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RESEARCH ARTICLE
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Study and optimization of operating conditions for use of sunflower oil in the production of ethyl and methyl biodiesel

Estudio y optimización de las condiciones operativas para el uso de aceite de girasol en la producción de biodiésel etílico y metílico

Estudo e otimização das condições operacionais para o uso de óleo de girassol na produção de biodiesel etílico e metílico

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ABSTRACT

Objective: In this paper, we study the production of biodiesel from sunflower oil, optimizing the process through the application of a fractional factorial design 2^{6-2} followed by the central composite design (CCD) response surface method. **Methods:** Transesterification was optimized using ethanol and methanol routes for the following parameters: reaction time, temperature, catalyst concentration, catalyst type, rotation, and alcohol:oil molar ratio. **Results:** We compared the cost of producing biodiesel using traditional soybean oil with sunflower oil and determined the costs with sunflower oil are less, since the operating conditions are milder for sunflower oil than those used with soybean oil. **Conclusions:** The optimized conditions were: for ethyl biodiesel, 35 minutes of reaction at a temperature of 308 K, 0.19 % KOH and 260 rpm; for methyl biodiesel, 60 min of reaction at 319 K, 0.42 % KOH and 189 rpm. This information is especially important in order to maintain control over the process.

Keywords: transesterification; optimization; response surface; pareto.

1 INTRODUCTION

Currently, 76 % of the biodiesel produced in Brazil comes from soybean oil and 17 % comes from beef fat. Other oilseeds with great production potential are welcome in order to enhance the choices of raw materials. Among these, the oilseed sunflower is highlighted. Among the important factors in its selection has been the growth in recent years in its production as well as particular characteristics of the plant[1-3] such as oil content (40–47 %) which is considerably greater than that of soybean oil (18–21 %)[4]. Sunflowers yield about 600 kg of oil per hectare versus 450 kg, on average, obtained from soybeans[5]. Sunflowers are planted in July/August, and soybeans in December, which could favor crop rotation, improving the soil and gaining the diversity of oilseed. Another point in favor of its use is that oilseed sunflower is a plant that does not require much care, has low water requirements, low cost and is tolerant to climatic variations as well as variations in the soil[6].

In Brazil, the leading production region is the Midwest, especially Mato Grosso, which is responsible for 67 % of the national production of sunflower. According to figures from the National Supply Company (Conab), production in Mato Grosso reached 75 million tons in the 2011/12 harvest, corresponding to a 53 % increase over the previous harvest, when the crop reached 49 million tons[7].

Many parameters can affect the transesterification reaction. Those known to greatly influence the reaction are: temperature, the alcohol/oil molar ratio, type and amount of catalyst and time [8-10]. The quality of biodiesel fuel can be influenced by various factors including production parameters[11].

Most biodiesel plants in operation in Brazil are adapted and optimized to work with soybean oil and, as the production of sunflower oil is increasing, it is important to know from the industrial point of view if the technical conditions used with oil soybean could also be used for biodiesel production using sunflower.

In this study biodiesel production from sunflower oil using methanol and ethanol has been optimized by applying a fractional factorial design 26-2 and using a central composite design (CCD) response surface methodology to optimize the reaction parameters and determine the relationships between reaction parameters.

2 METHODS

2.1 Reagents and materials

Refined sunflower oil obtained from a local market, absolute ethyl and methyl alcohol PA (Dynamic, 99.8%) and potassium and sodium hydroxide PA (Vetec 85%) were used for the alkaline transesterification reaction. The characterization of the oil and biodiesel were performed using a Metrohm automatic potentiometric titrator (model 808); ABBE Refractometer; Metrohm coulometric Karl Fischer titrator (model 831 KF), Kyoto densimeter (model DA-500); ISL viscometer (model VH2); Tanaka Flash Point Tester (model APM-7); and Rancimat (model 743).

2.2 Transesterification Reaction

In the transesterification reaction the catalyst was added to the alcohol and the mixture was agitated for 5 minutes and then added to the sunflower oil. After the alkaline transesterification reaction the system separated into two phases, with impure biodiesel at the top and glycerin at the bottom. The biodiesel was removed from the mixture and the pH was adjusted to near 7 and then washed 3 times with water at 80 °C. A high temperature wash water was necessary to solubilize and remove impurities. The yields of fatty acid methyl esters (FAME) and ethyl (FAEE) from the sunflower oil transesterification were calculated as described previously in ABNT NBR15342. Experiments were performed in duplicate, and the reaction conditions for each parameter are shown in table A.2 and A.3.

2.3 Statistical methods

To determine the experimental conditions as well as their simultaneous effects which influence the yield of the transesterification reaction, the variables reaction time, rotation, alcohol:oil molar ratio, type of catalyst, catalyst concentration and temperature were screened through a 26-2 fractional factorial design, resulting in 16 experiments coded -1 (low level) or +1 (high level). After identifying the most significant variables a central composite design (CCD) was used to determine the critical values for these variables and optimize the experiment. The models were built using the program Statistic 7.0.

