Optimization of methyl ester production from waste cooking oil in a batch tri-orifice oscillatory baffled reactor

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A B S T R A C T

Transesterification of vegetable oils is a common route for the production of biodiesel. This reaction is a slow mass transfer limited reaction that has been shown to benefit from process intensification reactors such as the Oscillatory Baffled Reactor (OBR). The use of waste cooking oil as a resource is an attractive alternative to other virgin vegetable oils that will enable the capital costs of biodiesel production to be largely decreased, thereby making biodiesel an affordable and competitive fuel. In this study, optimization of biodiesel, or fatty acid methyl ester (FAME) production from waste cooking oil (WCO) was investigated using a batch OBR (diameter = 0.06 m, height = 0.55 m) with multi-orifice baffles, which have been recommended for scale-up. Response Surface Methodology (RSM) was applied to study the effects and interaction of different operating parameters: oscillation frequency (in the range 2.4–4.9 Hz), inter-baffle spacing (in the range 0.05–0.09 m) and reaction temperature (in the range 40–60 °C). It was found that temperature is the main factor influencing reaction yield and the interaction between temperature and oscillation frequency is non-negligible. Inter-baffle spacing does not, however, have a significant effect on the reaction. This is different from the design recommendations of OBRs in the literature, which were originally developed for single orifice baffles. An optimal reaction yield of 81.9% was obtained with an oscillation frequency of 4.1 Hz and an inter-baffle spacing of 5 cm (i.e. approximately $1.5d_e$) at a temperature of 60 °C. However, similar reaction yields could be obtained for different values of inter-baffle spacing.

1. Introduction

Biodiesel is promoted as a renewable and sustainable supplement for petroleum diesel and has received much attention in research over the last decades as it is a biodegradable and non-toxic fuel source. Biodiesel, often referred to as fatty acid methyl ester (FAME), is characterized as the alkyl esters of long chain of fatty acids derived from vegetable oils or animal fats. Indeed, the feedstock plays the most important role in biodiesel production process cost, comprising 70–90% of the biodiesel price. Therefore, waste cooking oils (WCOs), which are two or three times cheaper than virgin vegetable oils, are of high interest in biodiesel production [1,2], thereby potentially making it a sustainable substitute for petroleum diesel. Furthermore, collecting and reusing WCOs as a biodiesel feedstock or other bio-sourced derivatives, such as bio-lubricants [3,4], bio-asphalts [5] and bio-based surfactants [6], instead of discarding them into sewers can significantly decrease costs of treating waste waters [3]. It should be pointed out that however, the use of WCO for biodiesel production may require extra pre-treatment processing due to the presence of free fatty acids (FFA), water and other impurities which can hinder the performance of the FAME producing reaction.

Amongst different biodiesel production technologies, including such as pyrolysis, alcoholysis, co-feeding with petroleum feedstock etc., transesterification has been one of the most common and preferred chemical modification processes [7,8]. In this reaction, glycerides react with a short chain alcohol, such as methanol or ethanol, in presence of an alkaline, acid or enzyme catalyst. At the beginning of the reaction, oil and methanol form an immiscible liquid-liquid mixture that is mass transfer controlled due to the low solubility of these reactants. As the reaction occurs, however, the intermediates (diglycerides, monoglycerides) and methyl ester act as an emulsifier and the reaction medium is an emulsion of fine drops (or pseudo-homogeneous phase) [9–12]. In the final stage of the reaction, the products (methyl esters and glycerol), which are immiscible, for two distinct liquid phases

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again. The high difference in densities between glycerol and methyl ester causes phenomena such as stratification, which can lead to an incomplete reaction if there is no sufficient mixing, since most of the catalyst resides in glycerol phase [13,14]. The most important limitation in biodiesel production, however, is the mass transfer process and it is therefore vital to mix the reactants, which have significantly different viscosities, effectively such that high interfacial area is created and mass transfer is enhanced. Previously, some important issues in biodiesel synthesis reaction, such as modeling of reaction kinetics and mass transfer, effects of different feedstocks and alcohols as well as other main reaction parameters have been investigated comprehensively in a mechanistic approach [14,15].

An oscillatory baffled reactor (OBR) is composed of a tube containing equally spaced orifice plate baffles. The oscillatory flow generates vortices near the baffles and thereby improves radial mixing and plug flow [16,17] and enhances heat and mass transfer [18,19]. In OBRs, the amplitude and frequency of oscillation are independent parameters that control the mixing process. The governing dimensionless groups for oscillatory flow mixing are [20]:

$$\mathrm{Re}_o = \frac{2\pi f x_0 \rho d_e}{\mu} \tag{1}$$

$$\mathrm{St} = \frac{d_e}{4\pi x_0} \tag{2}$$

where Re_o is the oscillatory Reynolds number, ρ is the fluid density, μ is the fluid viscosity, f is the oscillation frequency, x_0 is the center-to-peak oscillation amplitude and St is the Strouhal number. d_e is the effective tube diameter for OBRs with multi-orifice baffles [21]:

$$d_e = \sqrt{\frac{d^2}{n}} \tag{3}$$

where d is the tube diameter and n is the number of orifices in the baffle. Re_o describes the nature of the flow generated by the maximum oscillatory velocity $2\pi f x_0$. For $Re_o < 250$, the flow in the OBR is essentially axi-symmetrical and mixing intensity is low; for $Re_o > 2000$, the flow becomes turbulent; at intermediate values of Re_o, the flow is 3-dimensional and mixing is more intense than the laminar flow [22]. The Strouhal number (St) is a measure of vortex propagation inside each inter-baffle zone relative to the tube diameter: larger oscillation amplitudes cause smaller St values and improve the vortex formation. Mixing and eddy propagation within the OBR is also inherently related to the inter-baffle spacing. For a given oscillation amplitude, the inter-baffle space should be large enough for vortices to expand and propagate. If the inter-baffle distance is too large, the vortices will not propagate through the full volume of the inter-baffle zone and produce stagnant regions [23]. Generally, the most adapted inter-baffle spacing is that which covers the maximum length of eddies without causing suppression or stagnation [23,24]. Several early studies on OBRs with single orifice baffles have investigated the effect of baffle spacing on single phase mixing quality using qualitative flow visualization [25,26]; and gas-liquid mass transfer [24]. The results of these studies indicate an 'optimal' baffle spacing of 1.5 and 1.8 times the tube diameter, although an optimization approach was not used in their experiments. A baffle-spacing of 1.5 time the tube diameter is now considered as a basic design rule for OBRs. Later, in 1999, Smith used this recommendation for the design of multi-orifice baffled reactors, whereby he replaced the tube diameter by the effective tube diameter as given in Eq. (3) [27].

