OPTIMIZATION OF BIODIESEL PRODUCTION FROM FRYING OIL AND BOVINE TALLOW

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ABSTRACT

Nowadays, discussions about energy-related issues are in evidence. The dynamics of gradual depletion of non-renewable energy reserves, such as oil ones, and global warming have encouraged the search for renewable energy alternatives. The main objective of this work is to evaluate the influence of major operational variables on the transesterification reaction of mixtures of frying oil and bovine tallow, in the presence of methanol, using microwave technology. In an effort to optimize biodiesel production, a statistical design was performed, considering the solvent/feed ratio, the ratio between frying oil and bovine tallow, the amount of KOH, reaction time, and temperature as independent variables. The dependent variables analyzed were biodiesel yield and esters content, obtained by chromatographic analysis. The experiments and the analysis confirmed that a 9:1 solvent/feed molar ratio of, 1.5% catalyst, 35 seconds reaction time, and a mixture containing 70% of frying oil and 30% of bovine tallow provided yields above 89 %. The best conditions to reach 99.43 % of ester content used a 9:1 solvent/feed molar ratio, 0.5 % catalyst, 70%/30% frying oil/bovine tallow, and 35 seconds reaction time.

KEYWORDS

biodiesel; frying oil; bovine tallow; methanol; microwave

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1. INTRODUCTION

The global economy has become more dependent on the energy's market. The increase in economical development has a direct relationship with higher energy demands. Thus, the energy matrix, and the dynamics for new energy sources are becoming essential for economic agents such as businesses, governments, or individuals.

In this context, biodiesel is a source of renewable energy and because of that, it can be observed the increase development in its market. To achieve this target, a growing number of feedstocks are used as raw materials in biodiesel production. Biodiesel is produced by the transesterification of triglycerides with short chain alcohols, such as methanol or ethanol, usually catalyzed by an acid or a base.

Likewise, in Brazil, the use of biodiesel plays a promising role in the Country's energy scenario. It contributes to the economy by creating jobs in the primary sector, which are important to the Country's social development, and is priority of the current government administration (UBRABIO, 2016).

Raw materials used in the production of biodiesel are vegetable oils, animal fats, and waste oils and fats. These materials have triglycerides, glycerol, esters, and fatty acids in varied proportions. Monoglyceride or diglyceride esters are obtained from the direct esterification of fatty acids, meaning that the solution has some esters differing in concentration and type (Gazzoni, 2012).

It is important to provide an overview about the potential of vegetable oils for biodiesel production, especially with regards to the technological and economic aspects of this process. However, the major obstacle in the commercialization of biodiesel production from edible vegetable oil is its high production cost. Raw material costs account for almost 59 % of the biodiesel production total cost. The choice of raw material for biodiesel production relies largely on geographical factors. Depending on the nature and quality of the raw material, changes in the production process may be required (Zhang et al., 2003). However, there are some alternative raw materials that can be used for biodiesel production, like frying oil and bovine tallow. Waste cooking oil and fats are promising alternatives for edible vegetable oil,

because they pose significant disposal problems in many parts of the world (Mohammadshirazi et al., 2014).

Moreover, bovine tallow is an inexpensive commodity for biodiesel production in Brazil (Oliveira, 2004). Brazil has produced around 650,000 ton of bovine tallow per year. Because in recent years the Country has increased its meat production, Brazil has satisfactory amounts of beef tallow that can be used as raw material in biodiesel production (SBRT, 2016). According to Mendonça et al. (2011), Brazil is the world leader in exportation of beef and has one of the world's largest cattle inventory. Therefore, biodiesel production from beef tallow, a byproduct of the beef industry, is not only viable from a raw material supply standpoint, but it has an environmental importance, since most of the beef tallow is, at the present moment, either discarded in rivers or used for soap production, as boiler fuel or as a component of animal food supplements (Bankovic-lic et al., 2014).

