

Contents lists available at [ScienceDirect](http://ScienceDirect.com)

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Application of response surface methodology for optimization of biodiesel production by transesterification of soybean oil with ethanol

Giovanilton F. Silva^a, Fernando L. Camargo^b, Andrea L.O. Ferreira^{c,*}

^a *Tecnologias Bioenergéticas, R. Rômulo Proença S/N Bloco A, Pici, 60455-700, Ceará, Brazil*

^b *Escola de Engenharia de Piracicaba, Fundação Municipal de Ensino de Piracicaba, Av. Monsenhor Martinho Salgot 560 Vila Areião, 13414-040, São Paulo, Brazil*

^c *Chemical Engineering Department, Universidade Federal do Ceará, Campus do Pici, Bloco 709, Pici, 60455-760, Ceará, Brazil*

ARTICLE INFO

Article history:

Received 6 October 2008

Received in revised form 28 September 2010

Accepted 25 October 2010

Available online 26 November 2010

Keywords:

Biodiesel

Ethanol

Fuel

Optimization

Response surface

Soybean oil

ABSTRACT

In this paper, the transesterification of soybean oil with ethanol is studied. The transesterification process can be affected by differing parameters. The biodiesel production process was optimized by the application of factorial design 2⁴ and response surface methodology. The combined effects of temperature, catalyst concentration, reaction time and molar ratio of alcohol in relation to oil were investigated and optimized using response surface methodology. Optimum conditions for the production of ethyl esters were the following: mild temperature at 56.7 °C, reaction time in 80 min, molar ratio at 9:1 and catalyst concentration of 1.3 M.

© 2010 Elsevier B.V. Open access under the [Elsevier OA license](http://www.elsevier.com/locate/elsevier).

1. Introduction

Biodiesel has become more attractive recently, because of its environmental benefits and the fact that it is made from renewable resources [1]. The transesterification of vegetable oils with methanol or ethanol, as well as the main uses of the fatty acid ethyl esters, are reviewed in current literature [1–3]. The general aspects of this process and the applicability of different types of catalysts—acids, alkaline metal hydroxides, alkoxides and carbonates, enzymes and nonionic bases, such as amines, amidines, guanidines and triamino(imino) phosphoranes—are described at ambient or elevated pressures, as well as temperatures [2–5]. “Transesterification” is the general term used to describe the important class of organic reactions where one ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called “alcoholysis” (see Fig. 1). Several parameters, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification by reaction. Soap is produced when a higher free fatty acid or a greater number of water molecules is available.

There are many studies of the alcoholysis of triglycerides using homogeneous catalysts [6–10]. For homogeneous catalysts, high conversions are easy to achieve in less than an hour of reaction at temperatures from 40 to 65 °C [11,12]. Typically, higher temperatures are not used to avoid system pressures, which require pressure vessels.

Generally, the alcohols employed in the transesterification are short-chain alcohols, such as methanol, ethanol, propanol, and butanol. Ma et al. [13] reported that when transesterification of soybean oil using methanol, ethanol and butanol is performed, 96–98% of ester can be obtained after an hour of reaction.

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, and thereby produces a mixture of fatty acids, alkyl esters and glycerol [5]. The overall process is a sequence of three consecutive and reversible reactions in which di- and monoglycerides are formed as intermediates (see Fig. 2). The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol (an undesirable product).

Annual soybean oil production in Brazil is estimated at more than 1.8 million m³. Alcohol production in Brazil was initiated on a large scale in 1975 at the National Program for Alcohol (1975–1985). The sugarcane industry has played a significant political and economic role in Brazil historically. Currently, that industry employs between 0.8 and 1 million people directly, producing annually some 11.2 × 10⁶ ton of sugar and about 13 × 10⁹ L of ethanol, with an equivalent 220,000 barrels/day of gasoline imports [13–16]. Therefore, this study of the

* Corresponding author. Tel.: +55 85 3366 9611; fax: +55 85 3366 9610.

E-mail addresses: giovanilton@gmail.com (G.F. Silva), flcamargo@pinga.eep.br (F.L. Camargo), andrea@ufc.br (A.L.O. Ferreira).

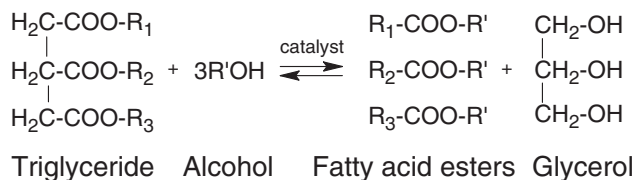


Fig. 1. Scheme of general transesterification reaction.

transesterification reaction using ethanol and optimization of process production of biodiesel is significant, as well as important for the environment.

The experiments discussed in this paper were designed to optimize the production process for biodiesel by transesterification of soybean oil with ethanol, where several parameters, including catalyst, alcohol/vegetal oil molar ratio, and temperature would influence the transesterification. This study's main objective was to develop an approach for better understanding the relationships between the variables (ethanol-to-oil ratio, catalyst concentration, reaction time and temperature) and the response (ethyl esters and glycerol)—to obtain the optimum conditions for biodiesel production using central composite rotatable design (CCRD) and response surface methodology (RSM). The CCRD has the advantage of predicting responses based on a few sets of experimental data, in which all parameters vary within a chosen range.