3 RESULTS

To evaluate the quality of the commercial sunflower oil used, tests were carried out to determine some of its physicochemical properties. The results are shown in table A.1. These properties are directly related to the yield and quality of the biodiesel produced[12]. Values found in the literature for saponification index, viscosity and specific mass [13-15] show a good agreement with the information presented in table A.1.

Table 1 - Physicochemical properties of sunflower oil.

Properties	Units	Value	Methods
Peroxide Index	meq kg^{-1}	9.890	ASTM D1563
Refractive Index (313.15K)	-	1.470	ASTM C1648
Saponification index	mg oleic acid g^{-1}	190	ASTM D5558
Acidity	mg KOH g^{-1}	0.780	ASTM D664
Content Water	mg kg^{-1}	793.2	ASTM D6304
Specific gravity	kg m^{-3}	920.1	ASTM D4052
Viscosity	mm^2 s^{-1}	41.00	ASTM D445 e D446
Oxidative Stability	hours	5.28	EN 14112
Flash Point	K	598.15	ASTM D93

Source: Author.

The influence of six independent variables was evaluated at two levels, as well as their simultaneous effects on the yield of biodiesel obtained in the transesterification reaction. Tables A.2 and A.3 show all the trials according to the matrix of the fractional factorial design 2^{6-2}, totaling 16 experiments, and the yield values from the ethyl and methyl transesterification reactions, respectively, with sunflower oil. The experiments were performed in duplicate.

Table 2 - Matrix for the 26-2 factorial design for ethyl biodiesel sunflower.

Time (min)	Rotation (rpm)	Ethanol:oil	Catalyst	Catalyst concentration (%)	Temperature (K)	Yield (%)
30 (-1)	100 (-1)	6:1 (-1)	NaOH (+1)	0.20 (-1)	308 (-1)	35.79/ 39.79
60 (+1)	100 (-1)	6:1 (-1)	NaOH (+1)	0.80 (+1)	308 (-1)	81.00/ 79.21
30 (-1)	200 (+1)	6:1 (-1)	NaOH (+1)	0.80 (+1)	328 (+1)	70.95/ 73.71
60 (+1)	200 (+1)	6:1 (-1)	NaOH (+1)	0.20 (-1)	328 (+1)	44.25/ 38.00
30 (-1)	100 (-1)	12:1 (+1)	NaOH (+1)	0.80 (+1)	328 (+1)	49.30/ 47.13
60 (+1)	100 (-1)	12:1 (+1)	NaOH (+1)	0.20 (-1)	328 (+1)	89.00/ 86.75
30 (-1)	200 (+1)	12:1 (+1)	NaOH (+1)	0.20 (-1)	308 (-1)	69.06/ 73.90
60 (+1)	200 (+1)	12:1 (+1)	NaOH (+1)	0.80 (+1)	308 (-1)	37.05/ 40.01
30 (-1)	100 (-1)	6:1 (-1)	KOH (-1)	0.20 (-1)	328 (+1)	87.07/ 82.44
60 (+1)	100 (-1)	6:1 (-1)	KOH (-1)	0.80 (+1)	328 (+1)	75.81/ 74.34
30 (-1)	200 (+1)	6:1 (-1)	KOH (-1)	0.80 (+1)	308 (-1)	80.12/ 85.03
60 (+1)	200 (+1)	6:1 (-1)	KOH (-1)	0.20 (-1)	308 (-1)	80.62/ 80.52
30 (-1)	100 (-1)	12:1 (+1)	KOH (-1)	0.80 (+1)	308 (-1)	73.90/ 78.50
60 (+1)	100 (-1)	12:1 (+1)	KOH (-1)	0.20 (-1)	308 (-1)	76.47/ 75.78
30 (-1)	200 (+1)	12:1 (+1)	KOH (-1)	0.20 (-1)	328 (+1)	87.74/ 87.95
60 (+1)	200 (+1)	12:1 (+1)	KOH (-1)	0.80 (+1)	328 (+1)	50.03/ 51.29

Source: Author.

Table 3 - Matrix for the 26-2 factorial design for methyl biodiesel sunflower.