Likewise, throughout the world, the availability of residual oil or frying oil is significant. The discharge of oil into sewers, springs, and rivers is frequent, despite it being considered an environmental "crime". These types of oil discharges difficult the operations in wastewater treatment plants, demanding secondary and tertiary treatments for contaminants. Frying oil is a viable and advantageous alternative feedstock for biodiesel production based on environmental and economic reasons. The environmental reason relies on the fact that it prevents pollution due to the reutilization of the oil while the economic reason is due to the low cost of the oil (Felizardo et al., 2006).

Many works that focus on the economic evaluation of biodiesel production from frying oil by transesterification reaction report that it is economically viable, indicating that ultrasonic and microwave processes can be more advantageous (Araujo et al., 2010; Felizardo et al., 2006; Mohammadshirazi et al., 2014).

The fatty acid composition is not the only characteristic that makes the raw material ideal for biodiesel production. The material also must have a minimum moisture content and acidity. In some cases, processes like drying and neutralization are applied as a pre-treatment to establish the

standard limits of moisture and acidity. Companies that produce biodiesel usually require that their suppliers of bovine tallow provide the material in ideal conditions for the production of biodiesel (Moura, 2008).

There are a few works in the literature revealing the potential different types of oil mixtures and other feedstock for biodiesel production. Issariyakul et al. (2008) investigated different mixtures of canola oil and cooking oil (100:0, 80:20, 60:40, 40:60, 20:80, 0:100) to produce biodiesel, at 50 °C, using KOH (1% w/w) as catalyst, and methanol and ethanol at 6:1 (alcohol to oil molar ratio), for 2 h and 600 rpm. They observed that a higher methyl ester yield could be attained when canola oil was added to the feedstock mixture, using methanol as solvent. Using ethanol, a higher amount of cooking oil (at least 60 % wt.%) was required to improve ethyl methyl ester. Likewise, the application of simultaneous optimization for biodiesel production from a mixture of beef tallow and vegetable oils has also received little attention.

The application of microwave technology in the production process of biodiesel is still sparse in the scientific literature and patents. Only a few works present the advantages of applying microwave-based techniques involving rapid heating of the reaction medium and the acceleration of reactions. Among the various routes used in the synthesis of biodiesel, transesterification and esterification using heterogeneous catalysts and non-catalytic routes are the systems where higher temperatures are applied, and for which the dielectric heating would be very promising. For systems that have been operated at moderate temperatures, especially transesterification reactions via homogeneous catalysis, basic microwave technology could be useful to accelerate reaction kinetics and promote greater purity in the final product (Azcan & Danisman, 2008).

There are studies involving the application of the microwave technology, such as the one performed by Azcan and Danisman in 2008, but none of them was done with a mixture containing the raw materials used in this work. Thus, biodiesel production from a mixture of frying oil and beef tallow, using the microwave technology, has become a prime option for the use of these residues.

Therefore, the objective of this work is to

evaluate the influence of the major operational variables, such as reaction time, solvent/feed ratio, temperature, and the effect of composition of the mixtures of frying oil and bovine tallow in the transesterification reaction, using methanol as solvent and microwave technology. Specifically, the purpose of this work is to reveal what is required to mix residual oil with other feedstocks to use them in the production of fuels, focusing on economic, environmental and safety concerns.

2. MATERIALS AND METHODS

2.1 Materials

The Federal Rural University of Rio de Janeiro donated the frying oil used in this work. The oil was collected from the University's restaurant. The oil was used without any previous treatment, except for a proper filtration process, whenever required, carried out in the restaurant itself to remove any leftover solid material. Biocapital Consultory and Participations S.A (Brazil) supplied the bovine tallow.

The chemicals used were methanol (P.A., 99.8 % purity), potassium hydroxide (P.A.), sulfuric acid (P.A.), n-hexane (P.A.), diethylether (P.A.), phenolphthalein (P.A.), glacial acetic acid (P.A., 99.7% purity), and potassium iodide, from Vetec Química Fina Ltda (Rio de Janeiro, Brazil); sodium chloride (P.A.), from ProAnálisi (Isofar, Rio de Janeiro, Brazil); chloroform (P.A.), from Quimex; and soluble starch, sodium thiosulfate, and hydrochloric acid, from Analyticals Montedison (Rio de Janeiro, Brazil).