2. Materials and methods

2.1. Materials

Refined soybean oil was purchased from Bunge Alimentos S.A. (Brazil); ethyl alcohol and acetic acid were acquired from Synth (Brazil); and NaOH, KOH, NaIO₄, NaCl, NH₄Cl, H₂SO₄, Na₂SO₄, Na₂CO₃, Na₂S₂O₄ and KIO₃ were obtained from Vetec (Brazil). Glycerol, hexane and tetrachlorocarbon were acquired from J.T. Baker, Phillipsburg, NJ (USA); and petroleum ether, phenolphthalein, oleic, linolenic and linoleic acid were obtained from Sigma-Aldrich, Milwaukee, WI (USA).

2.2. Transesterification reaction assays and analysis

The transesterification reaction was carried out with ethanol/oil ratio (i.e., 3:1, 6:1, 9:1, 12:1 and 15:1 M), using 0.1%, 0.5%, 0.9%, 1.3% and 1.7% w/v of NaOH, as an alkaline catalyst. The reactor (described in the later part) was preheated, and then the oil was added. When the reactor reached the temperature established for the reaction, the ethanol and the catalyst were added, in the amounts established for each experiment, taking that point in time as being time zero of the reaction. The reaction was carried out at 40, 50, 60, 70 and, 80 °C and the reaction times were 40, 60, 80, 100, and 120 min. The choice of said variables and their range were selected based on several outside sources and on preliminary studies in our laboratory. The combination of these variables (temperature, catalyst concentration, reaction time and molar ratio of alcohol to oil) was used in a factorial experimental design for biodiesel production optimization by transesterification of soybean oil with ethanol.

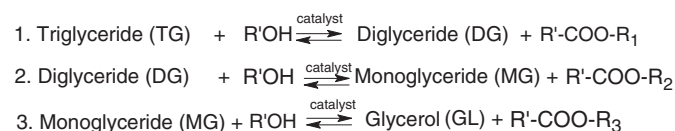


Fig. 2. Transesterification of triglyceride with alcohol of three consecutive and reversible reactions, where R' represents alkyl groups.

Refined soybean oil was used, and the free acid content of the oil was determined by titration according to AOCS methods, Ca 5a-40 to be 0.09%. The amount of used NaOH (dissolved in ethanol) was based on the amount needed to neutralize the unreacted acids (Official Methods and Recommended Practices of the AOCS, 1997).

The reaction product was allowed to settle overnight before the glycerol layer was removed from the bottom, in a separatory funnel, in order to collect the biodiesel layer from the top. The apparatus used for the transesterification reaction was a 1-L stainless steel jacketed batch reactor with mechanical stirring (two-blade propeller turbine agitator), sampling port and a reflux condenser, using cold tap water to condense ethanol vapor.

The ethyl esters obtained from the transesterification reaction were analyzed by gas chromatography using a Varian 3400 CX instrument (Varian, Walnut Creek, Calif., USA), equipped with a capillary injection system RTX-5MS, column (15 m × 0.25 mm), coated with a 0.25 μm film, with a split ratio of 100:1 and a sample size of 1 μL. The injector temperature was 240 °C, the oven temperature was programmed from 50 °C to 250 °C, and the detector temperature was 200 °C. The glycerol yield (Y_{glycerol}) was defined as a mass of glycerol from transesterification ($W_{\text{free glycerol}}$) per mass of triglyceride ($W_{\text{combined glycerol}}$) in the beginning of the assay.

2.3. Factorial experimental design and optimization of parameters

Temperature, ethanol-to-oil ratio, catalyst concentration and reaction time were chosen as independent variables, and the production of ethyl esters and glycerol were the dependent variables. The experimental range and levels of independent variables for biodiesel production are given in Table 1. For this study, a set of 30 experiments including the 2⁴ factorial experiments, 8 star points and 6 center points were carried out. Usually a low-order polynomial in some range of independent variables is employed for modeling. If the response is well modeled by a linear function of independent variables, then the approximating function is the first-order model. If there is curvature in the system, then a polynomial of higher degree must be used, such as the second-order model [17]. In this study, there was a curvature. Experiments were then employed to fit the second-order polynomial model, which indicated that 30 experiments were required for this procedure [17–19]. As already mentioned, a significant curvature effect was observed, then 8 star points, coded α, (runs 17 to 24 in Table 2) were added to the 22 experiments to form a central composite design (runs 1 to 16 and 25 to 30 in Table 2). The distance of the star points from the center point is given by $\alpha = 2^{n/4}$, where n is the factor numbers (for two factors, $\alpha = 2^{2/4} = 1.414$).

The coded values of the independent variables for the design of the experiment for biodiesel production and glycerol are given in Table 2. For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = \frac{(X_i - X_0)}{X} \quad (1)$$

Table 1

Experimental range and levels of independent process variables for biodiesel production.

Independent variable	Range and level				
	−α	−1	0	1	α
Molar ratio (x_1)	3:1	6:1	9:1	12:1	15:1
Catalyst concentration (wt.%) (x_2)	0.1	0.5	0.9	1.3	1.7
Temperature (°C) (x_3)	40	50	60	70	80
Time of reaction (min) (x_4)	40	60	80	100	120

Table 2
Full factorial central composite design matrix for biodiesel production.