Amongst the different studies on OBRs, several have focused on biodiesel and FAME production. Harvey et al. [20], evaluated the feasibility of a continuous OBR in the intensification of biodiesel production from rapeseed oil using single-orifice baffles in the presence of NaOH catalyst. Although no optimization process was done on the experimental factors (operating conditions or reactor geometry), it was found that the OBR allows methyl esters to be produced in much shorter residence times than the traditional batch stirred tank. The study shows that a product with a cetane number of 45 at 50 °C in just 30 min. In another study, Phan et al. [28] used continuous mesoscale OBRs in the laminar flow regime for the screening process conditions. They also studied the effect of baffle design and found that the sharp edged helical baffle design significantly improves the mixing of immiscible oil and methanol phases in the laminar regime, compared with the single orifice baffled reactor. At 50 °C and after a residence time of 10 min, the authors obtained methyl ester yields in the range of 78–85% depending on the methanol-to-oil ratio. Mazubert et al. [29] studied the process intensification of biodiesel production from waste cooking oil in a continuous glass OBR for relatively low temperatures and a few different oscillation conditions. At low temperature (27 °C), the Re_o in the range of 28–42 does not have a significant effect on reaction yield, which is between 82.3 wt% and 87.3 wt%. However, for low amplitude oscillations (Strouhal number equal to 0.16), reaction conversion was greatly diminished (38.1 wt%). At the highest achievable temperature in the reactor 44 °C (due to limitations of the glass), 92.1 wt% conversion was obtained in 6 min for a methanol-to-oil of 6:1 and 1% KOH catalyst. Syam et al. [30] used a mechanistic approach to investigate the effect of different operating parameters (temperature, catalyst type, methanol-to-oil molar ratio) on biodiesel production from Jatropha oil in a pulsed loop reactor with annular baffles. The methanol to oil molar ratio of 6:1, the potassium hydroxide catalyst with the recommended amount of 1% (per oil weight), and the reaction temperature of 60 °C were suggested as optimal operating parameters. Under these conditions, the authors obtained 99% yield of methyl esters in 10 min.

In all of the above-mentioned studies, the effect of OBR baffle spacing on biodiesel synthesis has not been investigated. Indeed, in these experimental set-ups, the baffle spacing was fixed at the so-called optimal value that was determined visually many years ago [22,23,24]. The effects of oscillation frequency and amplitude on methyl ester production are also not entirely straightforward. The objectives of this study are therefore to explore the effects of oscillation frequency and baffle spacing on FAME yield (after 5 min of reaction time) in a temperature range 40–60 °C. To do this, we have used RSM for experimental design and then to model the system and find the optimal operating parameters amongst those studied.

2. Material and methods

2.1. Materials

Methanol of 99% purity and potassium hydroxide of 98% purity (Merck) were used in methoxide production. Ethyl acetate (Fluka) and BSTFA (Sigma-Aldrich) were used for gas chromatography (GC) sample preparation. The waste cooking oil (WCO) with < 1% FFA, was obtained from the TMU University restaurant in Iran. Prior to the reaction, WCO was filtrated and preheated at 100 °C for about 3 h to vaporize its water content. The composition of WCO was determined by GC and is composed principally of oleic acid (32.9%wt), palmitic acid (30.4%wt) and linoleic acid (21.0%wt) with small amounts of stearic, linolenic and other fatty acids.

2.2. Experimental equipment

A vertical batch Oscillatory Baffled Reactor (OBR) with 0.06 m internal diameter and 0.55 m height and tri-orifice baffles (Fig. 1) following the dimensions given by Nogueira et al. [21] was fabricated in-house. The baffles had the capability of moving along the rod. The inter-baffle spacing, l, was varied between 0.05 m, 0.07 m and 0.09 m, corresponding to $1.45d_e$, $2d_e$ and $2.6d_e$, respectively. The multi-orifice baffle was chosen since multi-orifice baffles were initially designed for the scaling up of OBRs [27]. Indeed, this baffle type has shown to reproduce the fluid mechanics and axial dispersion, which are observed in lab-scale reactors, in larger scale equipment [31]. It is also expected to

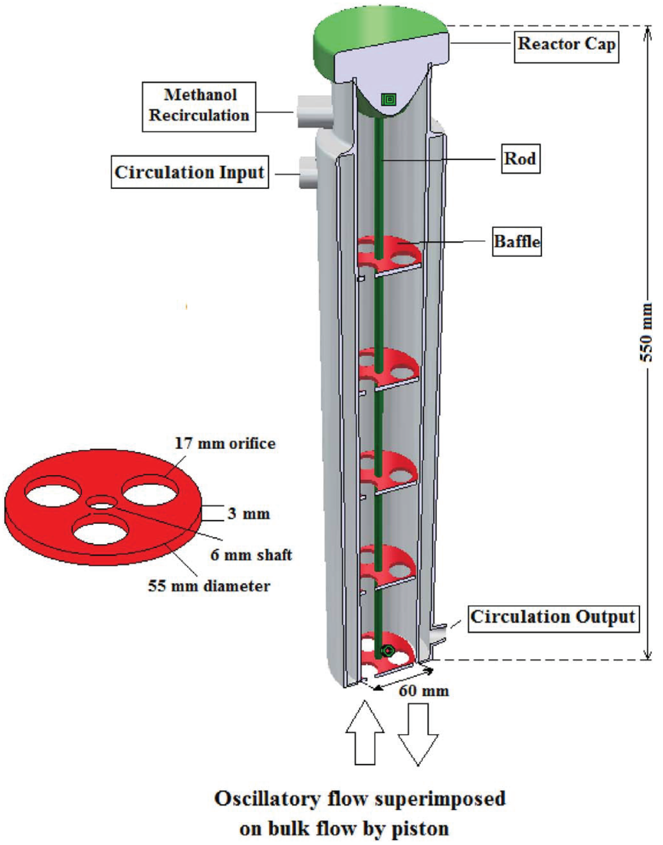

Fig. 1. Schematic view of a batch oscillatory baffled reactor.

