigate the interaction among the variables. Fig. 5 shows the effect of reaction temperature, catalyst amount and their reciprocal interactions on yield of biodiesel at a constant oil-to-methanol molar ratio of 6:1. It can be seen from this figure that the yield increases at the first stage followed by a decline with the increase of catalyst quantity. An increase in introduced quantities of catalyst increased the FAME content at a constant reaction temperature of 40°C and methanol-to-oil molar ratio of 6:1 within a catalyst amount of 1.3 (w/w%). Generally, the results show that addition of catalyst

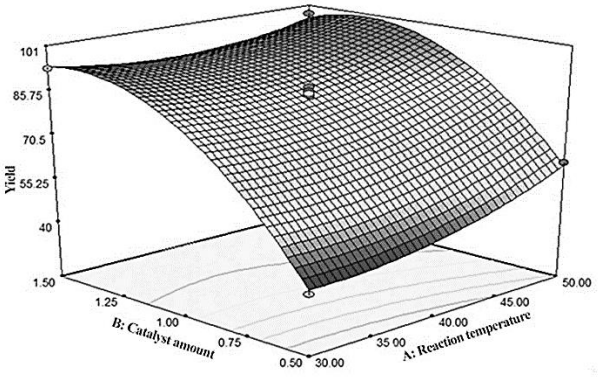

Figure 5. Response surface of yield of biodiesel vs. reaction temperature and catalyst amount.

caused a faster reaction of triglycerides, which increases the biodiesel yield [21,22]. However, addition of excessive catalyst would make the esterification of free fatty acids progress faster, and more water would be formed in a shorter time, and the excess water would deactivate the acidic hydroxyl groups since the hydration of these will occur when water is present [21]. Moreover, it can be seen from this figure that at low amounts of introduced catalyst, synthesis was significantly affected by reaction temperature; whereas at high catalyst amounts, the yield of biodiesel was only slightly affected by the reaction temperature.

At any designed quantity of catalyst from 0.5% to 1.5%, the augmentation of FAME contents resulted in a linear increase in reaction temperature. The increase in biodiesel yield is due to the fact that viscosity of oils decreases at high temperature and results in an increased reaction rate and shortened reaction time, thereby increasing the biodiesel yield [21]. Furthermore, the transesterification reaction is typically endothermic, so FAME yield increased with the increasing of the reaction temperature [23].

Fig. 6 represents the effect of different reaction temperatures and oil-to-methanol molar ratios on biodiesel synthesis at a catalyst amount of 1.0%. Methanol-to-oil molar ratio has a positive influence on biodiesel yield. This is because the transesterification reaction is an equilibrium reaction theoretically, so a greater amount of methanol is used to shift the reaction equilibrium to the right side [21,24]. This caused increased methyl esters production.

Methanol-to-oil molar ratio is found to have less effect on biodiesel yield than other variables as change in biodiesel yield with change in the methanol-to-oil ratio is very small. Therefore, lower molar ratio of methanol-to-oil would be more economical to use.

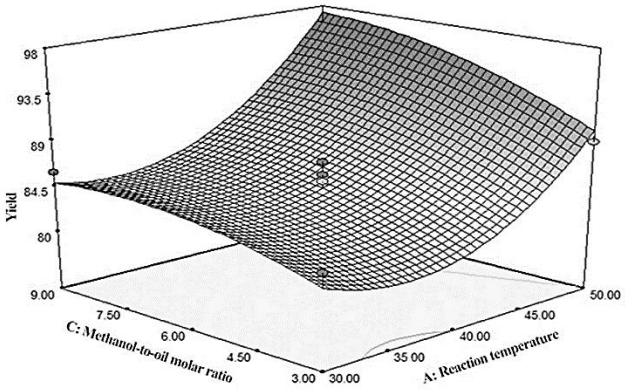

Figure 6. Response surface of yield of biodiesel vs. reaction temperature and methanol-to-oil molar ratio.

4. Optimization

By comparing the results shown in Figs. 5 & 6, the optimal condition for the maximal acquisition of FAME yield was achieved with a high reaction temperature and oil-to-methanol molar ratio, and a catalyst amount of 1.2–1.5 (w/w%).

Numerical optimization technique based on desirability function was carried out to determine the optimum conditions for the biodiesel yield. In order to provide an ideal case for biodiesel production, the goal for reaction temperature, catalyst amount, and methanol-to-oil molar ratio was set in range and biodiesel yield was set on maximize. The optimal values of the selected variables were obtained by solving the regression equation using (Stat-Ease, trial version) software. The optimal conditions for biodiesel yield estimated by the model equation were as follows: reaction temperature=47.0°C,

catalyst amount=1.29 (w/w%), and methanol- to-oil molar ratio=6:1. The theoretical FAME yield predicted under the above conditions was 96.64%. In order to verify the prediction of the model, the optimal reaction conditions were applied to three independent replicates for biodiesel synthesis**,** and the mean±standard deviation was determined. The average yield was 97.1 ± 0.5%.

Verification experiments were performed at the predicted conditions, indicating the validity and adequacy of the predicted models. The observed results were well accorded with the predicted results. As a result, the model developed was considered to be accurate and reliable.

5. The advantages of using ultrasonic irradiation for biodiesel production

A survey on the effect of ultrasound in the transesterification reaction was carried out at the optimal operating condition (reaction temperature=47.0°C, catalyst amount=1.29 (w/w%), and methanol-to-oil molar ratio=6:1). The reaction at the optimal operating conditions was carried out in the microreactor in the absence of ultrasonic waves. The experimental biodiesel yield at these conditions was found to be 53± 0.6%. This was result was related to three repetitions of the experiment.

The ultrasonic process under the optimum conditions obtained an increase of about 44%. It was found that the rate of ester formation under ultrasonic condition is significantly higher than non-ultrasonic condition due to the effective emulsification and mass transfer, which is induced by ultrasonic mixing.

In the present study, the case of ultrasonication in the microreactor, the residence time is greatly reduced compared with a conventional batch reactor due to the simultaneous application of ultrasonic irradiation and microreactor technology. In general, microreactors increase reaction rates and thereby reduce the reaction time because of their high mass and heat transfer rates and short molecular diffusion distance and ultrasonic due to the emulsification of the immiscible reactants [11,25].

It was found that the yield of the reaction in the absence of ultrasonic irradiation was 53% and by indirect sonication of the reaction mixture in the microtube, the yield increased up to 97.1%. This means that for equivalent levels of reaction yield, the operating parameters have been reduced. Furthermore, reaction temperature has been minimized to 47°C in this work while the optimal temperature ranges from 50°C to 60°C in past works. The optimum used molar ratio of methanol-to-oil was only 6:1.

6. Conclusions

In the present study, the microreactor technology coupled with ultrasound technique was applied for intensification of biodiesel production. The use of process intensification equipment for FAME production provides a means to reduce the mass transfer limitations related to transesterification reaction with less energy consumption.

The UA transesterification of soybean oil with methanol was studied and optimized. According to the second-order polynomial model the optimum reaction conditions were as follows: temperature of

47°C, catalyst amount of 1.29 (w/w%) and methanol-to-oil molar ratio of 6:1 which resulted in the FAME yield of 97.1.

At the optimal operation condition for the ultrasonic process, a higher yield of methyl esters was obtained in comparison with that of the non-ultrasonic layout. Besides, UA transesterification in microreactor also minimizes the reaction time, reaction temperature, alcohol-to-oil molar ratio and consequently, energy consumption. These results indicate that ultrasonic energy could be a valuable tool for transesterification of fatty acids from soybean oil in a microreactor.

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