Run	Independent variables				Responses	
	x_1	x_2	x_3	x_4	Ethyl esters (%)	Glycerol (%)
1	-1	-1	-1	-1	79	4.5
2	+1	-1	-1	-1	83	9.5
3	-1	+1	-1	-1	84	9.1
4	+1	+1	-1	-1	95	3.4
5	-1	-1	+1	-1	56	3.4
6	+1	-1	+1	-1	78	10.9
7	-1	+1	+1	-1	79	2.5
8	+1	+1	+1	-1	94	1.5
9	-1	-1	-1	+1	56	4.3
10	+1	-1	-1	+1	93	4.5
11	-1	+1	-1	+1	94	0.6
12	+1	+1	-1	+1	92	1.3
13	-1	-1	+1	+1	49	6.1
14	+1	-1	+1	+1	72	5.6
15	-1	+1	+1	+1	67	1.8
16	+1	+1	+1	+1	92	2.5
17	$-\alpha$	0	0	0	49	4.2
18	$+\alpha$	0	0	0	77	5.5
19	0	$-\alpha$	0	0	60	5.4
20	0	α	0	0	79	6.2
21	0	0	$-\alpha$	0	71	6.9
22	0	0	$+\alpha$	0	81	4.7
23	0	0	0	$-\alpha$	69	4.8
24	0	0	0	$+\alpha$	72	5.7
25	0	0	0	0	75	5.8
26	0	0	0	0	71	6.0
27	0	0	0	0	74	5.4
28	0	0	0	0	70	6.4
29	0	0	0	0	69	6.1
30	0	0	0	0	75	5.2

where X_0 is the average value of variables in high and low levels, and X is (variable at high level – variable at low level)/2. Where x_1 is a coded variable that represents the molar ratio, x_2 is a coded variable that represents the catalyst concentration, x_3 is a coded variable that represents the temperature and x_4 is a coded variable that represents the time of reaction.

The behavior of the system discussed is described by a quadratic equation, Eq. (2), which follows [20,21]. A multiple regression data analysis was carried out with the statistical package (StatSoft Inc., Tulsa, Okla., USA). The optimum values of selected variables were obtained by solving the regression equation and also by analyzing the response surface contour plots:

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

where Y is the predicted response; β_0 , β_j , β_{ij} and β_{jj} constant coefficients; x_i and x_j are the coded independent variables or factors; ε is random error.

3. Results and discussion

3.1. Regression equation for ethyl esters

It is known that the most important parameters affecting the efficiency of the biodiesel production are molar ratio (x_1), concentration of catalyst (x_2), temperature (x_3) and time (x_4) for reaction. In order to study the interaction factors (combined effect of these factors), experiments were performed varying physical parameters, using experimental design. By applying multiple regression analysis on the Table 2 data, the experimental results of the full factorial central composite design were fitted to the polynomial Eq. (2). The

Table 3
Regression analysis (ANOVA) for Eq. (3).

Sources of variation	Sum of squares	Degrees of freedom	Mean squares	F _{value}	Probability P
Model	0.7690	8	0.0961	122.6	0.00052
Residual	0.0165	21	0.0008		
Total	0.7855	29			

Correlation coefficients: $R^2 = 0.922$.
 $F(0.95, 8, 21) = 2.42$.

adjusted model obtained for ethyl esters production, as a function of the more significant variables, is shown in Eq. (3).

$$Y_{\text{Ethyl esters}} = 0.72 + 0.17x_1 + 0.13x_2 - 0.04x_3 + 0.05x_3^2 + 0.029x_4^2 - 0.06x_1x_2 + 0.07x_1x_3 + 0.072x_1x_4 \quad (3)$$

This fit of the model was checked with the coefficient of determination R^2 , which was calculated to be 0.922, indicating that 92.2% of the response variability could be explained by the previously discussed model. This study indicates that the model can be considered statistically significant according to the F-test with 95% of confidence, as the F-value of 122.6 is much higher than $F(8, 21)$, showing that the model is significant at 95% confidence level. The probability p -value is low (0.00052), indicating the significance of the model specified previously, according to the ANOVA Table 3.

According to Fig. 3, molar ratio (x_1) and concentration of catalyst (x_2) are the most significant variables for biodiesel production (effect of $x_1 = 16.463$ and effect of $x_2 = 12.701$), followed by their interaction molar ratio (L) with time (L) (x_1x_4) (effect of $x_1x_4 = 5.933$), as well as molar ratio (L) with temperature (L) (x_1x_3) (effect of $x_1x_3 = 5.912$). Molar ratio (x_1) has a substantially higher effect on the ethyl esters production compared to the catalyst concentration (x_2). Where (L) is the linear and (Q) is the quadratic interaction of variables. In the presence of an interaction effect, the variables cannot be analyzed separately, therefore the application of statistical methods reveals the interactions x_1x_4 , x_1x_3 and x_1x_2 are significant (effect of $x_1x_2 = -5.065$).

According to Fig. 3, temperature (L) has a negative effect in ethyl esters production (-3.773), however temperature has a positive quadratic effect (Q) (5.30); therefore, temperature-effect forecasts are not straightforward. Time (L) is not significant for ethyl esters production at the confidence interval considered (95%), but time (Q) presents a significant effect on biodiesel production (3.21). Note that the chosen optimum conditions took into consideration temperature and time interactions, which are important in defining the operational cost of biodiesel production on an industrial scale.