2.2 Experimental methodology

A pretreatment step was performed with bovine tallow samples to reduce their acidity index. Neutralization of bovine tallow was made by an acidic esterification to reduce the content of free fatty acid to less than 2 %. The acidic esterification was performed with 0.5 % H₂SO₄ as catalyst, an optimum concentration of 6:1 methanol/oil, at 45 °C, for 1 hour reaction time (Wyatt et al., 2005).

Initially, the methanol and KOH used as catalysts were mixed to prepare the alkoxide solution. The solvent/feed ratio (S/F) used in the experiments was established. The reaction was

Table 1. 2^4 Full Factorial Design for biodiesel production with microwave technology.

Independent variables	Levels		
	-1	0	1
Catalyst concentration (KOH) – X_1	0.5	1.5	1
Mixture – X_2	30/70*	50/50**	70/30***
Reaction Time (s) – X_3	10	22	35
S/F ratio – X_4	3:1	6:1	9:1

*30/70 – Mixtures: 30 % of frying oil + 70 % bovine tallow

**50/50 – Mixtures: 50 % of frying oil + 50 % bovine tallow

***70/30 – Mixtures: 70 % of frying oil + 30 % bovine tallow

done in a flat-bottomed flask (1000 mL) inside a domestic microwave oven at maximal power, at pre-determined times (10, 22, and 35 seconds). After reaching the reaction time, the products obtained were separated and purified. The separation was performed using a centrifuge (New Technique, Model NT 820), for 15 min at 3000 rpm, and a separation funnel. Glycerol was removed, and the obtained biodiesel was washed with a 5 % (w/w) aqueous solution of sodium sulphate, until the washing solution became clear. After the washing process, biodiesel was oven dried, for 1 hour at 105 °C, and then filtered with anhydrous sodium sulfate. The experimental procedures were done in the Biofuels and Applied Thermodynamic Laboratory at the Chemical Engineering Department of the Federal Rural University of Rio de Janeiro.

2.3 Experimental design

The response surface methodology (RSM) was used to determine the optimum operating ranges of each variable. The experiments were done according to a 2^4 full factorial design (FFD) with 4 center points (CP), comprising 20 experimental runs. The influence on the biodiesel yield (by weight and ester content) of the following independent variables was investigated: S/F ratio (methanol/oil molar ratio), different percentages of oils in the mixture, the amount of KOH, and reaction time. The effect of variables and their errors were calculated for a 95 % confidence level.

The values adopted for the independent variables are presented in Table 1. They were chosen according to the best operational results found in similar works using the same raw materials, bovine tallow and frying oil (Moura, 2010).

For each level combination in the planning matrix, the regression coefficients were also analyzed for each parameter, and the estimations were done with levels higher than 95 % and 92 % ($p < 0.05$ and $p < 0.08$) (Rodrigues & Iemma, 2005).

2.4 Chromatographic analysis

Identification and quantification of fatty acids in frying oil and bovine tallow samples were performed by gas chromatography, after the derivatization step of the oil to avoid clogging of the column (Felizardo et al., 2006). An INTECROM G 8000 equipped with a CP-CIL 88 FAME column (100 m length x 0.25 mm x 0.20 μ m thick film) was used with a FID detector.

The saponification reactions were performed in test tubes with screw caps. For each 200 to 500 mg of the lipid sample, 3 mL of 0.5 mol.L⁻¹ methanolic sodium hydroxide solution were added, and the samples were placed in a water bath (at boiling temperature for 30 min). Afterwards, the test tubes were cooled and 5 mL of the methylation reagent were added. The mixtures were heated at boiling temperature under reflux for 5 min. After cooling, 8 mL of sodium chloride saturated solution were added. The methyl esters migrated to the top of the solution and were solubilized by adding 2 mL of n-hexane.

The esters obtained were injected into a gas chromatograph. The chromatographic operating conditions were: 1 μ L injection volume, 140 °C initial temperature, 4 °C/min heating rate, 240 °C final temperature, 250 °C injector temperature, 280 °C detector temperature, 5 min initial time, 40 min total time, 70 kPa column pressure, 1:50 split, with 1 mL/min helium carrier gas flow rate, 300 mL/min synthetic air flow rate, 30 mL/min nitrogen flow rate. Biodiesel was also analyzed by gas

Table 2. Oils, fats, and derivatives analyses.

