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FAME production from residual materials: Optimization of the process by Box–Behnken model

E.M. Vargas[a,b], J.L. Ospina[a], L.A.C. Tarelho[b], M.I. Nunes[b,*]

[a] *Department of Chemical Engineering, University Jorge Tadeo Lozano, Bogotá, Colombia*
[b] *Centre for Environmental and Marine Studies, Department of Environment and Planning, University of Aveiro, Portugal*

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Abstract

In the worldwide more than 95% of biodiesel production feedstocks come from edible oils. The waste cooking oils (WCO) are an alternative feedstock for biodiesel production; its usage reduces significantly the cost of biodiesel production and has environmental benefits, e.g., a waste recovery instead of its elimination. This work aimed to optimize the process to produce fatty acid methyl esters (FAME) using the response surface methodology and a Box–Behnken experimental design from mixtures of refined palm oil (RPO) with WCO using a residual solid material as catalyst (biomass fly ashes). The influence on FAME yield of four operational variables (catalyst loading, methanol/oil molar ratio, RPO/WCO ratio and reaction temperature) was studied. The higher FAME yield achieved using the RMS method was 77.06% for: 14.63 wt% of catalyst loading, 5.42/1of methanol/oil molar ratio, 14.81 wt% of RPO in the oil mixture and 55 ° C for the reaction temperature.

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Keywords: Biomass fly ash; FAME; Optimization; Refined palm oil; Response surface methodology; Solid catalyst; Waste cooking oil

1. Introduction

It is imperative to find alternative fuels to the petroleum based ones in order to, along with environmental issues, prolong the petroleum supply. One of the most promising biofuel is biodiesel, an alternative diesel fuel derivate from renewable sources with high quality [1]. Globally, the cost of production has been the main barrier in commercializing biodiesel. In the literature, it is consensual that the oily feedstock is the major contributor, about 80% [2], for the total production costs. The waste cooking oils (WCO) are edible vegetable oils that have been previously used for frying or cooking and can constitute an additional source of raw material for biodiesel production. This feedstock can be two to three times cheaper that virgin vegetable oils [3]. Moreover, the catalyst

* Corresponding author.
E-mail address: isanunes@ua.pt (M.I. Nunes).

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commonly used in the biodiesel production is the sodium or potassium hydroxide, which have been economically unfeasible to recover from the process. On the other hand, biomass fly ashes are a residual materials with potential for catalyzing the reactions for Fatty Acid Methyl Esters (FAME) production [4]. Thus, this work aimed at optimizing the operational conditions for FAME production from oil mixtures of WCO and RPO using biomass fly ashes as catalyst (FAD). In line with the principles of circular economy, this work also aimed to contribute to make the biodiesel production process more environmentally friendly through the valorization of two waste streams: FAD and WCO.

The effect on FAME yield of four process variables were tested, namely: catalyst loading, methanol/oil, RPO/WCO ratio and reaction temperature. The Response Surface Methodology (RSM), based on a Box–Behnken model was adopted for designing experiments since it is required minimum data that give the best reaction condition for a desired response [5]. RSM can solve multivariate data which are obtained from properly designed experiments to solve multivariate equation simultaneously.

2. Methodology

WCO used in this work was provided by a collecting company of Bogotá, Colombia. The WCO was pre-treated by filtration and heating (at 110 °C for 1 h) to remove suspended particles and traces of water, respectively. The RPO was purchased at a local store in Bogotá. The oil mixtures were characterized in terms of moisture content, density, acid value (AV), Free Fatty Acid content (FFA), molecular weight (MW) and viscosity.

The biomass fly ashes (solid catalyst) were collected at the electrostatic precipitator of a thermal power-plant using residual forest biomass (derived from eucalyptus) as fuel, located in the Center Region of Portugal. They were dried at 120 °C for 5 h for the experiments; its characterization can be found in [4]. All the chemicals used were analytical grade except n-hexane (GC grade) and methyl heptadecanoate (analytical standard) from Sigma-Aldrich and Merck.