be a good design for transesterification since this reaction is limited by mass transfer and the interfacial area can be created by high shear rates, which are produced at the edges of the baffle orifices [32].

The OBR experimental rig consists of the vertically positioned jacketed OBR with a glass condenser (to return the possible methanol vapors into the reactor), the oscillation generating mechanism, a heating and circulation unit and a control unit. The oscillation generating mechanism is a set of 0.37 kW electromotor, gearbox and a reciprocating piston in the cylinder. The heat and circulation unit consists of a tank equipped with a thermocouple and a hot oil pump to circulate the heating fluid in the outer jacket of the OBR. The control unit allows regulation of the oscillation frequency using the inverter and the temperature via two PT-100 sensors (one is situated inside the OBR and the other in the heating tank).

2.3. Experimental procedure

In each experimental run, the WCO oil and the methoxide (solution of KOH and methanol) were poured inside the OBR with a methanol to oil molar ratio of 6:1 and a catalyst concentration of 1%, which have shown to provide the best reaction conversion in a number of studies [7,29,30,33]. The reactor temperature (40 °C, 50 °C and 60 °C) was stabilized before the oscillation generation mechanism started. The oscillation amplitude, x_o, was set to 0.03 m, which corresponds to 0.3l to 0.6l depending on the baffle spacing. The oscillation frequency ranged from 2.4 to 4.9 Hz. These parameters provided oscillatory Reynolds numbers, Re_o, approximately in the range 2000 to 4000, corresponding to turbulent flow and a Strouhal number of 0.09.

2.4. Product analysis

After 5 min of reaction time, a sample was taken from the OBR sampling port and was quickly quenched using icy water. The FAME and the glycerol were then separated using a centrifuge. Following this, about 50 mg of the FAME phase was poured into a micro-tube and 1 ml of internal standard solution for GC analysis (C17) with a concentration of 7 mg/ml was added. The samples were kept in a freezer at − 5 °C to completely stop the reaction before the GC analysis. Approximately 0.5 μl of prepared solution were injected into the GC system. The Clarus 580 Gas Chromatography instrument (Perkin Elmer) was equipped with a flame ionization detector (FID) and biodiesel capillary column (Varian CP9080) with a length of 30 m, internal diameter of 0.32 mm and stationary phase thickness of 0.25 mm. Helium gas was used as the mobile phase. The column temperature program was adjusted according to the EN 14103 standard: the column temperature was firstly set at 60 °C for 2 min, the temperatures was then increased at a rate of 10 °C/min until 210 °C and then at a rate of 5 °C/min until 230 °C where it remained constant for 10 min. The total required time for the product analysis was 31 min. In order to calculate the mass of methyl esters and the FAME yield after 5 min of reaction time in batch mode, the following formula was used [34,35]:

$$W_{FAME} = (\sum A - A_{IS})/A_{IS} \times \{(C_{IS} \times V_{IS} \times M)/m\} \quad (4)$$

$$Y\% = (W_{FAME} \times M_{Oil})/(W_{Oil} \times 3M_{FAME}) \times 100 \quad (5)$$

where W_{FAME} is the weight of methyl esters produced; A_{IS} is the peak area of the internal standard; V_{IS} is the volume of the internal standard solution (ml); M is the weight of biodiesel phase in the reaction mixture; M_{Oil} is the average molar weight of oil (g/mol); ΣA is the total area of peaks in the chromatogram; C_{IS} is the internal standard solution concentration (mg/ml); m is the weight of biodiesel for GC analysis; Y is the reaction yield percentage; W_{Oil} is the waste oil weight; M_{FAME} is the average molar weight (g/mol) of methyl esters produced.

2.5. Experimental design

Response surface methodology (RSM) is a collection of mathematical and statistical modeling techniques used for multiple regression analysis and to quantify the relationships between one or more measured responses and the vital input factors. There are typically two main purposes of considering a RSM model. Firstly, it can be employed to establish a relationship between independent operating parameters and a measured response that can then be used to predict the response for alternate values of the operating variables. Secondly, RSM can be used to determine the significance and the optimum settings of operating parameters that result in an optimum response over a predefined range of operating conditions. Another important advantage of using RSM is the fact that it decreases the number of required experiments for performance assessment in industrial applications [36]. There are however some limitations to RSM, like for many other modeling methods, including extrapolative prediction. A mechanistic modeling approach can provide some solutions [14,15], however, this may result in excessive experimental time and costs.

In this study, a 3-levels-3-factors Box-Behnken design was applied to evaluate the interaction of the independent variables, namely oscillation frequency, inter-baffle space and reaction temperature, in the OBR and their effects on the reaction yield of FAME. The Box-Behnken factorial design, including 12 factorial points and five center points, was applied for fitting a second-order response surface. The experimental runs were randomized to minimize the effects of unexpected errors in the observed responses. Moreover, five repeated center points were set to create uniform precision. Table 1 shows the encoded and physical levels of the independent variables used for the Box-Behnken experimental design and Table 2 tabulates the experimental runs performed and the resulting FAME yield for each run.

Using Design-Expert® Software (version 7), the least squares method was then used to suggest the best equation type to relate the experimental reaction yield to the operating variables.