Properties	Methods
Acid (mg KOH/g)	AOCS Bc 3d-63
Saponification (mg KOH/g)	SMAOFD 2.202
Refractive index at 25 °C	AOCS Cc 7-25
Iodine (g I ₂ /100 g)	AOCS Cd 1c-85
Moisture (%)	AOCS Bc 2-49
Viscosity at 40 °C (mm ² /s)	ASTM D 445
Density (kg/m ³)	ASTM D 4052

Table 3. Physicochemical properties of frying oil, bovine tallow, and their mixtures.

Physicochemical Properties	Frying Oil	Bovine tallow	70/30	50/50	30/70	ANP values
Acidity index (mg KOH/g)	0.54	1.74	0.55	1.45	1.67	0.50
Iodine index (g I ₂ /100g)	180.81	63.57	167.3	128.60	96.45	120
Saponification number (mg KOH/g)	197.90	197.90	191.40	192.10	192.40	-
Moisture (%)	0.19	0.18	0.19	0.18	0.18	< 0.2%
Density (kg/m ³)	909.68	902.31	905.52	906.04	906.29	850-900
Viscosity at 40 °C (mm ² /s)	36.41	46.99	42.16	43.09	46.61	3-6
Refractive Index at 25 °C	1.48	1.46	1.45	1.46	1.47	-

chromatography (GC), but it was necessary to filter each sample to retain particles that could damage the equipment.

2.5 Sample analysis

The analyses of frying oil and bovine tallow samples followed the international regulations of Standard Methods for the Analysis of oils, fats, and derivatives (SMAOFD, 2016), the American Oil Chemists Society Official and Tentative Methods (Sulistyo et al., 2008), and the American Society for Testing and Materials (ASTM, 2016). All the specification analyses of the raw materials are presented in Table 2. The analyses were done in triplicate.

triplicate, and Table 3 presents the average results of the physicochemical properties. Table 3 also presents the ANP values for each quality parameter for biodiesel. In particular, it must be pointed out that determination of the saponification number and refractive index is not mandatory by the National Regulatory Agency of Petroleum, Gas and Biofuels (ANP).

Reports in the literature (Fangrui et al., 1999; Fukuda et al., 2001; Ma & Hanna, 1999) show that the ideal conditions for biodiesel production, considering acidity, are values below 2.0 mg KOH/g. Table 3 shows 8.46 mg KOH/g for bovine tallow prior to the pre-treatment, thus, it was neutralized, reaching 1.74 mg KOH/g.

It could be observed that acidity values were below 2 mgKOH/g, and moisture contents for all samples were according to the limits established by ANP (2016).

The values for kinematic viscosity are in the range of 36 and 47 mm²/s, which are not in agreement with the ranges specified for these mixtures according to ANP. The viscosity increases with the length of the triglycerides and fatty acid carbon chain, and decreases when the unsaturation degree increases (Moretto & Fett, 1998).

3. RESULTS AND DISCUSSION

3.1 Physicochemical analysis of the oils and mixtures (FOT)

A physicochemical characterization of the oils and their mixtures was performed according to the acidity value, iodine value, saponification number, moisture, density, kinematic viscosity, and refractive index, after a pretreatment step, whenever necessary. The analyses were done in

Table 4. Composition of fatty acids found in frying oil, bovine tallow, and mixtures.

Fatty Acids			Molar Mass and Compositions					
Abbreviation	IUPAC Name	Name	Molar Mass	Frying Oil (%)	Bovine tallow (%)	70/30 (%)	50/50 (%)	30/70 (%)
C 14:0	Tetradecanoic acid	Myristic acid	242.39	2.92	2.27	0.63	1.20	1.48
C 16:0	Hexadecanoic acid	Palmitic acid	270.44	18.23	23.71	14.25	17.08	18.84
C 18:0	Octadecenoic acid	Stearic acid	298.50	1.66	16.25	7.15	-	11.89
C 18:1	9-octadecenoic acid	Oleic acid	296.48	19.49	34.96	27.37	10.31	30.55
C 18:2	9,12-octadecadienoic acid	Linoleic acid	294.47	49.65	12.54	47.99	31.69	29.56
C 18:3	Octadecatrienoic acid	Linolenic acid	292.45	6.52	-	4.66	0.29	2.49
C 20:0	Eicosanoic acid	Arachidonic acid	326.55	-	-	0.31	32.30	2.84