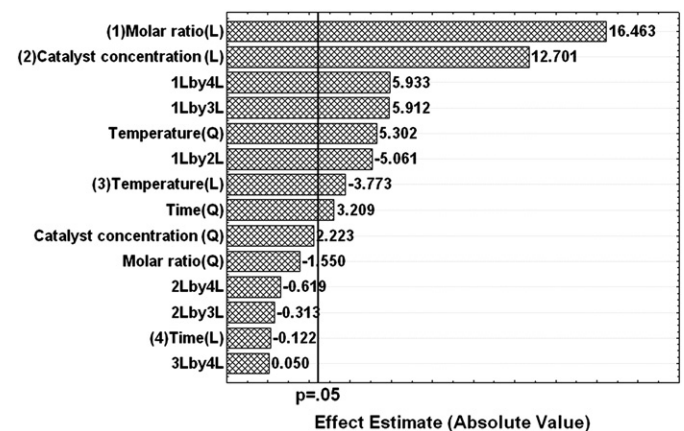


Fig. 3. Pareto chart of standardized effects on ethyl esters production. (L) is the linear and (Q) is the quadratic interaction of variables.

The response surface contours, which are the graphical results of interactive effects, are shown in Figs. 4, 5 and 6. Fig. 4 shows the response for the interactive factor temperature and catalyst concentration. As expected, Fig. 4 shows that ethyl esters conversion increases when high catalyst concentration is applied. However, as with the work of Vicente et al. [22], it was observed that temperatures (>60 °C) and catalyst concentrations ($>1.5\%$) led to the production of large amounts of soaps in this study. Furthermore, the addition of an excessive amount of catalyst increases emulsion formation.

The response surface corresponding to the second-order model indicates that for low temperatures, ethyl esters production increases with an increasing catalyst concentration. Maximum ethyl ester conversions are therefore obtained from large catalyst concentrations (1.7 wt.%). This is due to the second most significant factor being the catalyst concentration, and to its effect being positive (see Fig. 3).

When soybean oil and NaOH dissolved in ethanol react, there are two reaction pathways: transesterification to produce biodiesel and saponification to produce soap; therefore, forecasting the temperature effect is not straightforward. There are two equilibrium reactions. When saponification reaction is favored, NaOH is lost and the overall process rate decreases. NaOH is a catalyst on transesterification reaction and a reagent on saponification reaction. On the other hand, the transesterification reaction can be favored when adequate temperatures are used. Low temperature decreases the saponification reaction rate, thus transesterification reaction is favored. When temperatures increase, the reaction rates are obviously higher because molecules have more energy, but the saponification reaction rate speeds up, therefore the transesterification reaction yield decreases. That could be compensated for eventually through an increase of selectivity for biodiesel, but that was not the case (see Fig. 4). When operating at much higher temperatures, the transesterification reaction is faster than the saponification reaction, thus NaOH is again a catalyst. Therefore, temperature was tested as an important variable to enhance the reaction in biodiesel production. To summarize, defining the best temperature is clearly an optimization problem.

Fig. 5 shows the response for the interactive factors of temperature and molar ratio. Fig. 6 shows the response for the interactive factor of time and molar ratio. The 3D response surface plots indicate that the ethyl esters production increases when ethanol concentration increases (molar ratio: ethanol/oil) (see Fig. 5). Therefore, the maximum biodiesel conversions are obtained for high molar ratio. This is caused by the stoichiometry of transesterification, which

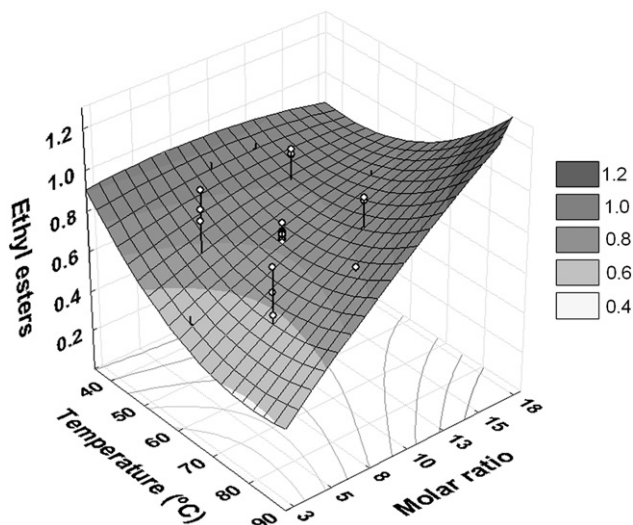


Fig. 5. Response surface contour for interaction on ethyl esters production between molar ratio and temperature.

requires a 3:1 M ratio of alcohol to triglyceride, since this reaction involves the conversion of one ester and an alcohol towards another ester and another alcohol, as an excess of alcohol is used to drive the reaction near completion. Consequently, the ethanol concentration results in a greater biodiesel conversion within a shorter time (see Fig. 6) [23–25]. On the other hand, an excessive amount of alcohol makes the recovery of glycerol difficult [1,5]; therefore, the ideal alcohol/oil ratio has to be established empirically, considering each individual process. Fillieres et al. [26] found a molar ratio between 9:1 and 12:1 to be the best for ethanol.