Table 1
The experimental matrix with the encoded and actual levels of independent variables.

Independent variables	Unit	Symbols	Levels of each factor		
			Coded values		
			− 1	0	1
Oscillation frequency	Hz	X_1	2.4	3.7	4.9
Inter-baffle space	cm	X_2	5	7	9
Reaction temperature	°C	X_3	40	50	60

Table 2
The Box-Behnken experimental design proposed by RSM.

	X_1	X_2	X_3	Response
Run	Frequency (Hz)	Space between baffles (m)	Reaction temperature (°C)	Conversion yield (%)
1	2.4	0.09	50	76.87
2	3.7	0.07	50	78.54
3	4.9	0.09	50	79.20
4	4.9	0.07	40	76.58
5	2.4	0.07	60	76.26
6	3.7	0.05	60	82.32
7	3.7	0.07	50	78.52
8	4.9	0.07	60	79.17
9	3.7	0.07	50	80.53
10	3.7	0.09	40	78.83
11	2.4	0.05	50	76.31
12	3.7	0.07	50	78.12
13	4.9	0.05	50	78.66
14	2.4	0.07	40	76.64
15	3.7	0.05	40	77.94
16	3.7	0.07	50	78.80
17	3.7	0.09	60	81.94

3. Results and discussion

3.1. RSM model and statistical analysis

The polynomial quadratic model suggested by the Design-Expert® Software that based on analysis of variance (ANOVA) is given in Eq. (6) in terms of coded factors.

$$Y = +78.90 + 0.94 \times X_1 + 0.2 \times X_2 + 1.21 \times X_3 - 0.00475 X_1X_2 + 0.74 X_1X_3 - 0.32 X_2X_3 - 2.12 \times X_1^2 + 0.98 \times X_2^2 + 0.38 \times X_3^2 \quad (6)$$

Where X_1 is the oscillation frequency, X_2 is the inter-baffle spacing and X_3 is the reaction temperature. The probability value (p-value) of this model is 0.0286, which is considered statistically significant if a significance level of 0.05 is assumed. Table 3, shows the RSM model statistics the ANOVA analysis.

In this case, X_1, X_3, and X_1^2 are significant model terms. The model indicates that the effect of baffle-spacing is not that significant. The lack of fit F-value of 1.49 implies the Lack of fit is not significant relative to the pure error.

3.2. Interaction of experimental operating parameters

3.2.1. Oscillation frequency and inter-baffle spacing ($X_1 \cdot X_2$)

Fig. 2(a) shows the surface plot and design points indicating the interaction between oscillation frequency and inter-baffle spacing on the reaction yield when the reaction temperature is 60 °C. Fig. 2(b) is a two-dimensional contour plot showing the reaction yield as a function of the oscillation frequency (X_1) and the inter-baffle spacing (X_2). It can be seen from these plots that the reaction yield increases about 4% when the oscillation frequency increases from about 2 Hz to approximately 4 Hz (Re_o = 3312), however, the inter-baffle space has little effect on the yield. Indeed, increasing the oscillation frequency increases the Reynolds number, leading to higher turbulence and eddy/vortex formation. This increased turbulence will promote drop breakup and an increase in interfacial area, which in turn enhances mass transfer and reaction yield [37]. However, at oscillation frequencies above approximately 4.5 Hz, no significant increase in biodiesel yield was recorded. This issue is attributable to reversible feature and the equilibrium position of the transesterification reaction. In other words, the maximum reaction conversion will not be affected unless a new equilibrium position is attained. Syam et al. [30] have also reported similar results. According to Fig. 2(b), the symmetric shapes of contour lines indicates that the inter-baffle spacing does not have a significant effect on reaction yield. The statistical analysis of the model also confirms this result by providing a p-value of 0.6 for inter-baffle spacing and this is much > 0.05. This suggests that the inter-baffle spacing of tri-orifice baffles in this range with the oscillation amplitude of 0.03 m, does not have a significant effect on vortex formation and the reaction yield in biodiesel synthesis.

3.2.2. Oscillation frequency and reaction temperature ($X_1 \cdot X_3$)

Fig. 3(a) and (b) show the surface plot with design points and the contour plot indicating the effect of the interaction of oscillation frequency and reaction temperature on reaction yield, respectively. According to these plots, it can be seen that the interaction of temperature and oscillation frequency has a non-negligible effect on methyl ester production, even though the p-value is > 0.05, which means that it is not that significant. At temperatures < 45 °C, oscillation frequency hardly affects reaction yield and at oscillation frequencies less than about 3 Hz, the yield is hardly affected by temperature. The former observation is due to the kinetics of the reaction whilst the latter observation indicates that the reaction is hindered at low frequencies due to a lack of interfacial area between reactants. As both oscillation frequency and reaction temperature increase, higher yields are obtained, thereby showing a synergistic effect of the oscillation frequency X_1 and temperature X_3.

3.2.3. Inter-baffle spacing and reaction temperature ($X_2 \cdot X_3$)

Fig. 4(a) and (b) depict the interactive effects of inter-baffle spacing and reaction temperature on the reaction yield using surface and contour plots for a frequency of 3.7 Hz. The contour plot in Fig. 4(b) shows that there appears to be only a slight interaction between inter-baffle space and temperature. Indeed, for a fixed reaction temperature, an increase in inter-baffle space does not cause any significant change in reaction yield; the yield depends mostly on temperature. This is an interesting result since according to the original studies on 'optimal' baffle spacing, the recommended value is 1.5d_e. In this study, the inter-baffle spacing varies between 1.45d_e and 2.6d_e, and there does not seem to be much impact on the process objective, i.e. the reaction yield, even though it can be noted that the highest yield is obtained at low values of baffle spacing close to 1.5d_e (5 cm). The fact that no significant effect of baffle spacing was observed may due to the fact that the flow regime is fully turbulent. It is expected that in fully turbulent conditions, small scale eddies are controlling the creation of interfacial area between reactants and therefore reaction yield and therefore the impact of inter-baffle spacing is attenuated. If the flow is not fully turbulent, the baffle spacing and oscillation amplitude have a greater effect on the propagation of vortices and mixing.