Time (min)	Rotation (rpm)	Ethanol:oil	Catalyst	Catalyst concentration (%)	Temperature (K)	Yield (%)
30 (-1)	100 (-1)	6:1 (-1)	NaOH (+1)	0.20 (-1)	308 (-1)	90.82/ 87.40
60 (+1)	100 (-1)	6:1 (-1)	NaOH (+1)	0.80 (+1)	308 (-1)	49.10/ 49.08
30 (-1)	200 (+1)	6:1 (-1)	NaOH (+1)	0.80 (+1)	328 (+1)	51.37/ 68.60
60 (+1)	200 (+1)	6:1 (-1)	NaOH (+1)	0.20 (-1)	328 (+1)	92.00/ 88.24
30 (-1)	100 (-1)	9:1 (+1)	NaOH (+1)	0.80 (+1)	328 (+1)	61.00/ 68.70
60 (+1)	100 (-1)	9:1 (+1)	NaOH (+1)	0.20 (-1)	328 (+1)	82.90/ 74.30
30 (-1)	200 (+1)	9:1 (+1)	NaOH (+1)	0.20 (-1)	308 (-1)	75.30/ 73.90
60 (+1)	200 (+1)	9:1 (+1)	NaOH (+1)	0.80 (+1)	308 (-1)	50.30/59.60
30 (-1)	100 (-1)	6:1 (-1)	KOH (-1)	0.20 (-1)	328 (+1)	92.70/90.00
60 (+1)	100 (-1)	6:1 (-1)	KOH (-1)	0.80 (+1)	328 (+1)	82.70/85.00
30 (-1)	200 (+1)	6:1 (-1)	KOH (-1)	0.80 (+1)	308 (-1)	55.84/53.00
60 (+1)	200 (+1)	6:1 (-1)	KOH (-1)	0.20 (-1)	308 (-1)	87.40/85.50
30 (-1)	100 (-1)	9:1 (+1)	KOH (-1)	0.80 (+1)	308 (-1)	85.50/77.18
60 (+1)	100 (-1)	9:1 (+1)	KOH (-1)	0.20 (-1)	308 (-1)	91.57/89.40
30 (-1)	200 (+1)	9:1 (+1)	KOH (-1)	0.20 (-1)	328 (+1)	77.70/84.09
60 (+1)	200 (+1)	9:1 (+1)	KOH (-1)	0.80 (+1)	328 (+1)	73.62/71.08

Source: Author.

Analyzing the Pareto chart, Figure A.1., for ethyl biodiesel, there was a negative effect of catalyst type and concentration, speed, time and molar ratio, all of which should therefore be kept at the low level (-1). On the other hand, temperature had a positive effect, indicating that for better performance in terms of yield, this parameter should be maintained at the high level (+1).

For a full analysis of the chart, interactions between variables also need to be taken into account, as they may be even more important than the individual variables.

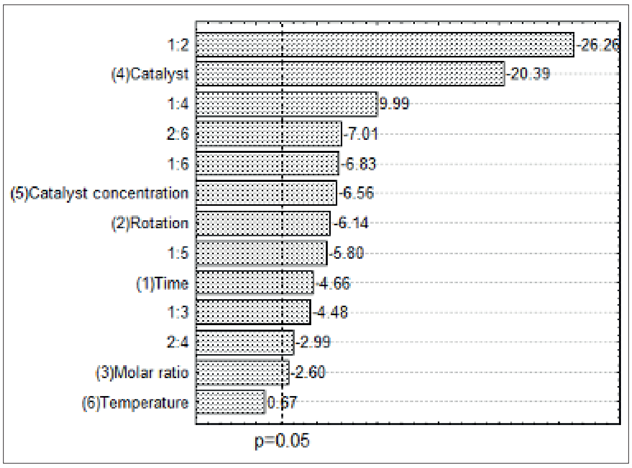
The interaction between (1) and (2) is significant and negative, implying that in interpreting the joint action of two factors, saved trends of the individual effects of the main variables leads to a decrease in the reaction yield. Therefore the variables time and temperature should be maintained at the high level (+1).

The use of potassium hydroxide (-1) as a catalyst was the most effective in transesterification, which also favored the interaction between (1) and (4).

The temperature should be maintained at wevel to promote interactions between (2) and (6) and (1) and (6). The effects of varying the catalyst concentration and molar ratio were negative, which necessitates also keeping them at low levels.

Interactions between (1) and (5), (2) and (3), and (2) and (4) were less significant than the others. For this reason they were disregarded in subsequent statistical analyses.

Figure 1 - Matrix for the 26-2 factorial design for ethyl biodiesel sunflower.



Source: Author.

Therefore, holding constant the variables: molar ratio (6:1), type of catalyst (KOH) and temperature (35 °C) for not significantly affecting the yield of the reaction or being qualitative variables, the matrix of the central composite design was obtained for ethyl sunflower biodiesel. It is illustrated in Table A.4.

Table 4 - Matrix of central composite design for ethyl biodiesel.