Higher production of ethyl esters is strongly favored when high molar ratio is employed for a certain time of reaction (x_4), temperature (x_3) and catalyst concentration (x_2) (see Figs. 5 and 6). The molar ratio (ethanol/oil) is a fundamental variable in the transesterification of the biodiesel production. This said molar ratio affects the separation and recovery of glycerol. A molar ratio of 6:1 is generally considered the most appropriate for methanol, although in this work, as has been indicated, we found the molar ratio 9:1 to be the best for ethanol. Nevertheless, the results are quantitatively similar to those of the literature [1,2,5,6,22–25].

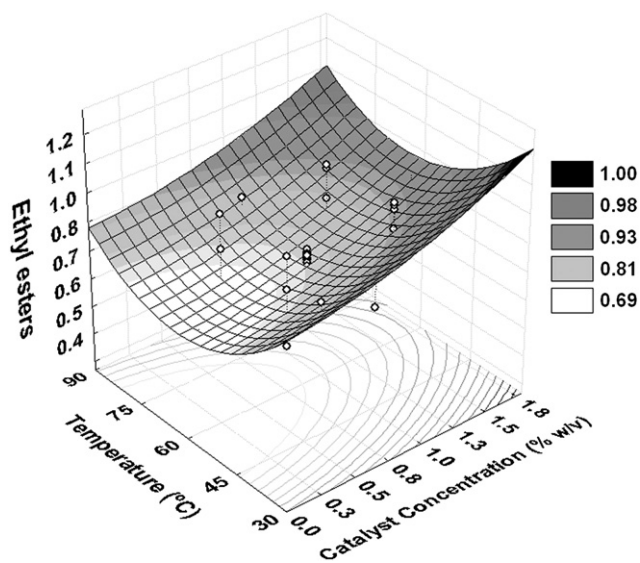


Fig. 4. Response surface contour for interaction on ethyl esters production between temperature and catalyst concentration.

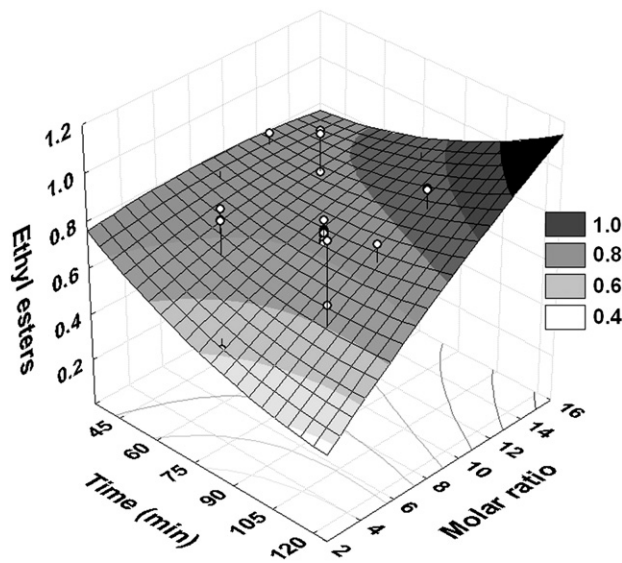


Fig. 6. Response surface contour for interaction on ethyl esters production between molar ratio and time.

Some researchers have hypothesized that the quality of esters (biodiesel yield) depends on the large excess of alcohol [5,26]. However, in this study, the high molar ratio of alcohol to vegetable oil only interfered in the glycerol separation, since there was an increase in solubility. When glycerol remains in solution, it helps driving the equilibrium back to the left, thereby lowering the yield of esters. The transesterification of soybean oil with ethanol was studied at molar ratios between 3:1 and 15:1. When temperature was high, higher ethyl ester yield was achieved (see Fig. 5), mainly when the molar ratio increased to values of 15:1. On the other hand, at lower temperatures (35 °C), the best results were for molar ratios between 9:1 and 12:1. For molar ratios less than 6:1, the reaction was incomplete. For a molar ratio of 15:1 the glycerol separation was difficult and the apparent yield of esters decreased, since some of the glycerol remained in the biodiesel phase. Therefore, molar ratio 9:1 seems to be the most appropriate. Several workers have found similar results for biodiesel production [26–28].

Fig. 7 shows the ethyl ester yield as function of molar ratio and catalyst concentration under experimental conditions defined by factorial design shown in Section 2. It is possible to observe that higher ethyl ester yields occur at higher molar ratio (>12:1) and at higher catalyst concentration (>1.3 wt.%). When molar ratio values were low (<6:1), yields increased with catalyst concentration. However, when molar ratio was kept in its higher level (15:1), a higher ethyl ester yield was always achieved. Thus, catalyst concentration is the most important factor in improving ethyl ester yields. However, excess catalyst can produce emulsions and the biodiesel that is produced has difficulty in the separation phase.

It has been reported that low catalyst concentration increases conversions with methanol-to-oil ratio [30]. In this present study, applying response surface design, we observed that for ethanol, ethyl esters production increases when catalyst concentration increases for low molar ratio.