The saponification number (SN) is a characteristic of vegetable oils, being inversely proportional to the average molecular weight of the fatty acids present in the triglycerides. This means that when the size of the fatty acid chain increases, oil saponification rate decreases (Kucek et al., 2007; Moura, 2008; Wyatt et al., 2005). The SN found for oils and mixtures thereof are within the range of 192 to 198 mg KOH/g.

The iodine index of the oils and mixtures is between 63 and 181 g I₂/100 g (McCormick et al., 2001). This analysis consists of an empiric method to measure the unsaturation degree present in the biofuel. According to Pereira (2007), when the iodine index increases, the unsaturation degree also increases; this is a sign that the vegetable oil and/or biofuel has a great tendency to oxidize. In the literature, it is possible to find iodine indexes for frying oil ranging between 69 and 143 g I₂/100 g (Demirbas, 2002; Silva et al., 2010).

3.2 Characterization of the frying oil and bovine tallow (FOT) mixture

3.2.1 Chemical composition

The mixtures were subjected to an alkaline methanolysis, and the obtained esters were analyzed by gas chromatography. The contents of fatty acids present in frying oil, bovine tallow, and mixtures are shown in Table 4. The values of the chemical composition in terms of fatty acids for

frying oil and bovine tallow are in agreement with data available in literature for the average composition of the oils (Moura, 2010; 2008).

Based on the values of Table 4, it was possible to calculate the average molecular weight of the frying oil (820.13 g/mol); bovine tallow (840.59 g/mol); 70/30 mixture (827.00 g/mol); 50/50 mixture (821.57 g/mol); and 30/70 mixture (837.14 g/mol). It could be also observed that the chemical composition of the oils and the mixtures were based mainly on palmitic, oleic, and linoleic fatty acids.

3.3 Transesterification reaction

The results concerning the biodiesel production were analyzed in terms of biodiesel yield (% R) and ester content (% E), as shown in Table 5. The biodiesel yield by weight (% R) was calculated with Equation 1:

$$\%R = \frac{m_{biod} \cdot MM_{oil}}{m_{oil} \cdot MM_{biod}} \cdot 100 \quad (1)$$

Where m_{biod} is the purified biodiesel mass, MM_{oil} is the average molar mass of the oil mixture, m_{oil} is the mass of the oil mixture, and MM_{biod} is the average molar mass of biodiesel.

The yield of ester (% E), or the ester content, produced with frying oil and bovine tallow, was named as BTFM, and was defined as the sum of the

Table 5. Results of biodiesel production according to the 2⁴ factorial design.

Coded variables					Independent variables				Dependent variables (Yields)	
Assay	X ₁	X ₂	X ₃	X ₄	X ₁	X ₂	X ₃	X ₄	*R (%)	**E (%)
1	-1	-1	-1	-1	0.5	30/70	10	3:1	81.17	97.33
2	-1	-1	-1	1	0.5	30/70	10	9:1	81.04	99.13
3	-1	-1	1	-1	0.5	30/70	35	3:1	70.84	98.75
4	-1	-1	1	1	0.5	30/70	35	9:1	65.98	99.06
5	-1	1	-1	-1	0.5	70/30	10	3:1	70.20	99.19
6	-1	1	-1	1	0.5	70/30	10	9:1	75.95	99.33
7	-1	1	1	-1	0.5	70/30	35	3:1	88.57	99.15
8	-1	1	1	1	0.5	70/30	35	9:1	75.78	99.43
9	1	-1	-1	-1	1.5	30/70	10	3:1	51.14	99.09
10	1	-1	-1	1	1.5	30/70	10	9:1	84.90	99.18
11	1	-1	1	-1	1.5	30/70	35	3:1	62.56	99.11
12	1	-1	1	1	1.5	30/70	35	9:1	59.17	99.11
13	1	1	-1	-1	1.5	70/30	10	3:1	68.23	99.11
14	1	1	-1	1	1.5	70/30	10	9:1	88.87	99.42
15	1	1	1	-1	1.5	70/30	35	3:1	60.88	99.26
16	1	1	1	1	1.5	70/30	35	9:1	85.00	98.42
17	0	0	0	0	1	50/50	22.5	6:1	80.30	99.14
18	0	0	0	0	1	50/50	22.5	6:1	78.90	99.13
19	0	0	0	0	1	50/50	22.5	6:1	75.63	99.10
20	0	0	0	0	1	50/50	22.5	6:1	78.56	99.04

