OPTIMIZATION OF THE REAL CONVERSION EFFICIENCY OF WASTE COOKING OIL TO FAME

by

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This work presents a polynomial regression model for the optimization of the content of fatty acid methyl esters and the conversion yield of waste vegetable oil to biodiesel. The equations are optimized to obtain the maximum fatty acid methyl esters yield, which is the product of the conversion yield and the fatty acid methyl esters content in the biodiesel. The independent variables considered are the type of catalyst used (KOH and NaOH), percentage of catalyst (0.6%, 1.0%, and 1.5% w/w with respect to oil), and the methanol: oil molar ratio (6:1, 7.5:1, and 9:1). The prediction models are obtained by using nine experimental points for each catalyst. The validation is developed with four main experimental points from the mapping. A polynomial relation is obtained as a consequence, which correlates each of the experimental variables with the fatty acid methyl esters and conversion yield. The optimization of the proposed models shows an error of 2.66% for the fatty acid methyl esters, and an error of less than 1% for the conversion yield are obtained. This work presents a straight forward methodology to obtain the best chemical conditions in the production of biodiesel by using a small number of experiments, obtaining good results. This methodology can be applied for biodiesel production from any raw material, recalculating each of the regression constants thus allowing to obtain the highest quantity of oil to be converted in fatty acid methyl esters.

Key words*: biodiesel, fatty acid methyl esters, waste cooking oil, factorial design, polynomial regression*

Introduction

The increase in the global energy demand, the scarcity and high prices of fossil fuels, and the environmental impact caused by the burning of these fuels are the incentives to look for other alternatives of energy sources. Another problem associated with this issue is the production and disposal of residues, which needs to be solved in an economical and environmentally friendly manner [1, 2]. One of the alternatives to tackle these problems is the use of biofuels since they can be obtained from a RES and their degradation does not cause damages to the environment. To date, the international agency of energy expects a significantly increase in energy consumption [3], estimating that for the year 2030 it should be 11861 million of tons, that means an increase of 22.8% higher than in 2015. On the other hand, it is estimated that the consumption of biofuels would be almost twice that in 2015, that is, from 57-105 millionns [4,

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5]. Moreover, it is expected that the energy use by means of biofuels will reach 109.4 million barrels per day by 2040 [6].

Among all the alternatives for biofuel production, waste cooking oil (WCO) is a promising one to produce biodiesel [7, 8]. The WCO is usually available at low cost since it is a waste product from kitchens [9, 10]. Additionally, the pollution of soils and water bodies caused by the inadequate disposal of WCO to drains or sewers can be avoided if it is reused properly [11-13]. The WCO is obtained from vegetable or animal fats mainly composed of triacylglycerols, which are long-chain fatty acids chemically joined to a glycerol skeleton (1,2,3-propanetriol) [14, 15]. The reaction conditions for each WCO depend on their chemical composition, of which density, viscosity, and the content of free fatty acids affect the formation of esters during the production of biodiesel [16]. All these characteristics vary for each WCO because of the different crop it comes from and the treatment it receives after disposal [17].

Several variables are important for the production of biodiesel, such as the alcohol: oil molar ratio, concentration, type of catalyst, temperature, stirring rate, and time of reaction [18]. Even when such variables such as temperature, stirring rate, and time of reaction are set constant during the biodiesel production process, it is still difficult to develop a detailed analysis of the process because of the simultaneous interactions of other variables, and the properties of the different raw materials available [19]. However, the production of biodiesel from WCO depends mainly on the content of free fatty acids and the transesterification reaction efficiency [20]. If the content of free fatty acids is above 3%, it is necessary to develop an acid catalysis (esterification) before the basic catalysis (transesterification) [21, 22]. The reagents used on the production of biodiesel are acid (homogeneous or heterogeneous), basic (homogeneous or heterogeneous), or enzymatic [23-25]. In general, most of the biodiesel production is carried out by using sodium hydroxide, potassium hydroxide, and sodium methylate as catalysts [26-28].