3.3. Process optimization

The optimal level of each operating parameter that gave the maximum response factor (reaction yield after 5 min) was determined using the regression polynomial equation obtained from RSM model. The optimum values of operating parameters of methyl ester production reaction in the OBR setup are indicated in Fig. 5.

The optimum values for experimental variables were oscillation

Table 3
Quadratic model statistics and ANOVA for RSM model.

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	1.58	0.3701	0.2247	− 0.2403	64.17	
2FI	1.73	0.4206	0.0730	− 1.6515	137.18	
Quadratic	1.04	0.8549	0.6682	− 0.3310	68.86	Suggested
Cubic	0.94	0.9313	0.7253		+	Aliased

Source	Sum of squares	df	Mean-square	F-value	p-Value	
Model	44.23	9	4.91	4.58	0.0286	Significant
X_1-frequency	7.09	1	7.09	6.61	0.0370	
X_2-baffle spacing	0.32	1	0.32	0.30	0.6001	
X_3-temperature	11.74	1	11.74	10.94	0.0130	
$X_1{\cdot}X_2$	9.025E-005	1	9.025E-005	8.413E-005	0.9929	
$X_1{\cdot}X_3$	2.21	1	2.21	2.06	0.1944	
$X_2{\cdot}X_3$	0.40	1	0.40	0.38	0.5595	
X_1^2	18.89	1	18.89	17.61	0.0041	
X_2^2	4.02	1	4.02	3.74	0.0943	
X_3^2	0.60	1	0.60	0.56	0.4783	
Residual	7.51	7	1.07			
Lack of fit	3.96	3	1.32	1.49	0.3461	Not significant
Pure error	3.55	4	0.89			
Std. Dev.	1.04					
C.V. %	1.32					

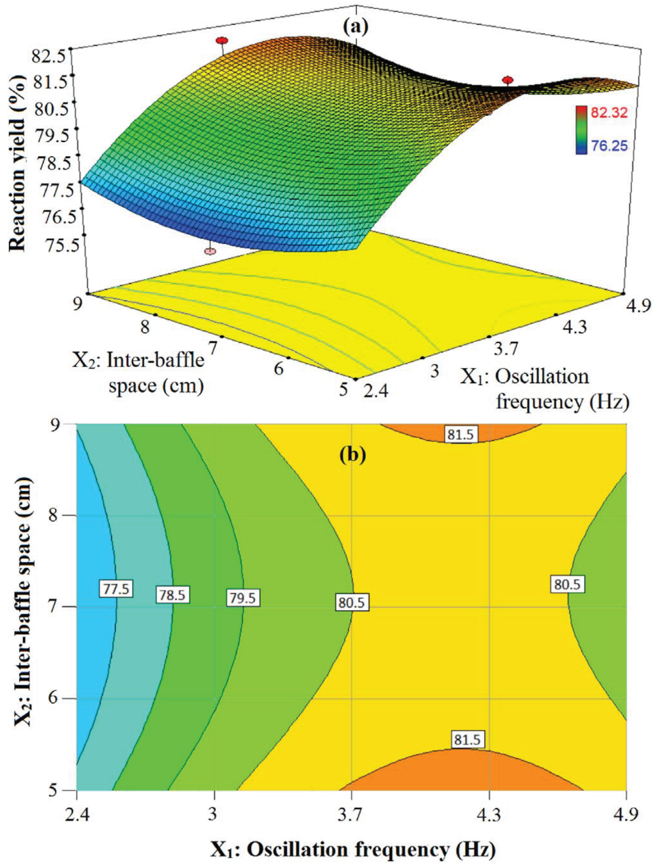

Fig. 2. Effect of interaction between oscillation frequency and inter-baffle space on reaction response ($X_1{\cdot}X_2$) when X_3 = 60 °C. (a) surface response; (b) contour plot.

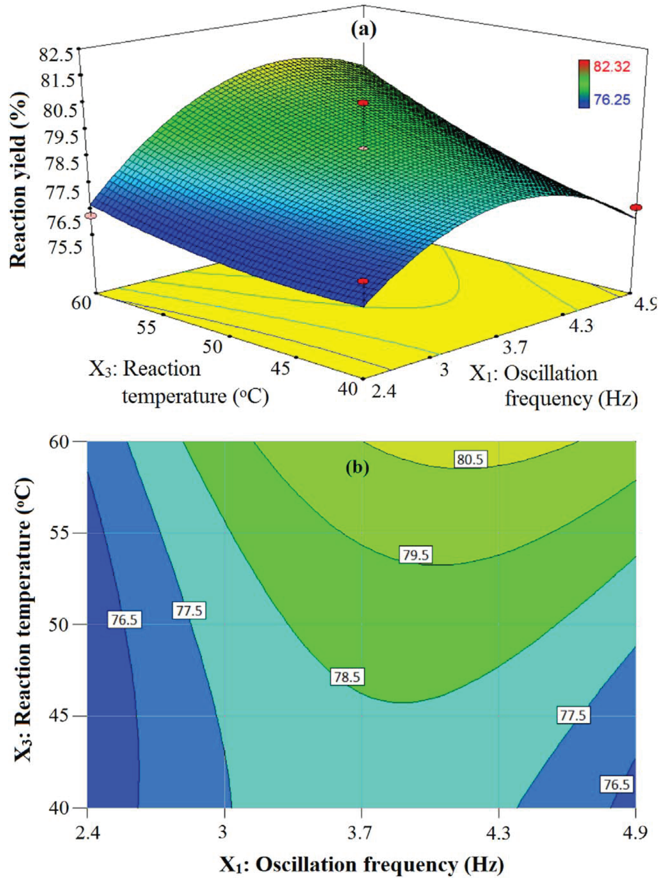

Fig. 3. Effect of interaction between oscillation frequency and reaction temperature on reaction yield ($X_1{\cdot}X_3$) when X_2 = 5 cm. (a) surface response; (b) contour plot.

frequency of 4.1 Hz, the inter-baffle spacing of 5 cm and a reaction temperature of 60 °C. Applying these optimum values, the reaction yield was predicted 81.9% with a desirability of 0.93. In order to confirm the predicted optimum values, they were applied in an experimental run and the reaction yield was measured as 82.0%. This proves excellent agreement of the RSM model with the experimental measurements. However, it is interesting to note that a reaction yield of 81.7% can be obtained for a baffle spacing of 9 cm, a frequency of 4.1 Hz and 60 °C. This again shows that the baffle spacing does not have a significant impact on reaction performance.