The optimum values of selected variables were obtained by solving the regression Eq. (3). The optimum values of the process variables for maximum ethyl esters production are shown in Table 4, when a yield of 95% was achieved. The ester yield increased as the molar ratio also increased up to a value of 12:1. The best results were for molar ratios between 9:1 and 12:1. The reaction was incomplete for molar ratios less than 6:1. For a molar ratio of 15:1, the glycerol separation was difficult and the apparent yield of esters decreased, because of a

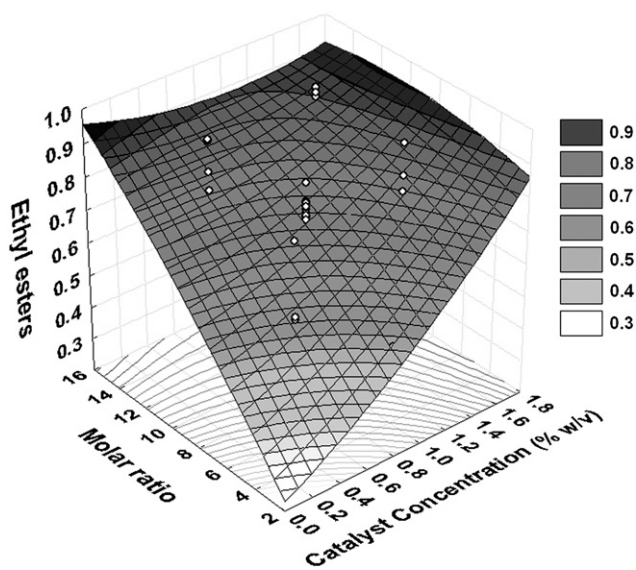


Fig. 7. Response surface contour for interaction on ethyl esters production between time and catalyst concentration.

Table 4
Optimum values of the process parameter for maximum efficiency.

Parameters	Optimum values
Ethyl esters (%)	95
Molar ratio (x_1)	9:1
Catalyst concentration (wt.) (x_2)	1.3
Temperature (°C) (x_3)	40.0
Time (min) (x_4)	80

portion of the glycerol remaining in the biodiesel phase. Table 4 indicates that the value molar ratio for ethanol (9:1) was higher than the molar ratio found by Freedman et al. [29] in the methanol (6:1). However, it was lower than the molar ratio found by Encinar et al. [31], who studied the transesterification of *Cynara* oil with ethanol (12:1). Therefore, molar ratio 9:1 seems to be the most appropriate. Thus, reaction with ethanol uses a molar ratio higher than the reaction with methanol. Therefore, the phase separation becomes more difficult when molar ratio of ethanol increases due to its miscibility increasing for both phases (glycerol and ethyl ester).

The optimum-value temperature was 40.0 °C. This temperature is below the boiling point of alcohol. Therefore, molar ratio (ethanol/oil) is used between 6:1 and 12:1, since it did not evaporate. The transesterification rate increases as the temperature increases. However, the maximum operating temperature cannot exceed the boiling point of the reactants. Encinar et al.'s [31] study of the ethanolysis of refined *Cynara cardunculus* oils achieved the best results at 75 °C. This temperature was higher than the one in this present experiment. However, transesterification may occur at different temperatures, depending on the oil used. In addition, ethanol/oil presents the difference in solubility as a function of temperature.

The highest ethyl ester yields were achieved when the reaction time was 80 min. Other authors reported that similar yields of biodiesel may be obtained following ethanolysis or methanolysis; however, the reaction times required to attain them are very different: methanolysis is quicker than ethanolysis [32].

The optimum value of catalyst concentration was at 1.3% w/v. This value agrees with the values duly presented in the literature [1,5,6]. As a typical catalyst concentration for transesterification reactions (0.5 to 1.5 wt.%), the results that were obtained agreed with those obtained from the response surface analysis, confirming that the RSM was effectively used to optimize biodiesel production.

3.2. Regression equation for glycerol

The adjusted model obtained for glycerol production, as a function of the more significant variables, is shown in Eq. (4). According to the ANOVA (see Table 5), the response presented high correlation coefficients (>0.95) and the model can be considered statistically significant according to the F-test with 95% of confidence. The calculated values discussed previously were greater than the listed values, F-value of 32, which are higher than $F(7,22)$. The coefficient of

Table 5
Regression analysis (ANOVA) for Eq. (4).

Sources of variation	Sum of squares	Degrees of freedom	Mean squares	F _{value}	Probability P
Model	0.4770	7	0.0681	32	0.0014
Residual	0.0468	22	0.0021		
Total	0.5238	29			

Correlation coefficients: $R^2 = 0.960$.
 $F(0.95,7,22) = 2.46$.

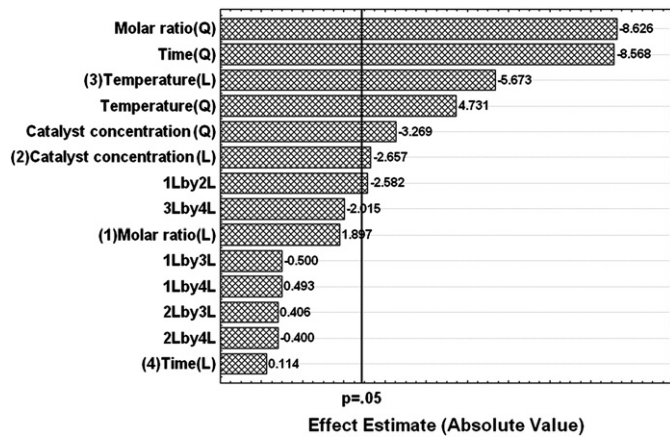


Fig. 8. Pareto chart of standardized effects on glycerol production.

determination R^2 , calculated to be 0.960, indicated that 96.0% of the variability in the response could be explained by the following model.

$$Y_{Glycerol} = 0.21 - 0.1x_1^2 - 0.03x_2 - 0.04x_2^2 - 0.075x_3 + 0.05x_3^2 - 0.1x_4^2 - 0.043x_1x_2 \quad (4)$$

Fig. 8 presents the Pareto Chart of standardized effects at $p = 0.05$. All the standardized effects were in absolute values (to verify which were positives and negatives). According to Fig. 8, molar ratio (Q) is the most significant variable for glycerol production. The molar ratio (Q), time (Q), temperature (L) and concentration of catalyst (Q) have a negative effect on glycerol production.