Several works are focused on the study of the variables involved in the production of biodiesel from oils. An optimization of the fatty acid methyl esters (FAME) from WCO, considering variables such as chemical composition and temperature, is conducted in [7], achieving curve fittings up to 99.9% on a statistical model of FAME prediction. The optimization of FAME from castor oils, considering variables such as the alcohol: oil molar ratio, the percentage of catalyst (KOH), and temperature is presented in [18]. The optimization of FAME from flax oil, considering variables such as the alcohol: oil molar ratio, the percentage of catalyst, temperature, and time of reaction is presented in [29]. The production of biodiesel from castor oil, taking into account the catalyst concentration, methanol: oil molar ratio, reaction temperature, and time of reaction is presented in [30]. The optimization of the mass-flow rate of water for the cleaning process, in order to clean the biodiesel produced is shown in [31]. The optimization of the FAME yield for the production of biodiesel from papaya oil by transesterification, using a 700 W microwave and magnetic agitation is discussed in [32]. All these works have the esters content in the biodiesel as the only response factor. Some of them are focused on the chemical composition, and others are focused on the chemical and physical variables of the reaction. However, to the best of the author's knowledge, no publication is focused on the percentage of oil that is converted to biodiesel, in order to know the real efficiency of the conversion of oil to FAME.

This paper presents the production of biodiesel from WCO with the method of transesterification, changing the type of catalyst, the percentage of catalyst, and the alcohol: oil molar ratio. A polynomial regression model is used for the prediction and optimization of conversion, real FAME content, and FAME yield. Moreover, the optimum values for conversion, real FAME content, and FAME yield are obtained by maximizing these polynomials for each catalyst.

Materials and methods

Raw materials and reagents

The WCO collected from several restaurants located in the city of Salamanca, Mexico, is used in this work to produce biodiesel. The WCO is vacuum filtered with a No. 1 Whatman brand paper filter to retain the suspended solids up to 11 μm with the aim of eliminating elements such as sulfate, calcium, or carbonates. For the filtration process, the oil is heated over a period of 10 minutes at a constant temperature of 80 °C in order to decrease the viscosity and eliminate the water content in it. The oil characterization is developed by following the ISO and ASTM standards, *i.e.*, the ISO 6883-2017 is used to obtain the density, the ASTM D445 is used to obtain the viscosity, and the NMX-F-101-SCFI-2012 is used to obtain the acidity percentage. The acidity index is measured three times during the production process to verify that it remains constant, which assures that the process is truly carried out with the method of transesterification. Analytical methanol with a 99% purity (Baker brand) is used to avoid undesirable parameters in the chemical reaction. Potassium hydroxide (KOH) flake technical grade with a 98% purity (Merk brand) and NaOH pearl technical grade with a 98% purity (Merk brand) are used as catalysts.

Parameters considered for the experiments

From among the six variables that influence the transesterification process of WCO, *i.e.*, alcohol: oil molar ratio, type of catalyst, catalyst concentration, temperature, stirring rate, and time of reaction, only the first three variables are considered here because it is well known that the optimum temperature for this type of process is 60 °C [7, 29], a time of reaction higher that 90 min assures that the process is completed [7, 33], and the stirring rate has no influence for a small amount of an oil-alcohol such as the one used here [7]. Table 1 shows the eight parameters considered in this work to produce biodiesel from WCO. Nine mapping points are used for the development of the experiments in order to obtain a refined response surface, as shown by the black circles of fig. 1. This design of experiments allows exploring four regions of the 3^2 experimental design. The eighteen experiments (nine for each catalyst) are performed in a random manner to minimize the error associated with the systematic trend in the variables. Also, four replicas of each of the eighteen runts are performed for statistical analysis. The experimental matrix of the factorial design is given in tab. 2.

Table 1. Parameters considered for the experiments

Fixed parameters	Value
WCO	200 g
Type of alcohol	Methanol
Temperature	60 °C
Agitation speed	600 rpm
Time of reaction	120 minutes
Variable parameters	Value
Type of catalyst	NaOH and KOH
Catalyst concentration	0.6, 1.0, 1.5 %.w/w
Methanol: oil molar ratio	6:1, 7.5:1, 9:1

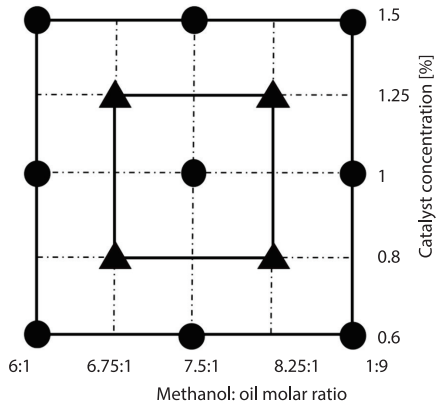

Figure 1. Experimental mapping used for the experiments; black circles are used for validation and black triangles are used for prediction