The optimal reaction yield was also determined by changing the

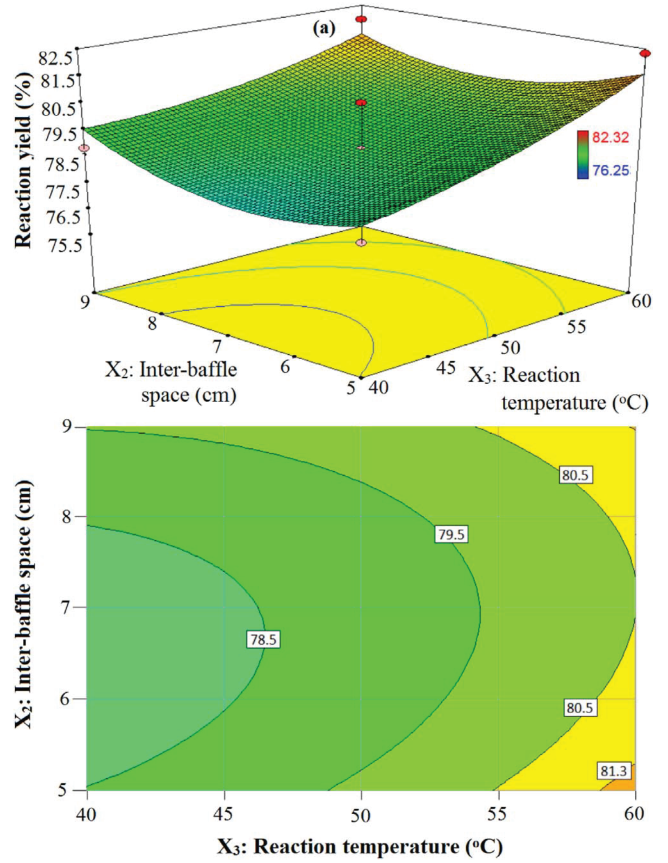

Fig. 4. Effect of interaction between inter-baffle space and reaction temperature on reaction response ($X_2 \cdot X_3$) when X_1 = 3.7 Hz. (a) surface response; (b) contour plot.

optimization criteria on the different operating parameters. If we consider a reduction in the global energy consumption of the process, one may want to find the maximal reaction yield for minimum reaction temperature and/or oscillation frequency. The maximum reaction yield obtained when both reaction temperature and oscillation frequency are minimized is 78.% and it increases to 80.3% when only oscillation is minimized. For both of these results, the optimal oscillation frequency and inter-baffle spacing are 3.6 Hz and 7 cm, respectively. This again shows another value for inter-baffle spacing, thereby reinforcing the low impact of this parameter on FAME yield.

According to Likozar et al. [14], on the process economics of biodiesel production, the cost of operating at higher temperatures is much less important than the costs of feedstock and catalyst. Therefore, it appears that the best operating conditions for FAME production in the current system are approximately 4 Hz and a temperature of 60 °C, regardless of inter-baffle spacing.

4. Conclusion

Response surface methodology successfully modeled and optimized biodiesel production in a batch oscillatory baffled reactor in turbulent flow. The RSM model was used to study the effects of oscillation frequency, inter-baffle spacing and reaction temperature and their interactions on the yield of methyl esters. The model suggested by RSM was a quadratic polynomial equation with a p-value of 0.0286.

It was found that the main parameter affecting reaction yield was temperature, but the interaction of temperature and oscillation frequency is also important. Indeed, if the frequency is too low, resulting in bad mixing, the temperature has very little impact on the reaction yield. However, the results show that it is not useful to use an oscillation frequency that is too high. After a certain limit, an increase in frequency no longer has a positive effect on the reaction. It is expected that this is due to the fact that interfacial area between the reactants has reached an equilibrium value and thereby resulting in no further improvement in reaction yield. The impact of inter-baffle spacing on reaction was found, however, to be very low. Although the optimum reaction yield was found for an inter-baffle spacing of 5 cm (1.45d_e), an oscillation frequency of 4.1 Hz and 60 °C, similar reaction yields can be obtained at other values of the inter-baffle spacing. This result is different from the original recommendations of OBR design, which state that the best inter-baffle spacing is 1.5d_e. Indeed, this widely accepted recommendation was obtained from qualitative flow visualization in single phase non-reactive flows in an OBR with single orifice baffles, and it was directly applied reactors with multi-orifice baffles with no further testing. The transesterification reaction studied here is a mass transfer limited liquid-liquid (multiphase) reaction that requires high interfacial area between reactants. The fact that inter-baffle spacing is not significant in this application suggests that the 'optimal' baffle spacing depends on the application and the process objective, which is in the current case, the generation of interfacial area to enhance the reaction. The current study is also carried out in the turbulent flow regime and it appears that the turbulence alone is sufficient to generate the required interfacial, therefore attenuating the effect of inter-baffle spacing, which in lower Reynold number flows, is important for mixing and vortex propagation.

An optimum reaction yield of 81.9% after only 5 min was found for an inter-baffle spacing of 5 cm (1.45d_e), an oscillation frequency of 4.1 Hz and 60 °C, which was confirmed by an independent experimental test. Nevertheless, since the inter-baffle spacing has a negligible impact, it appears that a range of operating conditions with a frequency of approximately 4 Hz and a temperature of 60 °C can allow similar reaction yield.