*R = Biodiesel yield mass, **E = Ester content

Table 6. Effects of factors and standard errors corresponding to the mass yield in BFTM

Factors	Effects	Regression Coefficients	Standard Error	tcal*	p-Value**
Mean	74.284	74.284	0.439	169.326	< 0.0001
X ₁ :KOH	-6.098	-3.049	0.981	-6.216	0.008
X ₂ :Mixture	7.335	3.668	0.981	7.477	0.005
X ₃ :Time	-4.090	-2.045	0.981	-4.169	0.025
X ₄ :molar ratio	7.888	3.944	0.981	8.041	0.004
Interactions					
X ₁ X ₂	4.218	2.109	0.981	4.299	0.023
X ₁ X ₃	-2.543	-1.271	0.981	-2.592	0.081
X ₁ X ₄	11.145	5.573	0.981	11.361	0.001
X ₂ X ₃	5.835	2.918	0.981	5.948	0.010
X ₂ X ₄	1.543	0.771	0.981	1.572	0.214
X ₃ X ₄	-7.368	-3.684	0.981	-7.510	0.005

* t statistical test, ** significance probability of the t-test

percentage of all ethyl esters identified and quantified by chromatographic analysis.

3.3.1 Yield analysis

The assays were based on the variance analysis (ANOVA), used to obtain some statistical parameters, such as the mean and the sum of standard errors (SS).

Interactions between variables and standard errors were calculated to evaluate the effects of the independent variables on the total yield of the biodiesel from frying oil and bovine tallow mixtures (BFTM). Statistical values (as main effects), regression coefficients, interactions, and standard errors are presented in Table 6.

Table 6 indicates that factors X₂ and X₄ and

Table 7. Analysis of variance (ANOVA) for model regression.

Source of variation	SS	DF*	MS**	F-Calc	F-Tab
Regression	1636.367	8.00	204.546	4.90	2.95
residual	458.765	11.00	41.706		
Lack of fit	447.217	6			
Pure error	11.547	3			
TOTAL SS	2095.132	19.00			
R ²	0.781				

* degree of freedom, ** mean square.

interactions X_1X_4 and X_3X_4 are statistically significant. Therefore, factors X_1 and X_3 and interactions X_1X_2 , X_1X_3 , X_2X_3 , and X_2X_4 exceeded the P-value (probability of error value), indicating that they are not statistically significant. The variables with positive values indicate that an increase in their levels provide a higher total yield, and the negative ones indicate an opposite effect.

It is important to note that the interaction between KOH and molar ratio is the one that affected most the yield in biodiesel production. This influence is positive, confirming that the yield increases when the interaction values also increase. This can be explained due to the easy phase separation between biodiesel and glycerin,

and due to the excess S/F molar ratio that was higher in amount than the stoichiometric factor, therefore, shifting the equilibrium in the direction of the products.

The result of analysis of variance (ANOVA), which was carried out to determine the significance and the fitting of the model, as well as the effect of significant individual terms and their interaction on the chosen responses, are presented in Table 7. The P-value is used as a tool to check the significance of each regression coefficient, which also indicates the interaction effect of each cross product. The smaller the P-value is, the higher the significance of the corresponding coefficient will be. The results are in agreement

Figure 1. Distribution of residuals: predicted *versus* observed values of BFTM production.