Table 2. Experimental matrix of the 3^2 factorial design, for each of the catalysts used

Run	Catalyst	Percent of catalyst	Methanol: oil
1/10	KOH/NaOH	0.60	6.:1
2/11	KOH/NaOH	1.00	6:1
3/12	KOH/NaOH	1.50	6:1
4/13	KOH/NaOH	0.60	7.5:1
5/14	KOH/NaOH	1.00	7.5:1
6/15	KOH/NaOH	1.50	7.5:1
7/16	KOH/NaOH	0.60	9:1
8/17	KOH/NaOH	1.00	9:1
9/18	KOH/NaOH	1.50	9:1

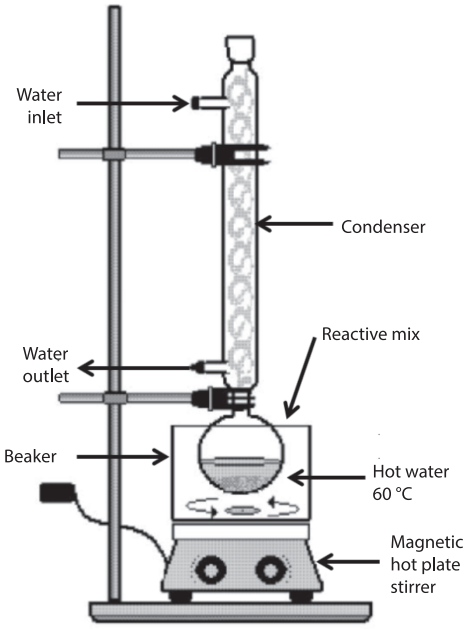

Figure 2. Scheme of the test facility

Transesterification

The transesterification process starts with the preheating of 200 ±1 g of WCO to a temperature of 60 ±1 °C, and the corresponding catalyst dissolution (NaOH or KOH) with the corresponding quantity of methanol for each sample. Subsequently, the reagents were put in a shaking plate and are warmed up in a water bath of 3 L at 60 ±0.5 °C during a two-hour period. A condenser is used to avoid the loss of reagents by evaporation. In order to describe the set-up more specifically, fig. 2 is presented.

Cleaning and drying of the biodiesel

After two hours of reaction, the products, *i.e.*, biodiesel and glycerin are separated by decanting over a period of 24 hours. The biodiesel is subsequently cleaned with water at 60 °C. Then, the biodiesel is dried to eliminate water residues from the cleaning process. The drying process is conducted on a heating plate at 120 °C for a period of 30 minutes. Finally, the biodiesel is stored on a recipient.

Characterization of the biodiesel

The biodiesel characterization tests were carried out within the following three days after it was obtained to avoid the natural degradation effects. The biodiesel characterization was performed with the following standards: the ASTM 1298 is used to measure density by means of a buoyant densimeter manufactured by ISOLAB with an uncertainty of ±0.1, the ASTM D445 is used to measure the kinematic viscosity by making use of a Cannon-Fenske viscosimeter with a time and temperature uncertainty of ±0.1 second and ±0.1 °C, respectively, and EN 14103: 2011 is used to measure the FAME percentage by gas chromatography. The chromatograph used in this work is a VARIAN 450GC with a Supelco column of 30 m × 25

mm × 0.25 μm, and a heptadecanoate (C_{17}) as an internal pattern, with an uncertainty of ±0.01 in the concentration of this internal pattern.

Prediction models

Regression model

A second order polynomial regression model:

$$\theta = \phi_1 + \phi_2 x + \phi_3 y + \phi_4 x^2 + \phi_5 y^2 + \phi_6 xy + \phi_7 x^2 y + \phi_8 xy^2 \tag{1}$$

is used to predict the conversion of WCO to FAME as well as the real FAME content on the biodiesel. Where θ is the response variable (conversion or real FAME content), ϕ_i – the regression constants, x – the independent variable which represents the alcohol: oil molar ratio, and y – the independent variable which represents the catalyst concentration.