Time (min)	Rotation (rpm)	Catalyst concentration (%)	Yield (%)
30 (-1)	200 (-1)	0.1 (-1)	91.18
30 (-1)	300 (+1)	0.1 (-1)	91.67
30 (-1)	200 (-1)	0.3 (+1)	87.98
30 (-1)	300 (+1)	0.3 (+1)	91.29
40 (+1)	200 (-1)	0.1 (-1)	87.67
40 (+1)	300 (+1)	0.1 (-1)	91.92
40 (+1)	200 (-1)	0.3 (+1)	89.46
40 (+1)	300 (+1)	0.3 (+1)	91.84
27 (-1.41)	250 (0)	0.2 (0)	91.87
43 (+1.41)	250 (0)	0.2 (0)	92.80
35 (0)	250 (0)	0.03 (-1.41)	92.71
35 (0)	250 (0)	0.4 (+1.41)	92.78
35 (0)	166 (-1.41)	0.2 (0)	91.13
35 (0)	334 (+1.41)	0.2 (0)	89.27
35 (0)	250 (0)	0.2 (0)	92.55
35 (0)	250 (0)	0.2 (0)	93.12
35 (0)	250 (0)	0.2 (0)	93.26
35 (0)	250 (0)	0.2 (0)	93.08
35 (0)	250 (0)	0.2 (0)	93.19
35 (0)	250 (0)	0.2 (0)	93.22

Source: Author.

Analyzing the Pareto chart, Figure A.2, for methyl biodiesel, the variables observed with negative effect are the type and concentration of catalyst, molar ratio and rotation, which must be kept at the low level (-1). On the other hand, there are positive effects for temperature and time, indicating that for better performance in terms of yield, this parameter should be maintained at the high level (+1).

The factors catalyst type and concentration should be kept at the low level (0.2% and KOH, respectively).

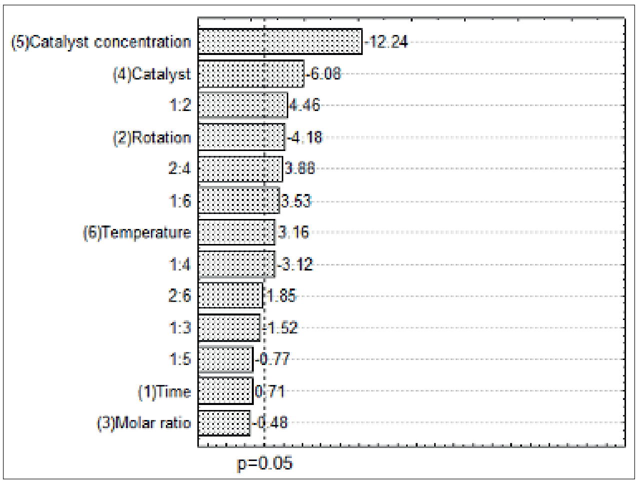
For a full analysis of the chart, the interactions between variables need to be taken into account, because they may be even more important than the main variables.

The interaction between (1) and (2) is positive, implying that interpret the joint action of two factors, saved trends of the individual effects of the main variables, induces an increase in the reaction yield. Porting should be maintained, the time variable at the high level (+1) and rotation at the low level (-1). Thus, the interaction between (2) and (4) will also be complied.

The interaction (1) and (6) is positive. Therefore, the variables time and temperature should be retained at the high level (+1).

The variable molar ratio did not influence the process statistically. However, for lower reagent consumption, it was kept at the low level (-1).

Figure 2 - Matrix for the 26-2 factorial design for ethyl biodiesel sunflower.



Source: Author.

Therefore, holding the variables molar ratio (6:1), type of catalyst (KOH) and time (60 minutes) constant, because they do not significantly affect the yield of the reaction, the matrix of the central composite design obtained for methyl biodiesel from sunflower is shown in Table A.5.

Table 5 - Matrix of central composite design for methyl biodiesel.

Time (min)	Rotation (rpm)	Catalyst concentration (%)	Yield (%)
303 (-1)	70 (-1)	0.20 (-1)	74.53
303 (-1)	70 (-1)	0.60 (+1)	68.88
303 (-1)	230 (+1)	0.20 (-1)	84.99
303 (-1)	230 (+1)	0.60 (+1)	77.36
343 (+1)	70 (-1)	0.20 (-1)	48.25
343 (+1)	70 (-1)	0.60 (+1)	33.73
343 (+1)	230 (+1)	0.20 (-1)	82.67
343 (+1)	230 (+1)	0.60 (+1)	80.87
289 (-1.41)	150 (0)	0.40 (0)	77.00
357 (+1.41)	150 (0)	0.40 (0)	53.23
323 (0)	15 (-1.41)	0.40 (0)	0.00
323 (0)	285 (+1.41)	0.40 (0)	85.03
323 (0)	150 (0)	0.06 (-1.41)	69.31
323 (0)	150 (0)	0.74 (+1.41)	86.69
323 (0)	150 (0)	0.40 (0)	95.26
323 (0)	150 (0)	0.40 (0)	94.60
323 (0)	150 (0)	0.40 (0)	96.10
323 (0)	150 (0)	0.40 (0)	95.60

Source: Author.

The contours of the response surface are the result of interactions between variables. From Figures A.4 and A.5 is possible to obtain a three-dimensional visualization of the variation in two independent variables in relation to the dependent variable, which is the yield of the transesterification reaction.