Figure 2. Surface plot of the yield as a function of the interaction of catalyst concentration and type of mixture.

with other works already published in the literature (Charoenchaitrakool & Thienmethangkoon, 2011; Lee et al., 2011; Shin et al., 2012) with respect to the significant variables.

The F-test indicated that the regression analysis was significant, since the F_{cal} value (4.90) was higher than F_{tab} one (2.95), and the model does not need any adjustment. The correlation coefficient (R^2) provides a measure of the proportion of variance explained by the regression equation to responses variation (Costa Neto et al., 2000). In general, R^2 is expressed in percentage, and 78 % was the R^2 value of this model.

The residue distribution (predicted values *versus* observed ones) is shown in Figure 1. One can notice that the average values are close to the red line and the deviations between them are distributed normally; positive and negative deviations are in the same proportion, with no tendentious behavior.

The response surface was estimated with Equation 2, where X_1 , X_2 , X_3 , and X_4 are the variables describing factors β_0 (intersection point), β_1 , β_2 , β_3 , and β_4 (referring to the linear effects) and the interaction effects between the variables are the regression coefficients obtained by the method

applying the least squares methodology. Equation 2 is the model that describes the response surface for the BFTM biodiesel efficiency.

$$R = 74.284 - 3.049 \cdot X_1 + 3.668 \cdot X_2 - 2.045 \cdot X_3 + 3.944 \cdot X_4 + 2.109 \cdot X_1X_2 + 5.573 \cdot X_1X_4 + 2.918 \cdot X_2X_3 - 3.684 \cdot X_3X_4 \quad (2)$$

A similar and acceptable accuracy of the model ($R^2 = 0.85$) was also found by another work using only frying oil as raw material, 65 °C of temperature reaction, 45 min of time, a methanol:oil molar ratio of 9, and using NaOH concentration of 0.72 w/w, obtaining 92.05 % ester yield (Atapour et al., 2014).

The response surface defines the most appropriate condition that can maximize the yield of BFTM. Figure 2 shows the variation of the yield (%) as a function of catalyst concentration and type of mixture. A mixture of 70/30 and 0.5 % of catalyst led to yields with mass higher than 85 %.

The variation of the yield (%) as a function of time and type of mixture is shown in Figure 3. Yields higher than 77 % by weight were also obtained with a mixture of 70/30 in 35 seconds of reaction.

Figure 3. Surface plot of the yield as a function of the interaction of time and type of mixture.

The variation of the biodiesel yield (%) as a function of the alcohol:oil molar ratio and type of mixture is shown in Figure 4. Again, yields higher than 81 % were attained using a mixture of 70/30 % and an alcohol:oil molar ratio of 9:1.

3.3.2 Ester conversion analysis

Table 8 shows the effects of the variables X_1 , X_2 , X_3 , and X_4 and of interactions X_1X_2 , X_1X_3 , X_1X_4 , X_2X_3 , X_2X_4 , and X_3X_4 , as previously presented for the yield

in mass, but now as a function of ester conversion. The data presented in Table 8 are statistically significant, with type of mixture and molar ratio as the main effects observed. The variables X_1 and X_3 exceeded the p-value, indicating that they are not statistically significant. The interaction between the content of KOH and the mixture is the one that produces a more significant effect on responses of the ester content.

Table 8. Effects of the factors and standard errors corresponding to the yield for the ester content BFTM.

Factors	Effects	Regression coefficients	Standard Error		P-Value
Mean	99.024	99.024	0.010	9841.084	< 0.0001
Main Effects					
X_1 :KOH	0.166	0.083	0.022	7.389	0.005
X_2 :Mixture	0.319	0.159	0.022	14.167	0.001
X_3 :Time	0.064	0.159	0.022	2.833	0.066
X_4 :molar ratio	0.261	0.131	0.022	11.611	0.001
Interactions					
X_1X_2	-0.389	-0.194	0.022	-17.278	<0.0001
X_1X_3	-0.289	-0.144	0.022	-12.833	0.001
X_1X_4	-0.371	-0.186	0.022	-16.500	<0.0001
X_2X_3	-0.261	-0.131	0.022	-11.611	0.001
X_2X_4	-0.289	-0.144	0.022	-12.833	0.001
X_3X_4	-0.324	-0.162	0.022	-14.389	0.001

Figure 4. Surface plot of the yield as a function of the interactions of alcohol:oil molar ratio and type of mixture.