Generalized regression model

For the generalized regression equation, the type of catalyst used is considered. Thus, a second order polynomial regression with three independent variables is obtained:

$$\begin{aligned}\eta = \zeta_1 + \zeta_2 x + \zeta_3 y + \zeta_4 z + \zeta_5 x^2 + \zeta_6 y^2 + \zeta_7 zx + \zeta_8 zy + \zeta_9 xy + \\ + \zeta_{10} x^2 z + \zeta_{11} xyz + \zeta_{12} zy^2 + \zeta_{13} x^2 y + \zeta_{14} xy^2 + \zeta_{15} zx^2 y + \zeta_{16} zxy^2 + \zeta_{17} x^2 y^2\end{aligned} \tag{2}$$

where η is the generalized response variable (conversion or real FAME content) and z – the independent variable which represents the type of catalyst (1 for NaOH and –1 for KOH).

The FAME yield, C+conversion, and real FAME content

The real FAME content, F, which represents the amount of oil converted to fatty acid methyl esters present in the sample, is calculated:

$$F = CY \tag{3}$$

where Y is the value of the FAME yield which is obtained by gas chromatography and C – the conversion:

$$C = \frac{m_{\text{bio}}}{m_{\text{oil}}} \tag{4}$$

where m_{oil} is the initial mass of WCO and m_{bio} – the mass of the biodiesel obtained.

Validation method

In order to ensure that eqs. (1) and (2) represent good models to predict the conversion and real FAME content, the predictions are validated with the experiments described in tab. 3 and represented by the black triangles of fig. 1. Also, four replicas of each of the eight validation runs are performed for statistical analysis.

The prediction error is defined as the deviation of the predictions obtained with eqs. (1) and (2), with respect to the experimental data.

Table 3. Validation of the experiments

Run	Catalyst	Percent of catalyst	Methanol : oil
19/23	KOH/NaOH	0.80	6.75:1
20/24	KOH/NaOH	1.25	6.75:1
21/25	KOH/NaOH	0.80	8.25:1
22/26	KOH/NaOH	1.25	8.25:1

Results and discussion

Properties of the waste cooing oil

The average acidity of the waste cooking oil used in the experiments is 0.7% with a variation of 1% on the measurements. The dynamic viscosity is 65.2 mPa·s, and the density is 925 kg/m^3. These characteristics show that the WCO is not used many times before being disposed of. Additionally, the transesterification only is needed to obtain the biodiesel because the average acidity is found to be below 3%. Table 4 shows the physical and chemical properties of WCO.

Table 4. Physical and chemical properties of WCO

Properties	WCO	Standard
Acidity percentage [%]	0.72 ±0.04	NMX-F-101-SCFI-2012
Kinematic viscosity, ν [mm^{2}s^{-1}]	70.46	ASTM 445
Density, ρ [kgm^{-3}]	925	ASTM D1298
Fatty acid composition	Molar weight [gmol^{-1}]	[%.w/w]
Palmitic (C16:0)	256.40	11.71
Stearic (C18:0)	284.48	4.42
Oleic (C18:1)	282.47	29.96
Linoleic (C18:2)	280.44	4836
Linolenic (C18:3)	272.43	5.72

Properties of the biodiesel obtained

The results of the biodiesel density and viscosity are given in tab. 5. It is observed that these two properties are independent of both, the methanol: oil molar ratio and the type of catalyst, because their values remain almost constant for the tests developed.

Adjustment of the equations

The ϕ_i constants of eq. (1) and eq. (2), for the conversion and the real FAME content, are obtained by applying a polynomial regression the data obtained from the experiments. The values of the determination coefficients are given in tab. 6. It can be seen that the values of r^2 are above 95% for each case, and the values of the adjusted r^2 are above 85% for each case. These results suggests that the values predicted by the equations are well acceptable.

Experimental and predicted results for conversion

The experimental results of the conversion obtained for each run, and for each catalyst (runs 1-9 for NaOH and runs 10-18 for KOH), are given in tab. 7. The statistical error of the experimental results, given by the standard deviation, is observed to be less than 2% for each of the experimental runs.