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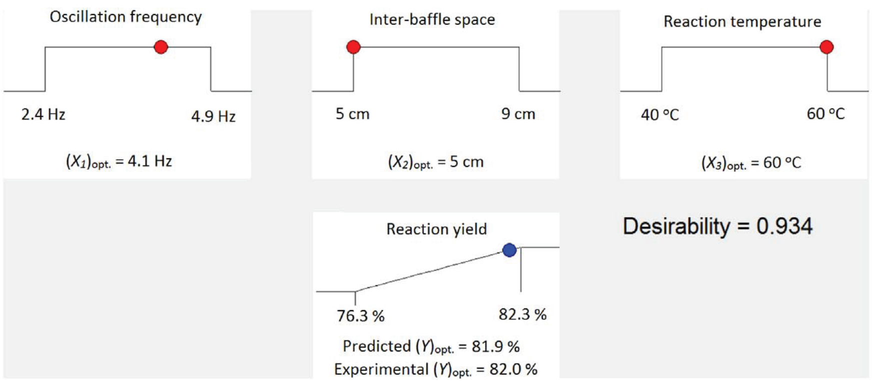

Fig. 5. The Optimal levels of the operating parameters.

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References

[1] A. Molaei Dehkordi, M. Ghasemi, Transesterification of waste cooking oil to biodiesel using Ca and Zr mixed oxides as heterogeneous base catalysts, Fuel Process. Technol. 97 (2012) 45–51, http://dx.doi.org/10.1016/j.fuproc.2012.01.010.

[2] G. Knothe, K.R. Steidley, A comparison of used cooking oils: a very heterogeneous feedstock for biodiesel, Bioresour. Technol. 100 (2009) 5796–5801, http://dx.doi.org/10.1016/j.biortech.2008.11.064.

[3] E. Wang, X. Ma, S. Tang, R. Yan, Y. Wang, W.W. Riley, M.J.T. Reaney, Synthesis and oxidative stability of trimethylolpropane fatty acid triester as a biolubricant base oil from waste cooking oil, Biomass Bioenergy 66 (2014) 371–378, http://dx.doi.org/10.1016/j.biombioe.2014.03.022.

[4] M.D. Soufi, B. Ghobadian, G. Najafi, M. Sabzimaleki, F. Jaliliantabar, Performance and exhaust emissions of a SI two-stroke engine with biolubricants using artificial neural network, Energy Procedia, Elsevier Ltd, 2015, pp. 3–9.

[5] D. Sun, G. Sun, Y. Du, X. Zhu, T. Lu, Q. Pang, S. Shi, Z. Dai, Evaluation of optimized bio-asphalt containing high content waste cooking oil residues, Fuel 202 (2017) 529–540, http://dx.doi.org/10.1016/j.fuel.2017.04.069.

[6] Q.-Q. Zhang, B.-X. Cai, W.-J. Xu, H.-Z. Gang, J.-F. Liu, S.-Z. Yang, B.-Z. Mu, The rebirth of waste cooking oil to novel bio-based surfactants, Sci Rep 5 (2015) 9971, http://dx.doi.org/10.1038/srep09971.

[7] A. Abbaszaadeh, B. Ghobadian, M.R. Omidkhah, G. Najafi, Current biodiesel production technologies: a comparative review, Energy Convers. Manag. 63 (2012) 138–148, http://dx.doi.org/10.1016/j.enconman.2012.02.027.

[8] G. Fogassy, N. Thegarid, G. Toussaint, A.C. van Veen, Y. Schuurman, C. Mirodatos, Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units, Appl. Catal. B Environ. 96 (2010) 476–485, http://dx.doi.org/10.1016/j.apcatb.2010.03.008.

[9] H. Noureddini, D. Zhu, Kinetics of transesterification of soybean oil, J. Am. Oil Chem. Soc. 74 (1997) 1457–1463.

[10] M. Busto, S.A. D'Ippolito, J.C. Yori, M.E. Iturria, C.L. Pieck, J.M. Grau, C.R. Vera, Influence of the axial dispersion on the performance of tubular reactors during the noncatalytic supercritical transesterification of triglycerides, Energy Fuel 20 (2006) 2642–2647.

[11] O.S. Stamenković, Z.B. Todorović, M.L. Lazić, V.B. Veljković, D.U. Skala, Kinetics of sunflower oil methanolysis at low temperatures, Bioresour. Technol. 99 (2008) 1131–1140.

[12] G. Guan, M. Teshima, C. Sato, S. Mo Son, M. Faisal Irfan, K. Kusakabe, N. Ikeda, T. Lin, Two-phase flow behavior in microtube reactors during biodiesel production from waste cooking oil, AICHE J. 56 (2010) 1383–1390.

[13] A.N. Phan, A.P. Harvey, Characterisation of mesoscale oscillatory helical baffled reactor-experimental approach, Chem. Eng. J. 180 (2012) 229–236, http://dx.doi.org/10.1016/j.cej.2011.11.018.

[14] B. Likozar, A. Pohar, J. Levec, Transesterification of oil to biodiesel in a continuous tubular reactor with static mixers: Modelling reaction kinetics, mass transfer, scale-up and optimization considering fatty acid composition, Fuel Process. Technol. 142 (2016) 326–336, http://dx.doi.org/10.1016/j.fuproc.2015.10.035 (Research article).

[15] B. Likozar, J. Levec, Transesterification of canola, palm, peanut, soybean and sunflower oil with methanol, ethanol, isopropanol, butanol and tert-butanol to biodiesel: Modelling of chemical equilibrium, reaction kinetics and mass transfer based on fatty acid composition, Appl. Energy 123 (2014) 108–120, http://dx.doi.org/10.1016/j.apenergy.2014.02.046.