Concerning the FAME process optimization a Box–Behnken experimental design was carried out to assess the effect of four process variables on yield to FAME – Y. The response surface methodology (RSM) was used to optimize these (independent) variables, maximizing the response variable (Y). Table 1 shows the experimental ranges and factor levels tested in this work. Twenty-nine experiments were performed in a batch reactor, with 5 repetitions of the center point.

Table 1. Ranges and factor levels of process variables used in the Box–Behnken experimental design.

Real variables	Coded variables	Level		
		Low (−1)	Medium (0)	High (+1)
Catalyst loading [wt%]	A	5%	10%	15%
Methanol/oil [molar ratio]	B	3	6	9
Reaction temperature [°C]	C	45	50	55
RPO/WCO ratio [wt%]	D	0 (M3)	50 (M2)	100 (M1)

In each experiment, the final mixture (FAME) was separated from glycerol, washed, dried and characterized in terms of FAME content by gas chromatography. The yield of FAME was calculated using Eq. (1).

$$\text{Yield to FAME} = \frac{\text{mass of FAME produced}}{\text{mass of oil used in the experiment}} \quad (1)$$

The statistical analysis performed to the experimental results, consisted on a quadratic polynomial model fitting for predicting the response (i.e., FAME yield) as a function of independent variables and their interactions according to Eq. (2):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} {x_i}^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

In Eq. (2) Y is the predicted response for the process, βo is the intercept coefficient (offset), βi are the linear terms, βii are the quadratic terms, βij are the interaction terms, xi and xj are the coded independent variables, and ε is the error [6]. Data were analyzed with Design-Expert 7.0.0 software trial version.

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3. Results and discussion

3.1. Materials

The results of the characterization of the oil mixtures prepared for this study are shown in Table 2.

Table 2. Properties of the oil mixtures used in this work.

	M1	M2	M3
WCO [wt%]	0	50	100
RPO [wt%]	100	50	0
Moisture [wt%]	0.067 ± 0.010	0.170 ± 0.003	0.197 ± 0.012
Density [g/mL]	0.908 ± 0.008	0.913 ± 0.010	0.906 ± 0.003
AV [mgKOH/g]	0.307 ± 0.004	3.958 ± 0.082	4.934 ± 0.252
FFA [wt%]	0.172 ± 0.005	1.979 ± 0.041	2.453 ± 0.056
MW [g/mol]	843.152 ± 9.522	886.338 ± 1.208	857.825 ± 4.014
Viscosity [mm^2/s]	14.902 ± 0.193	17.122 ± 0.123	19.185 ± 0.392

With the exception of the density and the MW, all the properties characterized of the three oil mixtures are statistically different with a confidence level of 95%. Thus, as the percentage of WCO increases in the blend, higher are the moisture and the FFA contents, the acid value and the viscosity, while the remaining properties (density and MW) are similar within mixtures.

The properties of M1 (i.e., 100% RPO) are similar to those reported by Kansedo et al. [7] and by Singh and Singh [8]. Concerning the waste cooking oils properties, they are quite dependent of the vegetable oil feedstocks and their frying practices and conditions. The WCO (M3) used in this work has properties similar to those reported by Wan Omar and Saidina Amin [9] and Lam and Lee [10] and it can be categorized as yellow grease (FFA $<$ 15%) [11].

Regarding the FAD catalyst's acid and basic strength, the latter can be considered as intermediate ($9.3 \leq pKa < 12.2$) due to the high basicity of the metal-oxygen groups (Lewis bases) present in the calcium compounds on the surface of the catalyst; while its acid strength can be classified as low ($6.8 \leq pKa < 7.2$) [4,12].

3.2. Statistical analysis and fitting models

A second order polynomial model based on the coded values was obtained with multiple regression analysis of the experimental results. The model equation was:

$$Y = 55.95 + 9.89A + 4.00B + 18.51C - 17.58D - 1.36AB - 2.10AC - 6.76AD - 4.00BC + 2.42BD - 3.88CD - 6.92A^2 - 7.70B^2 - 8.57C^2 - 19.99D^2 \quad (3)$$

This model has a good fit ($R^2 = 0.8959$) as shown in Fig. 1c and Table 3. This table summarizes the analysis of variance (ANOVA) performed.