Once the polynomial regressions are developed, and considering the estimated values of conversion given by the alcohol: oil molar ratio, x, the catalyst concentration, y, and the type of catalyst, z, the relations:

$$C_{\mathrm{NaOH}} = 73 - 7.7x + 118y + 1.1x^2 - 106.9y^2 + 1.3xy - 1.57x^2y + 10.74xy^2 \tag{5}$$

$$C_{\mathrm{KOH}} = 387.57 - 69.6x - 346.72y + 4.033x^2 + 45.74y^2 + 77.92xy - 4.189x^2y \tag{6}$$

Table 5. Properties of the biodiesel obtained

Run	Density at 15 [°C]*		Kinematic viscosity at 40 [°C]**	
	ρ [kgm^{-3}] ±1		ν [mm^{2}s^{-1}] ±0.01	
	NaOH	KOH	NaOH	KOH
1/10	886	889	5.72	5.43
2/11	884	887	5.50	6.23
3/12	885	885	5.62	5.73
4/13	886	888	5.45	5.81
5/14	886	887	5.80	6.18
6/15	888	886	5.73	6.27
7/16	887	888	5.42	5.57
8/17	885	887	5.70	5.52
9/18	888	887	5.76	5.59
19/23	886	887	5.29	6.12
20/24	886	888	5.85	5.45
21/25	886	887	5.65	6.20
22/26	886	887	5.72	5.50
Average	886.10	887.20	5.63	5.82

* Specification of EN14214:2001 for density is ρ_{min}= 860 kg/m^3 and ρ_{max}= 900 kg/m^3
** Specification of EN14214:2001 for kinematic viscosity is ν_{min} = 3.5 mm^2/s and ν_{max} = 5.0 mm^2/s
Local barometric pressure is 88.26 kPa. The value is verified by using a barometric sensor Bme280

Table 6. Determination coefficients of the regressions

Catalyst	S	r^2 [%]	Adjusted r^2 [%]
Conversion			
NaOH	2.96	98.34	86.68
KOH	0.15	99.98	99.85
Generalized	2.61	96.85	86.60
FAME			
NaOH	2.67	98.16	85.32
KOH	2.13	98.55	88.39
Generalized	0.19	99.97	96.76

$$C = 246.7 - 40.8x - 149.8y - 94.5z + 2.57x^2 - 13.89y^2 + 22.6zx + \\ + 97zy + 44.3xy - 1.47x^2z - 20.3xyz - 2.88x^2y - 12.41y^2z + 1.31zx^2y \quad (7)$$

are obtained. The results for the conversion obtained by using these equations, in terms of the prediction error, are also given in tab. 7, where runs 1-9 are for NaOH and runs 10-18 are for KOH. It can be observed that better values of conversion are obtained when KOH is used as a catalyst. That is, the maximum value of conversion when using KOH is 100% and the maximum value of conversion when using NaOH is 92%. It can also be observed that smaller predicted errors are obtained when using KOH as a catalyst. Moreover, can also be observed that the prediction of the validation runs show a bigger error than the predictions of the experimental

Table 7. Experimental values and predicted errors for the conversion

Run	NaOH			KOH		
	Experimental values [%]	Error		Experimental values [%]	Error	
		Eq. (5) [%]	Eq. (7) [%]		Eq. (6) [%]	Eq. (7) [%]
1/10	92	0.35	1.01	100	0.02	0.32
2/11	92	1.33	1.11	9.3	0.13	1.85
3/12	75	0.29	0.59	88	0.09	0.17
4/13	90	1.45	1.60	93	0.13	0.67
5/14	92	1.94	2.00	93	0.01	0.52
6/15	7	1.31	0.96	92	0.18	0.69
7/16	91	0.40	1.48	93	0.07	1.54
8/17	84	1.30	3.85	92	0.18	0.47
9/18	74	0.62	2.20	86	0.16	1.54
Average		0.99	1.64		0.11	0.86
19/23	90	3.69	3.08	90	4.78	5.61
20/24	83	4.41	2.96	91	1.17	2.13
21/25	91	0.95	0.26	90	3.00	3.28
22/26	77	7.91	8.77	89	3.30	3.39
Average		4.18	3.77		3.06	3.60

design runs. This is something expected because the experimental design runs are used to obtain the ϕ_i and ζ_i constants. Another way to observe the comparison between the experimental data and the results of the predictions involves using parity diagrams. Figure 3 shows the results for conversion. It is observed that the equations predict the experimental results accurately. A small deviation between the numerical and experimental values is observed and is attributed to the adjustment error. All the averages for the predictions on the points considered for the validation are below 1.64% in all cases. This shows that the equations can be used to predict well the points that are not taken into account during the regression, *i.e.*, runs 19-22 for NaOH and runs 23-26 for KOH.