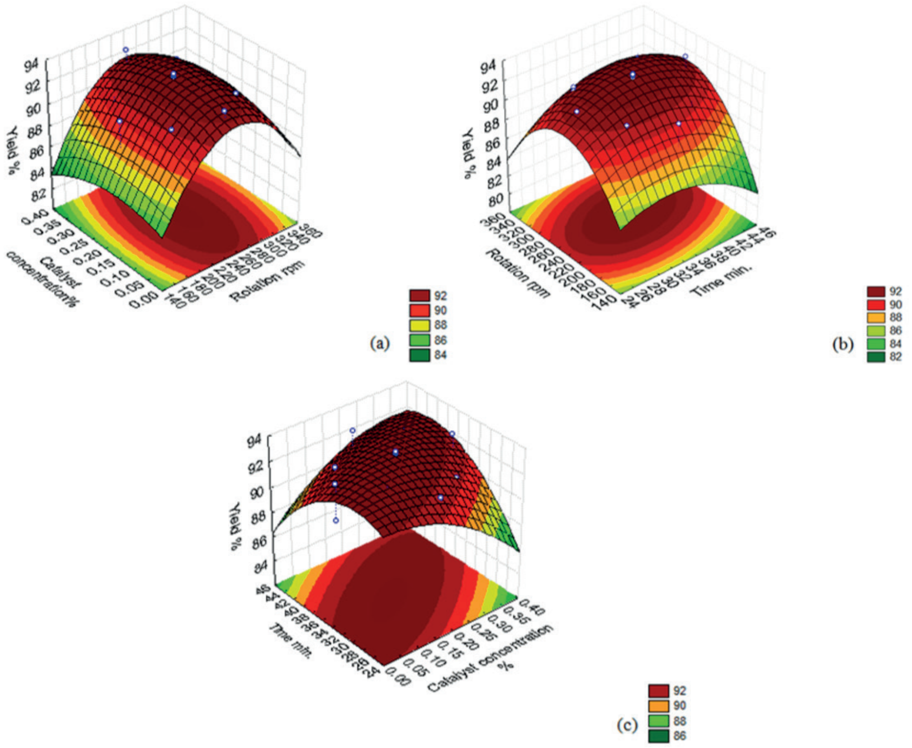
Figure A.4 shows the response surfaces obtained from the CCD according to the quadratic equation:

(a) Biodiesel yield (%) = 53.318 + 0.214 x [Rotation] – 0.0005 x [Rotation]^2 – 37.893 x [Catalyst concentration] – 39.041 x [Catalyst concentration]^2 + 0.001 x 34.999 x [Rotation] + 1.322 x 34.999 x [Catalyst concentration] + 0.023 x [Rotation] x [Catalyst concentration] + 4.755. The solution of this quadratic equation represents the optimized process conditions, where maximum performance is obtained when the rotation is 260 rpm and the catalyst concentration is 0.19%.

(b) Biodiesel yield (%) = 53.318 + 0.885 x [Time] – 0.021 x [Time]^2 + 0.214 x [Rotation] – 0.0005 x [Rotation]^2 + 0.001 x [Time] x [Rotation] + 1.322 x 0.199 x [Time] + 0.023 x 0.199 x [Rotation] – 9.140. The solution of this quadratic equation represents the optimized process conditions, where maximum performance is obtained when the time is 35 minutes and the rotation is 260 rpm.

(c) Biodiesel yield (%) = 53.318 + 0.885 x [Time] – 0.021 x [Time]^2 – 37.893 x [Catalyst concentration] – 39.041 x [Catalyst concentration]^2 + 0.001 x 249.999 x [Time] + 1.322 x [Time] x [Catalyst concentration] + 0.023 x 249.999 x [Catalyst concentration] + 21.352. The solution of this quadratic equation represents the optimized process conditions, where maximum performance is obtained when the time is 35 minutes and the catalyst concentration is 0.19%.

Figure 4 - Responses surfaces for the yield of ethyl transesterification. In (a) catalyst concentration x rotation, (b) rotation x time, (c) time x catalyst concentration.



Source: Author.

It can be noted from figure A.4. (a), that the process of alkaline transesterification via the ethylic route is controllable over a range of catalyst concentrations from 0.05 to 0.35% (m / m) and with a rotation (ethanol:oil) between 200 and 310 rpm. Thus, the tolerance of the process is 0.2 ± 0.15% mass/mass for the catalyst concentration and 255 ± 55 rpm for the rotation.

According to figure A.4. (b), the process is controllable over a range of rotation of 200 – 310 rpm, with a reaction time between 26 and 44 min. Thus, the tolerance of the process is 255 ± 55 rpm for the rotation and 35 ± 9 for the time.

According to figure A.4. (c), the process is controllable over a range of catalyst concentrations from 0.05 to 0.35% mass/mass, with a reaction time between 26 and 44 min. Thus, the tolerance of the process is 0.2 ± 0.15% mass/mass for the catalyst concentration and 35 ± 9 for the time.