Table 3. ANOVA results of the response surface quadratic model.

Source of variations	Sum of squares	Degrees of freedom	Mean square	F-value	p-value
Model	12 384.28	14	884.59	8.61	0.0001
Residual	1438.88	14	102.78		
Lack of fit	744.28	10	74.43	0.43	0.8736
Pure error	694.59	4	173.65		
Total	13 823.15	28			
	$R^2 = 0.8959$	Adj $R^2 = 0.7918$	Pred $R^2 = 0.6114$	C.V[a]= 26.62%	S.D.[b]= 10.14

[a]C.V = coefficient of variation.

[b]S.D = standard deviation.

The low p-value (0.0001) of the model means that it is statistically significant. On the other hand, the F-value of 0.43 implies that the lack of fit is not significant relative to the pure error. There is an 87.36% chance that this value

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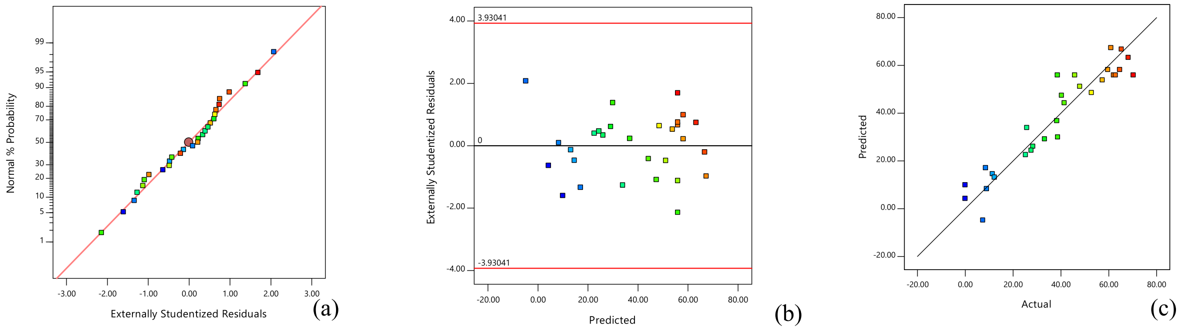

Fig. 1. Evaluation of RSM for FAME yield (%): (a) Residual normal probability plot, (b) Residual versus predicted response plot, (c) Predicted versus actual values plot.

could occur due to noise; non-significant lack of fit is good. The "Pred R^2" of 0.6113 is in reasonable agreement with the "Adj R^2" value of 0.7918. The coefficient of determination of the model was good ($R^2 = 0.8959$).

Finally, the statistical significance of each parameter of the model was evaluated and results are shown in Table 4. According to these results, the most influencing variables on the quadratic model response were reaction temperature (C), with a positive effect, and RPO/WCO ratio (D) with a negative effect. In addition, the individual effects, two-level interaction between variables and their single squared values were found not to have a significant impact on the process yield.

Table 4. ANOVA results for the coefficients of the variables in the multiple regression coded model.

Model parameters	Estimate coefficient	F-value	p-value
A	9.89	11.43	0.0045
B	4.00	1.87	0.1934
C	18.51	40.01	<0.0001
D	−17.58	36.08	<0.0001
AB	−1.36	0.07	0.7924
AC	−2.10	0.17	0.6846
AD	−6.77	1.78	0.2033
BC	−4.00	0.62	0.4429
BD	2.42	0.23	0.6401
CD	−3.88	0.59	0.4567
A^2	−6.92	3.03	0.1039
B^2	−7.70	3.75	0.0734
C^2	−8.57	4.64	0.0491
D^2	−19.99	25.22	0.0002

In order to validate the fitting model statistical graphical methods were performed. A normal probability plot of residuals is shown in Fig. 1a where it is observed that the points are located approximately along a straight line, thus one can intuitively conclude that the residuals follow a normal distribution. Plot of residuals versus fitted response values (predicted) is depicted in Fig. 1b which shows that the residuals are randomly distributed or, in other words, residuals are located on a horizontal curve and the number of points that exist in the above and below of horizontal line is equal. Moreover, residual values are located between ±3.00; typically, a threshold of three standard deviations is employed as a definition of an outlier [13]. The actual FAME yield versus the predicted values is plotted in Fig. 1c. This graph also confirms that the fitted model describes properly the experimental results. In short, this analysis confirm the accuracy and reliability of the proposed model.