The variation of the experimental results was statistically verified by the performance of the residue analysis. The analysis of variance for this model (Table 9), through the F-test, indicated that the regression is significant since the value of F_{cal} (6.581) is higher than the F_{tab} (3.02), as shown for the yield evaluation.

The correlation coefficient for the ester content was 0.855 (85%), not requiring any adjustment to the model. The distribution of the residues is presented in Figure 5, where one can see that

observed and predicted values are well distributed.

Equation 3 is the model that describes the response surface for the esters content of BFTM.

$$E = 99.024 + 0.083 \cdot X_1 + 0.159 \cdot X_2 + 0.131 \cdot X_4 - 0.194 \cdot X_1X_2 - 0.144 \cdot X_1X_3 - 0.186 \cdot X_1X_4 - 0.131 \cdot X_2X_3 - 0.144 \cdot X_2X_4 - 0.162 \cdot X_3X_4 \quad (3)$$

Figures 6 and 7 show higher ester contents in the biodiesel produced, 99.3 % and 99.2 %, respectively.

Table 9. Analysis of variance (ANOVA) for model regression.

Effect	SS	DF*	MS**	F-Calc	F-Tab
Regression (R)	3.352	9.00	0.372	6.581	3.020
residual (r)	0.566	10.00	0.057		
Lack of fit	0.560	5.00			
Pure error	0.006	3			
TOTAL	3.918	19			
R ²	0.855				

* degree of freedom, ** mean square

Figure 5. Distribution of residues predicted as a function of observed values for esters content of BFTM biodiesel.

Figure 6. Surface plot of E (%) as a function of the interactions of catalyst concentration and type of mixture.

respectively, using a lower catalyst concentration and a higher reaction time. The best type of mixture applied was the one with 70% of frying oil and 30% of tallow. Another conclusion based on the response surface methodology is that the higher ester content (99.1 %) was obtained when a higher alcohol:oil molar ratio and a mixture of 70/30 were applied (Figure 8).

Mendonça et al. (2011) adopted the same strategy for optimization using only beef tallow as raw material for the biodiesel production. Mixture percentage was not an independent variable in the design factorial. The best operational conditions were 7.5:1 of alcohol:oil molar ratio, using methanol as solvent, 1.5% of catalyst, 20 min of reaction time and 50 °C to achieve a conversion

Figure 7. Surface plot of E (%) as a function of the interactions of time and type of mixture.

Figure 8. Surface plot of E (%) as a function of the interactions of alcohol:oil molar ratio and type of mixture.

yield of 88.4 % with a purity of 99.4 %. The authors also concluded that a linear model was sufficient to establish the effect of the variables, and to have a model similar to the one proposed in this work. The molar ratio had a significant and positive influence on the yield, as observed in this work with the mixture.

The best conditions to optimize the two variables studied in biodiesel production, E and R%, were almost the same. Higher values of R% and E, and the best values of viscosity ($5.60 \text{ mm}^2 \cdot \text{s}^{-1}$) were obtained using a mixture of 70 % of frying oil and 30 % of tallow, a low catalyst concentration and higher reaction time (35 seconds).

4. CONCLUSIONS

This research allows the optimization of biodiesel production from blends of frying oil and bovine tallow, using a full factorial design. In the biodiesel production, one could note that all the independent variables influenced the total yields of the reaction. Parameters like alcohol:oil molar ratio of 1:9, 1.5 % of catalyst, 35 seconds of reaction time, and a mixture of 70/30 provided yields above 89 %. When analyzing ester content, higher values were obtained when using an alcohol:oil molar ratio of 1:9, 0.5 % of catalyst and a mixture containing 70% of frying oil and 30% of bovine tallow, for 35 seconds. Biodiesel was produced with an ester content of 99.43 %. Mixtures containing more frying oil and tallow are better, and the best operational time was 35 seconds of reaction.

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