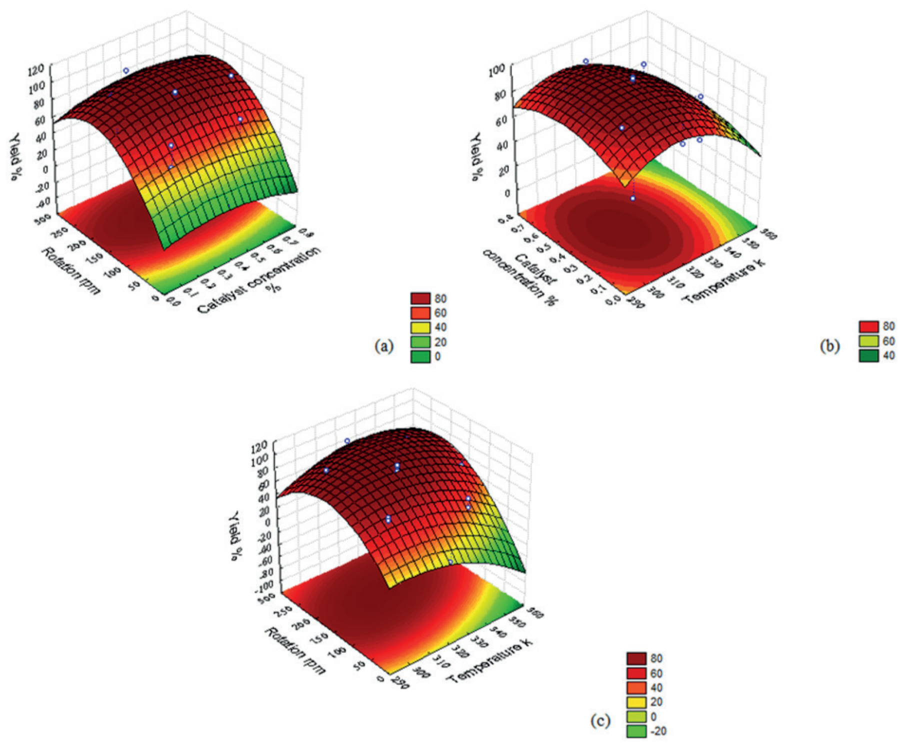
Figure A.5 shows the responses surfaces obtained from the CCD according to the quadratic equation:

(a) Biodiesel yield (%) = -10.4460 + 0.7289 x [Rotation] – 0.0026 x [Rotation]^2 + 75.7338 x [Catalyst concentration] – 104.6317 x [Catalyst concentration]^2 + 0.0048 x 50 x [Rotation] - 0.095 x 50 x [Catalyst concentration] + 0.0839 x [Rotation] x [Catalyst concentration] + 1.4932. The solution of this quadratic equation represents the optimized process conditions, where maximum performance is obtained when the rotation is 189 rpm and the catalyst concentration is 0.42%.

(b) Biodiesel yield (%) = -10.4460 + 1.1224 x [Temperature] – 0.0218 x [Temperature]^2 + 75.7338 x [Catalyst concentration] -104.6317 x [Catalyst concentration]^2 + 0.0048 x 150 x [Temperature] - 0.095 x [Temperature] x [Catalyst concentration] + 0.0839 x 150 x [Catalyst concentration] + 50.5259. The solution of this quadratic equation represents the optimized process conditions, where maximum performance is obtained when the temperature is 319 K and the cathlyst concentration is 0.42%.

(c) Biodiesel yield (%) = -10.4460 + 0.7289 x [Rotation] – 0.0026 x [Rotation]^2 + 75.7338 x [Temperature] – 104.6317 x [Temperature]^2 + 0.0048 x 50 x [Rotation] – 0.095 x 50 x [Temperature] + 0.0839 x [Rotation] x [Temperature] + 1.4932. The solution of this quadratic equation represents the optimized process conditions, where maximum performance is obtained when the rotation is 189 rpm and the temperature is 319 K.

Figure 5 - Responses surfaces for the yield of methyl transesterification.In (a) rotation x catalyst concentration, (b) catalyst concentration x temperature and (c) rotation x temperature.



Source: Author.

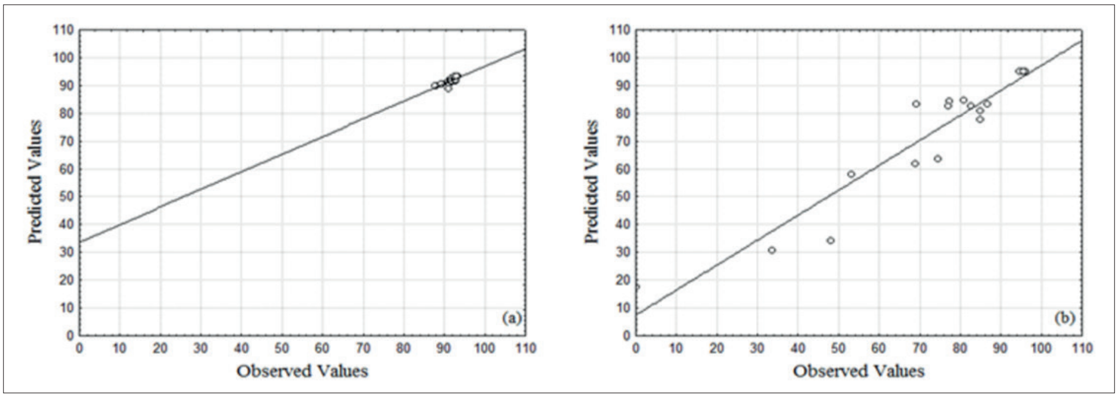
It can be noted from figure A.5. (a) that the process of alkaline transesterification via the methylic route is controllable over a range of catalyst concentrations from 0.2 to 0.6% (m / m), with a rotation between 130 and 250 rpm. Thus, the tolerance of the process is 0.4 ± 0.2% mass/mass for the catalyst concentration and 190 ± 60 rpm for the rotation.