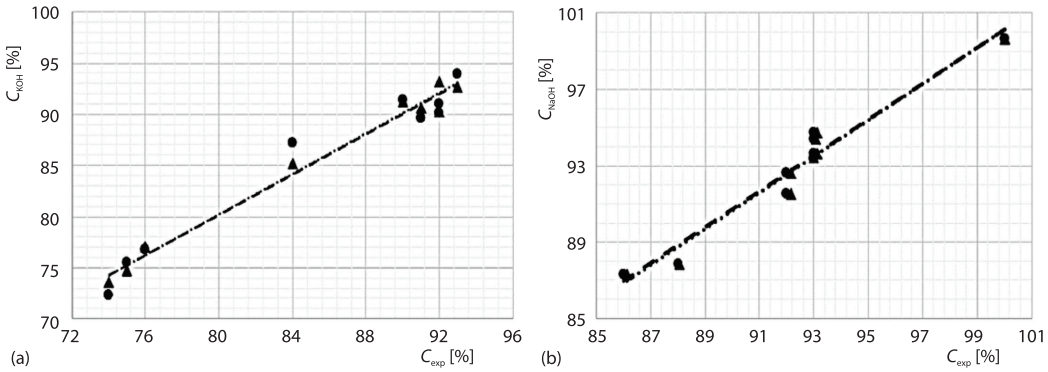

Figure 3. Parity diagram of experimental and calculated values of the conversion for (a) NaOH and (b) KOH, black triangles represent the values obtained using eq. (5) for NaOH and eq. (6) for KOH, and the black dotted line is their fitting curve, black dots represent the values obtained using eq. (7), and the black dashed line is their fitting curve

Experimental and predicted results for the real FAME content

The experimental results of the real FAME content obtained for each run, and for each catalyst (runs 1-9 for NaOH and runs 10-18 for KOH), are given in tab. 8. The statistical error of the experimental results, given by the standard deviation, is observed to be less than 2% for each of the experimental points. Once the polynomial regressions are developed, and considering the estimated values of the real FAME content given by the alcohol: oil molar ratio, x, the catalyst concentration, y, and the type of catalyst, z, the relations:

$$Y_{NaOH} = -306 + 128.1x + 232y - 9.33x^2 + 122.9y^2 - 110.6xy + 9.35x^2y - 13.33xy^2 \tag{8}$$

$$Y_{KOH} = -93 + 52x - 8y - 4.27x^2 + 122.6y^2 - 14.1xy + 3.39x^2y - 21.48xy^2 \tag{9}$$

$$\begin{aligned} Y = {} & -654.8 - 106.49z + 214.79x + 1091.6y - 15.114x^2 - 340y^2 + \\ & +38.04xz + 120.21yz - 330.7xy - 2.532zx^2 - 48.27xyz + 0.18y^2z + \\ & +24.259x^2y + 109.37xy^2 + 2.978x^2yz + 4.076xy^2z - 8.452x^2y^2 \end{aligned} \tag{10}$$

are obtained. The results for the real FAME content obtained by using these equations, in terms of the prediction error, are also given in tab. 8, where runs 1-9 are for NaOH and runs 10-18 are for KOH. It can be observed that better values of conversion are obtained when NaOH is used as a catalyst. That is, the maximum value of conversion when using KOH is 99.5% and the maximum value of conversion when using NaOH is 96.3%. It can also be observed that smaller predicted errors are obtained when using KOH as a catalyst. Moreover, it can also be observed that the prediction of the validation runs show a bigger error than the predictions of the experimental design runs. This is something expected because the experimental design runs are used to obtain the ϕ_i and ζ_i constants.