[16] M.R. Mackley, X. Ni, Mixing and dispersion in a baffled tube for steady laminar and pulsatile flow, Chem. Eng. Sci. 46 (1991) 3139–3151, http://dx.doi.org/10.1016/0009-2509(91)85017-R.

[17] M.R. Mackley, X. Ni, Experimental fluid dispersion measurements in periodic baffled tube arrays, Chem. Eng. Sci. 48 (1993) 3293–3305, http://dx.doi.org/10.1016/0009-2509(93)80213-A.

[18] M. Palma, R. Giudici, Analysis of axial dispersion in an oscillatory-flow continuous reactor, Chem. Eng. J. 94 (2003) 189–198, http://dx.doi.org/10.1016/S1385-8947(03)00057-3.

[19] J.P. Solano, R. Herrero, S. Espín, A.N. Phan, A.P. Harvey, Numerical study of the flow pattern and heat transfer enhancement in oscillatory baffled reactors with helical coil inserts, Chem. Eng. Res. Des. 90 (2012) 732–742, http://dx.doi.org/10.1016/j.cherd.2012.03.017.

[20] A.P. Harvey, M.R. Mackley, T. Seliger, Process intensification of biodiesel production using a continuous oscillatory flow reactor, J. Chem. Technol. Biotechnol. 78 (2003) 338–341, http://dx.doi.org/10.1002/jctb.782.

[21] X. Nogueira, B.J. Taylor, H. Gomez, I. Colominas, M.R. Mackley, Experimental and computational modeling of oscillatory flow within a baffled tube containing periodic-tri-orifice baffle geometries, Comput. Chem. Eng. 49 (2013) 1–17, http://dx.doi.org/10.1016/j.compchemeng.2012.09.015.

[22] P. Stonestreet, P.M.J. Van Der Veeken, The effects of oscillatory flow and bulk flow components on residence time distribution in baffled tube reactors, Chem. Eng. Res. Des. 77 (1999) 671–684.

[23] M.S.R. Abbott, A.P. Harvey, G.V. Perez, M.K. Theodorou, Biological processing in oscillatory baffled reactors: operation, advantages and potential, Interface Focus. 3 (2013) 20120036, http://dx.doi.org/10.1098/rsfs.2012.0036.

[24] X. Ni, S. Gao, Mass transfer characteristics of a pilot pulsed baffled reactor, J. Chem. Technol. Biotechnol. 65 (1996) 65–71, http://dx.doi.org/10.1002/(SICI)1097-4660(199601)65:1 < 65::AID-JCTB352 > 3.0.CO;2-1.

[25] C.R. Brunold, J.C.B. Hunns, M.R. MACKLEY, J.W. THOMPSON, Losses for oscillatory, Chem. Eng. Sci. 44 (1989) 1227–1244.

[26] P. Gough, X. Ni, K.C. Symes, Experimental flow visualisation in a modified pulsed baffled reactor, J. Chem. Technol. Biotechnol. 69 (1997) 321–328, http://dx.doi.org/10.1002/(SICI)1097-4660(199707)69:3 < 321::AID-JCTB717 > 3.0.CO;2-Q.

[27] K.B. Smith, The Scale-Up of Oscillatory Flow Mixing, PhD Thesis, Univ. Cambridge, 1999, https://core.ac.uk/download/pdf/1334175.pdf.

[28] A.N. Phan, A.P. Harvey, M. Rawcliffe, Continuous screening of base-catalysed biodiesel production using new designs of mesoscale oscillatory baffled reactors, Fuel Process. Technol. 92 (2011) 1560–1567, http://dx.doi.org/10.1016/j.fuproc.2011.03.022.

[29] A. Mazubert, J. Aubin, S. Elgue, M. Poux, Intensification of waste cooking oil transformation by transesterification and esterification reactions in oscillatory baffled and microstructured reactors for biodiesel production, Green Processes Synth. 3 (2014) 419–429, http://dx.doi.org/10.1515/gps-2014-0057.

[30] A.M. Syam, R. Yunus, T.I.M. Ghazi, T.S.Y. Choong, Synthesis of Jatropha curcas oil-based biodiesel in a pulsed loop reactor, Ind. Crop. Prod. 37 (2012) 514–519, http://dx.doi.org/10.1016/j.indcrop.2011.07.030.

[31] K.B. Smith, M.R. Mackley, An experimental investigation into the scale-up of oscillatory flow mixing in baffled tubes, Chem. Eng. Res. Des. 84 (2006) 1001–1011, http://dx.doi.org/10.1205/cherd.05054.

[32] A. Mazubert, D.F. Fletcher, M. Poux, J. Aubin, Hydrodynamics and mixing in continuous oscillatory flow reactors—part I: effect of baffle geometry, Chem. Eng. Process. Process Intensif. 108 (2016) 78–92, http://dx.doi.org/10.1016/j.cep.2016.07.015.

[33] M.G. Kulkarni, A.K. Dalai, Waste Cooking Oil is an Economical Source for Biodiesel: a Review, (2006), pp. 2901–2913.

[34] L.T. Thanh, K. Okitsu, Y. Sadanaga, N. Takenaka, Y. Maeda, H. Bandow, Ultrasound-assisted production of biodiesel fuel from vegetable oils in a small scale circulation process, Bioresour. Technol. 101 (2010) 639–645, http://dx.doi.org/10.1016/j.biortech.2009.08.050.

[35] X. Yin, H. Ma, Q. You, Z. Wang, J. Chang, Comparison of four different enhancing methods for preparing biodiesel through transesterification of sunflower oil, Appl. Energy 91 (2012) 320–325, http://dx.doi.org/10.1016/j.apenergy.2011.09.016.

[36] A.I. Khuri, S. Mukhopadhyay, Response surface methodology, Wiley Interdiscip. Rev. Comput. Stat. 2 (2010) 128–149, http://dx.doi.org/10.1002/wics.73.

[37] M.E. Mackay, M.R. Mackley, Y. Wang, Oscillations flow within tubes containing wall or central baffles, Chem. Eng. Res. Des. 69 (1991) 506–513.