According to figure A.5 (b), the process is controllable over a catalyst concentration range from 0.2 to 0.6% (m / m) at a temperature between 303 and 328 K. Thus, the tolerance of the process is 0.4 ± 0.2% mass/mass for the catalyst concentration and 42.5 ± 12.5 K for the temperature.

According to figure A.5 (c), the process is controllable over a range of rotations from 130 to 250 rpm at a temperature between 303 and 328 K. Thus, the tolerance of the process is 190 ± 60 rpm for the rotation and 42.5 ± 12.5 K for the temperature.

The regression was statistically significant for ethyl and methyl biodiesel (Fcalculated < Ftabulated), in agreement with the results shown in figure A.3.

Figure 3 - Matrix for the 26-2 factorial design for ethyl biodiesel sunflower.



Source: Author.

The model's regression F-value (5.59 for FAEE and 21.68 for FAME) and p-value (0.0006 for FAEE and <0.0001 for FAME), imply that it is significant at a 95% confidence level. The p-value is employed to verify the significance of each coefficient; it also indicates the effects of their interaction. The ANOVA table is in table A.6.

Table 6 - ANOVA for responde surface model analysis of variance table for ethyl biodiesel (FAEE) and methyl biodiesel (FAME).

	Source	Sum of aquares	Degrees of freedom	Mean square	F value	p-value
FAEE	Regression	8282.29	14	591.60		
	Residual	1798.24	17	105.79	5.59	0.0006
	Total	10080.53	31	-		
FAEE	Regresion	6130.13	14	437.87		
	Residual	343.40	17	20.2	21.68	<0.0001
	Total	6473.53	31	-		

Source: Author.

Papers in the literature on optimizing the transesterification of soybean oil using ethanol report that maximum efficiency is achieved when the parameters molar ratio, catalyst concentration, temperature and time are, respectively: 9:1, 1.3%, 40 ° C and 80 min[16]. Table A.7 presents the optimized conditions of the transesterification reaction using sunflower oil. It can be observed that all the parameters optimized for FAEE with sunflower oil generate savings in the process compared to soybean oil because they utilize milder condition. The optimized parameters molar ratio, catalyst concentration, temperature and time are, respectively: 6:1, 0.19%, 35 °C and 35 min; thus the best conditions for an oleaginous source may not be the most suitable for another source.

Table 7 - Optimized variables the transesterification reaction for ethyl biodiesel (FAEE) and methyl biodiesel (FAME).

Variable	FAEE	FAME
	Parameter	
Time	35 minutes	60 minutes
Temperature	308 k	319 K
Molar ratio (alcohol:oil)	6:1	6:1
Catalyst	KOH	KOH
Catalyst concentration	0.19%	0.42%
Rotation	260 rpm	189 rpm

Source: Author.

Table A.8 shows some physic-chemical properties of the biodiesel obtained under the optimized conditions, and even fits those parameters analyzed according to the specification parameters listed in Technical Regulation n° 14 / 2012 of the National Agency of Petroleum, Natural Gas and Biofuels (ANP), American Society of Testing and Materials ASTM D-6751 and Comité Européen de Normalisation EN 14214.

Table 8 - Physicochemical properties of ethyl biodiesel (FAEE) and methyl biodiesel (FAME) produced by alkaline transesterification of sunflower oil..

Physical Properties	Units	FAEE	FAME	Method
Saponification index	mg oleic acid g^{-1}	57.6	57.5	ASTM D-5558
Density	kg m^{-3}	870.0	868.0	ASTM D-4052
Acidity Index	mg KOH g^{-1}	0.47	0.48	ASTM D-664
Cetane Index		48.1	50.4	ASTM D-976
Viscosity	mm^2 s^{-1}	4.0	4.0	ASTM D-445 e D-446
Oxidative Stability	h	1.2	2.0	EN 14112
Flash Point	K	457	465	ASTM D-93
Total glycerin	% mass	0.09	0.14	ASTM D-6584
Free glycerin	% mass	0.019	0.018	ASTM D-6584

Source: Author.