Table 8. Experimental values and predicted errors for the FAME yield

Run	NaOH			KOH		
	Experimental values [%]*	Error		Experimental values [%]*	Error	
		Eq. (5) [%]	Eq. (7) [%]		Eq. (6) [%]	Eq. (7) [%]
1/10	84.8	0.49	0.05	80.5	0.29	0.03
2/11	75.7	1.44	0.25	89.5	1.18	0.03
3/12	80.8	0.04	0.28	95.3	0.05	0.19
4/13	96.3	1.06	0.15	90.3	1.36	0.05
5/14	79.7	2.04	0.14	94.1	1.24	0.20
6/15	75.2	1.42	0.50	86.8	1.40	0.20
7/16	88.1	0.57	0.11	87.5	0.06	0.05
8/17	89.0	1.08	0.34	99.5	1.42	0.08
9/18	88.5	0.23	0.46	79.9	0.48	0.36
Average		0.93	0.25		0.83	0.13
19/23	85.6	2.13	2.78	89.9	0.27	0.04
20/24	81.3	8.56	9.50	86.8	6.61	5.98
21/25	92	3.46	4.18	93.1	2.63	2.48
22/26	78.7	2.87	1.71	87.8	5.98	5.54
Average		4.26	4.54		3.87	3.51

* Specification of EN14214:2001 for FAME is min = 96:5%

Figure 4 shows the parity diagrams for the real FAME content. It is observed that the equations predict the experimental results accurately. A small deviation between the numerical and experimental values is observed and is attributed to the adjustment error. As for the case of conversion, all the averages for the predictions on the points considered for the validation are below 1.64% in all cases. This shows that the equations can be used to predict well the points that are not taken into account during the regression, *i.e.*, runs 19-22 for NaOH and runs 23-26 for KOH.

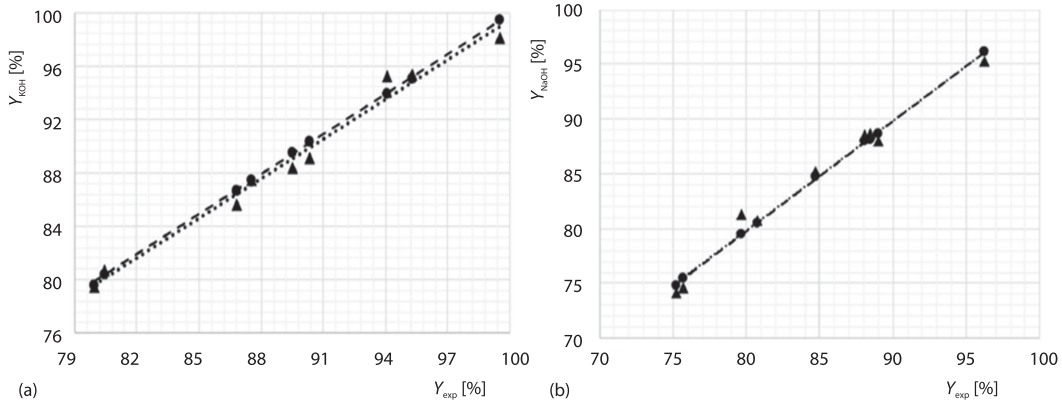

Figure 4. Parity diagram of experimental and calculated values of the real FAME content for (a) NaOH and (b) KOH; black triangles represent the values obtained using eq. (8) for NaOH and eq. (9) for KOH, and the black dotted line is their fitting curve

Maximization of conversion, real FAME content, and FAME yield

Once the validation of the equations is carried out and showing that errors below 5% are obtained for the predictions, the functions are maximized, establishing an upper limit of 100%. This maximization is performed by direct derivation of the objective function. Table 9 gives the maximum theoretical values for conversion, real FAME content, and FAME yield. These maximum theoretical values are given for each catalyst. Additionally, the theoretical values are compared with the experimental ones, and their difference is given as an error. A maximum error of 0.88% for conversion, a maximum error of 2.66% for real FAME content, and a maximum error of 3.4% for FAME yield are obtained. These results also indicate that the models can be used to predict the process well.

Table 9. Results of the optimization of the equations and experimental validation

Catalyst	Value in the equation	Optimal values [%]	Experimental values [%]	Error [%]
Conversion				
NaOH	$x = 6, y = 0.5, z = 1$	93.40	94.20	0.85
KOH	$x = 6, y = 1, z = -1$	100	99.80	0.20
FAME yield				
NaOH	$x = 7.444, y = 0.5, z = 1$	99.80	97.20	2.66
KOH	$x = 9.333, y = 1, z = -1$	98.20	96.70	1.55
Real FAME content				
NaOH	$x = 8.5, y = 0.5, z = 1$	86.20	89.20	3.34
KOH	$x = 9, y = 1, z = -1$	82.10	81.80	0.37

Other remarks

Other works similar to the one presented here are found in the literature [7, 29, 33, 34]. However, these works consider the FAME yield and the conversion as indices for the analysis of the transesterification process.