Fig. 9 shows molar ratio (x_1) and time (x_4) effects on glycerol production. As shown already, these parameters (time and molar ratio) are significant. According to Fig. 9, higher glycerol formation is strongly favored when molar ratio is kept between 6.0 and 12.0 for a given time. At a higher molar ratio, one can observe that glycerol production increases initially, reaching a maximum level at intermediate time (level 0 or 80 min), and then decreases at high time (level + α or 120 min). This is the result of negative effects of time and molar ratio quadratic coefficients. In the ethanolysis of soybean oil, a 10:1 M ratio released significantly more glycerol than a 3:1 M ratio. The response surface in Fig. 9 shows that the maximum glycerol production is obtained in the region of the stationary point.

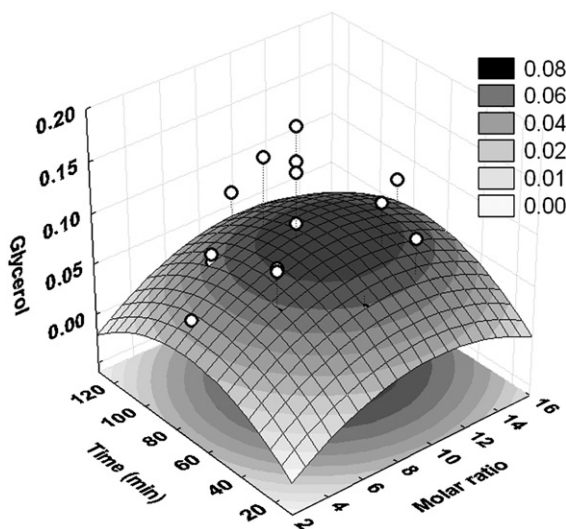


Fig. 9. Response surface contour for interaction on glycerol production between molar ratio and time.

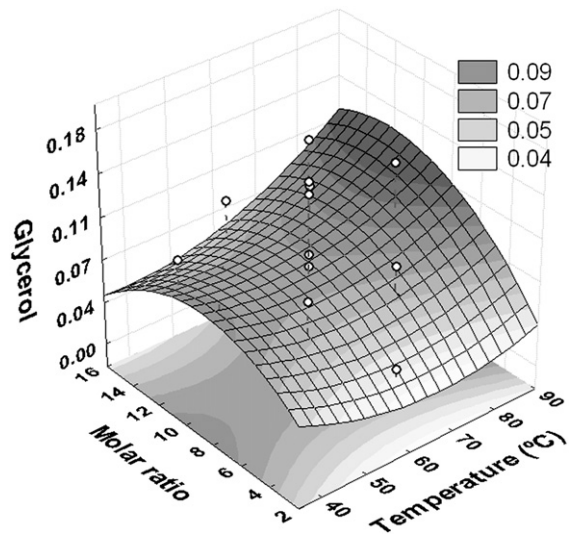


Fig. 10. Response surface contour for interaction on glycerol production between temperature and molar ratio.

Fig. 10 shows glycerol production as being a function of temperature and molar ratio. In Fig. 10, lowering the reaction time and high molar ratio values can attain higher glycerol formation. Molar ratio clearly influenced the reaction rate and ethyl esters yield. Combining the results presented in Figs. 9 and 10, biodiesel production is favored, while higher glycerol formation is minimized (applying low molar ratio values, high times of reaction, and high temperature levels).

According to Fig. 10, glycerol production increases when molar ratio is kept between 9 and 10 for a given temperature. Glycerol formation can be minimized when temperature (x_3) or molar ratio (x_1) decreases.

4. Conclusions

This research studied the variables affecting soybean oil ethanolysis and was carried out under laboratory conditions. Consequently, using response surface analysis, it was possible to study the effect of key parameters on biodiesel conversion. Process optimization was accomplished by applying factorial design and response surface methodology.

This study clearly shows that response surface methodology was a suitable method to optimize the operating conditions in order to maximize the ethyl esters production and minimize the glycerol production. Graphical response surfaces were used to locate the optimum point. A full factorial central-composite design (30 assays) was successfully employed for experimental design and results analysis. Satisfactory prediction equations were derived for both, with the ethyl esters and glycerol using RSM. The optimum concentration for molar ratio, catalysts, time and temperature were, 9:1, 1.3 wt.%, 80 min and 40.0 °C, respectively.

The catalyst tested, sodium hydroxide, gave the highest ethyl ester yield for the concentration of 1.3%. The best results were obtained at 40.0 °C. This temperature influenced the reaction time, increasing the reaction time of 80 min.