The influence on FAME yield of each independent variable studied is shown as response surface plots in Fig. 2. Fig. 2a relates the catalyst loading (wt%) and the RPO/WCO ratio in oily mixture (wt%) with FAME yield. Higher yields (71 wt%) are obtained with high catalyst loading (15 wt%) and moderate RPO/WCO ratio, i.e., up to 15 wt%. RPO/WCO ratios greater than 15 wt% have a negative effect on FAME yield for any of the catalyst loadings tested. Fig. 2b shows the effects of RPO/WCO and methanol to oily mixtures ratios on FAME yield. It is observed that the methanol to oil ratio does not influence significantly the FAME yield as RPO/WCO ratio.

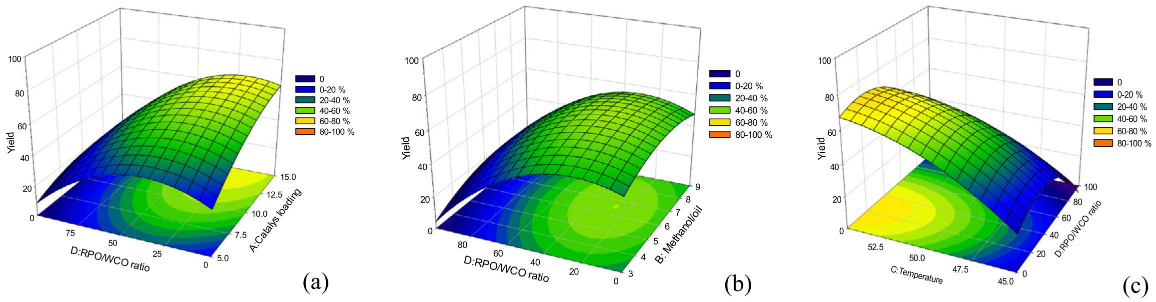

Fig. 2. Response surface plots of FAME yield (%) as a function of: (a) catalyst loading (wt%) and RPO/WCO ratio (wt%), (b) RPO/WCO ratio (wt%) and methanol/ oil, (c) reaction temperature (^{o}C) and RPO/WCO ratio (wt%).

Finally, Fig. 2c shows the influence of reaction temperature and RPO/WCO ratio on FAME yield. In the tested range, temperature has a positive and significant effect on FAME yield.

An important objective of this study was to find optimal operational conditions to achieve maximum FAME yield, combining the several independent variables studied. The RMS suggested that the highest FAME yield was 77.06%, which can be obtained by using 14.63 wt% of catalyst loading, 5.42/1 methanol/oil molar ratio, 14.81 wt% of RPO in the oil mixture and 55 °C for the reaction temperature.

4. Conclusions

Aiming to partially replace, by residual materials, some of the raw-materials, usually used in the biodiesel production process, one studied the performance of biomass fly ashes (as a catalyst) and a waste cooking oil (as an oil feedstock). The following operational variables were tested: reaction temperature, catalyst loading, RPO/WCO and methanol/oil ratios, using the Box–Behnken experimental design. One observed that, for the tested ranges, the reaction temperature, RPO/WCO ratio and the catalyst loading were the most significant variables affecting the FAME yield, while methanol/oil molar ratio had no a significant influence (p-value > 0.05).

To achieve the higher FAME yield c.a. 77.06% registered in this work, the RMS pointed out the following operational conditions: 14.63 wt% of catalyst loading, 5.42/1 of methanol/oil molar ratio, 14.81 wt% of RPO in the oil mixture and 55 °C for the reaction temperature.

The results obtained in this work are promising since they demonstrate the feasibility of valorizing a WCO and FAD in the production of biodiesel contributing, this way, to a circular economy.

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