The FAME yield is analyzed in [29] for the transesterification of flaxseed oil, concluding that the optimum reaction conditions are an alcohol: oil molar ratio of 5.9:1, a KOH catalyst concentration of 0.51 (%.w/w), and a temperature of 59 °C. The present work shows that for the waste cooking oil used, the optimum reaction conditions are an alcohol: oil molar ratio of 9.33:1, a KOH catalyst concentration of 1.00 (%.w/w), with a temperature of 60 °C. The difference in alcohol: oil molar ratio and catalyst concentration is due to the higher content of free fatty acids in the waste cooking oil compared with the flaxseed oil. According to the results reported in [34] the optimum temperature for the transesterification of WCO is 60 °C, and the alcohol: oil molar ratio is 8:1. These results are in good agreement with the results of the present work, where the temperature used is 60 °C, and the optimum alcohol: oil molar ratio is 7.44:1. In [33] it is reported that the optimum alcohol: oil molar ratio for the transesterification of cotton-seed cooking oil is 7:1. This result once more is in good agreement with the alcohol: oil molar ratio of 7.44:1 found in the present work. Finally, a polynomial optimization method for the transesterification of WCO is used in [7], finding that the optimum amount of KOH used as catalyst is 2.00 (%.w/w), and the conversion is 94%. Anew, these results are in good agreement with the ones presented here; that is, an optimum amount of KOH used as catalyst of 1.00 (%.w/w), and a conversion of 100%. Also, the temperature used in both works is 60 °C.

Some other more recent works present optimization alternatives as the one performed by [35], where an experiment is carried out with Calophyllum inophyllum-Ceiba pentandraoil although it is not mentioned a general efficiency of the process, but the quantity of obtained methyl esters. On the other hand, recently in [29] authors show that the bipolynomial regression model when applied to FAME presents a good fit, but again, it is not mentioned the amount of oil that was converted into biodiesel, only the amount of FAME present in the obtained biodiesel. It is important to emphasize that even though the biodiesel has been studied for many years, day-to-day several research works are published where optimizations are carried out, since it is necessary to perform them according to each raw material, besides being the same oil, factors such as the type of land where the farming is made or the plant family can change the fatty acids, being this variable important at the moment to perform the transesterification reaction [18, 36-38].

Although these works published already in the literature use the FAME yield and the conversion as indices to characterize the efficiency of the transesterification process, non-e of them report the use of the real FAME content, which is one of the main contributions of the present work.

Conclusions

In this work is presented a polynomial regression model for the optimization of the content of FAME and the conversion yield of waste vegetable oil to biodiesel.

The equations obtained for the prediction of the conversion, real FAME content, and FAME yield show an error of less than 5%. It is also observed that the use of KOH as a catalyst produces a higher amount of apparent methyl esters and a lower FAME percentage, when compared to NaOH. In addition, the real FAME content, which is the real amount of waste cooking oil converted to biodiesel, shows values of about 90% for the best reaction conditions of the optimized equations; that is, values of about 89.2-97.2% are obtained when NaOH is used, and values of about 94.2-99.8% are obtained when KOH is used.

Despite the many optimization models available in the literature, straightforward experimental methodologies to find the best reaction conditions for a specific raw material are not presented. In this work, not only the FAME yield and conversion are optimized, also the real FAME content of waste cooking oil to fatty methyl esters is optimized. This allows to find the best reaction conditions for a specific raw material by using a very few numbers of experiments.

The presented methodology in this work can be applied for the optimization in the production of biodiesel from any raw material, recalculating each one of the regression constants, with this, allowing to obtain the highest amount of oil to be converted into FAME.

Nomenclature

C – C = convertion oil to F
F – real FAME content
r – linear correlation coefficient
Y – FAME yield

Greek symbols

ρ – density
ν – kinematic viscosity

Acronyms

FAME – fatty acids methyl esters
WCO – waste cooking oil

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