4 DISCUSSION

All physico-chemical properties of the biodiesels were within the accepted standards except oxidative stability, which was less than the specified limit. This can be explained by virtue of the fact that 89 % of sunflower oil is comprised of unsaturated fatty acids and the higher the degree of insaturation, the higher the rate of degradation of an oil [17]. Therefore to render these products fit for use as biodiesel is necessary to use an additive to improve oxidative stability[18].

5 CONCLUSION

Fractional factorial design and central composite design was used to optimize reactions of methyl and ethyl transesterification in sunflower oil. The purpose is to achieve the highest yield of biodiesel by performing a few experiments with the minimal expenditure of energy and reagents.

By the ethyl route the interaction between time and rotation had the greatest influence on the reaction and the effect was negative and the methyl route the variable catalyst concentration also had greater influence with negative effect. In both routes potassium hydroxide was an ideal catalyst. The molar ratio was the variable with less effect on the reaction.

Using Sunflower oil for biodiesel production the process cost is less since the operating conditions are milder than those used with soybean oil. The optimized conditions were: for ethyl biodiesel, 35 minutes of reaction at a temperature of 308 K, 0.19 % KOH and 260 rpm; for methyl biodiesel, 60 min of reaction at 319 K, 0.42 % KOH and 189 rpm. This information is especially important in order to have control over the process so as to favor the transesterification reaction, since this reaction competes with the saponification reaction.

The physico-chemical parameters of the biodiesel from sunflower oil m*et all* the specifications of the ANP - National Agency of Petroleum, Natural Gas and Biofuels, ASTM D6751-American Society of Testing and Materials and EN - Comité Européen de Normalisation, except oxidative stability. It is necessary to add additives to biodiesel from sunflower oil before it can be used.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

REFERENCES

[1] ATABANI, A. E. *et al.* A comprehensive review on biodiesel as an alternative energy resource and its characteristics, **Renewable and Sustainable Energy Reviews**, 16 (2012) 2070-2093.

[2] RATHMANN, R. SZKLO; A. SCHAEFFER, R. Targets and results of the Brazilian Biodiesel Incentive Program – Has it reached the Promised Land?, **Applied Energy**, 97 (2012) 91-100.

[3] ANP, Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, in, 2012.

[4] BERGMANN, J. C. *et al.* Biodiesel production in Brazil and alternative biomass feedstocks, **Renewable and Sustainable Energy Reviews**, 21 (2013) 411-420.

[5] BIODIESEL BR. O poder das flores, in, 2013.

[6] SANTOS, A. D. *et al.* Characterization and kinetic study of sunflower oil and biodiesel, **J Therm Anal Calorim**, 106 (2011) 747-751.

[7] C.N.d. Abastecimento, in, 2013.

[8] KILIÇ, M. *et al.* Optimization of biodiesel production from castor oil using factorial design, **Fuel Processing Technology**, 111 (2013) 105-110.

[9] LEE, H. V. *et al.* Process optimization design for jatropha-based biodiesel production using response surface methodology, **Fuel Processing Technology**, 92 (2011) 2420-2428.

[10] SRIVASTAVA, A.; PRASAD, R. Triglycerides-based diesel fuels, **Renewable and Sustainable Energy Reviews**, 4 (2000) 111-133.

[11] ATABANI, A. E. *et al.* Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production, **Renewable and Sustainable Energy Reviews**, 18 (2013) 211-245.

[12] LIMA, A. P.; SANTOS, D. Q., NETO, W. B. Aplicação do Planejamento Fatorial e Método da Superfície de Resposta para Otimizar a Produção de Biodiesel Etílico de Óleo de Milho, **Revista Virtual de Química**, 5 (2013) 10.

[13] AMINI-NIAKI, S. R.; GHAZANFARI, A. Comparison of fuel and emission properties of petro diesel and sunflower biodiesel prepared by optimized production variables, Fuel, 109 (2013) 384-388.

[14] GHANEI, R. *et al.* Variation of physical properties during transesterification of sunflower oil to biodiesel as an approach to predict reaction progress, **Fuel Processing Technology**, 92 (2011) 1593-1598.

[15] TSOUTSOS, T. *et al.* Effect of wastewater irrigation on biodiesel quality and productivity from castor and sunflower oil seeds, **Renewable Energy**, 57 (2013) 211-215.

[16] SILVA, G. F., CAMARGO; F. L., FERREIRA, A. L. O. Application of response surface methodology for optimization of biodiesel production by transesterification of soybean oil with ethanol, **Fuel Processing Technology**, 92 (2011) 407-413.

[17] ZULETA, E. C. *et al.* The oxidative stability of biodiesel and its impact on the deterioration of metallic and polymeric materials: a review, **Journal of the Brazilian Chemical Society**, 23 (2012) 2159-2175.

[18] JORGE, N. *et al.* Alterações físico-químicas dos óleos de girassol, milho e soja em frituras, **Química Nova**, 28 (2005) 947-951.