Based on the study results, the conclusion is that ethanol can substitute for the methanol, when it is applied in optimized conditions, as presented here. As a result, the biodiesel produced comes from renewable sources (ethanol derived from sugar cane and soybean oil).

The innovation in this manuscript is the combined use of ethanol and soybean oil to produce a fuel from 100% renewable energy

sources, since methanol used for biodiesel production is produced from fossil fuels.

5. Nomenclature

ANOVA	analysis of variance;
CCRD	central composite rotatable design;
F	F-value, test statistic of F distribution;
L	linear variable;
p	p-value, smallest level of significance that would lead to the rejection of null hypothesis in test statistic;
Q	quadratic variable;
R ²	coefficient of determination;
RSM	response surface methodology;
X	independent variables;
x	coded variables;
Y	dependent variable, predicted response;
α	star point of factorial design;
β	constant coefficients of mathematical model;
ε	random error of mathematical model.

Acknowledgement

The authors thank the Brazilian research-funding agency CNPq.

References

- [1] F. Ma, M.A. Hanna, Biodiesel production: a review, *Bioresour. Technol.* 70 (1999) 1–15.
- [2] M. Mittelbach, Lipase catalyzed alcoholysis of sunflower oil, *J. Am. Oil Chem. Soc.* 67 (1990) 168–175.
- [3] U. Schuchardt, R. Sercheli, V.R. Matheus, Transesterification of vegetable oils: a review, *J. Braz. Chem. Soc.* 9 (1998) 199–210.
- [4] B. Freedman, R.O. Butterfield, E.H. Pryde, Transesterification kinetics of soybean oil, *J. Am. Oil Chem. Soc.* 63 (1986) 1375–1380.
- [5] H. Noureddini, D. Zhu, Transesterification of soybean oil, *J. Am. Oil Chem. Soc.* 74 (1997) 1457–1463.
- [6] G. Antolín, F.V. Tinaut, Y. Briceño, V. Castaño, C. Pérez, A.I. Ramírez, Optimisation of biodiesel production by sunflower oil transesterification, *Bioresour. Technol.* 83 (2) (2002) 111–144.
- [7] R.O. Feuge, T. Grose, Modification of vegetable oils. VII. Alkali catalyzed interesterification of peanut oil with ethanol, *J. Am. Oil Chem. Soc.* 26 (3) (1949) 97–102.
- [8] C.G. De Filippis, M. Scarsella, M. Sorrentino, Transesterification process for vegetable oils: a simple control method of methyl ester content, *J. Am. Oil Chem. Soc.* 72 (11) (1995) 1399–1404.
- [9] V. Jordan, B. Gutsche, Development of environmentally benign processes for the production of fatty acid methyl esters, *Chemosphere* 43 (2001) 99–105.
- [10] A.K. Agarwal, Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines, *Prog. Energy Combust. Sci.* 33 (2007) 233–271.
- [11] K.G. Georgogianni, M.G. Kontominas, P.J. Pomonis, D. Avlonitis, V. Gergis, Conventional and in situ transesterification of sunflower seed oil for the production of biodiesel, *Fuel Process. Technol.* 89 (2008) 503–509.
- [12] K.G. Georgogianni, M.G. Kontominas, P.J. Pomonis, D. Avlonitis, V. Gergis, Alkaline conventional and in situ transesterification of cottonseed oil for the production of biodiesel, *Energy Fuels* 22 (3) (2008) 2110–2115.
- [13] F.R. Ma, L.D. Clements, M.A. Hanna MA, Biodiesel fuel from animal fat. Ancillary studies on transesterification of beef tallow, *Ind. Eng. Chem. Res.* 37 (1998) 3768–3771.
- [14] M.A.V. Borrero, J.T.V. Pereira, E.E. Miranda, An environmental management method for sugar cane alcohol production in Brazil, *Biomass Bioenergy* 25 (2003) 287–299.
- [15] R.J. Moreira, J. Goldemberg, The alcohol program, *Energy Policy* 27 (1999) 229–245.
- [16] F. Rosillo-Calle, A.B.L. Cortez, Towards ProAlcool II—a review of the Brazilian bioethanol programme, *Biomass Bioenergy* 14 (1998) 115–124.
- [17] D.C. Montgomery, *Design and Analysis of Experiments*, 5th ed. Wiley, New York, 2001.
- [18] B. Barros Neto, I.S. Scarminio, R.E. Bruns, *Como Fazer Experimentos—Pesquisa e desenvolvimento na ciência e na indústria*, 1st ed, Editora UNICAMP, Campinas, 2001, pp. 83–296.
- [19] V. Calado, D.C. Montgomery, *Planejamento de Experimentos usando Statistica*, 1st ed. E-Papers Editora, Rio de Janeiro, 2003.
- [20] G.E.P. Box, W.G. Hunter, J.S. Hunter, *Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building*, John Wiley, New York, 1978.
- [21] G.E.P. Box, K.B. Wilson, On the experimental attainment of optimum conditions, *J. R. Stat. Soc. B* 13 (1951) 1–45.
- [22] G. Vicente, A. Coteron, M. Martinez, J. Aracil, Application of the factorial design of experiments and response surface methodology to optimize biodiesel production, *Ind. Crops Prod.* 8 (1998) 29–35.
- [23] F.J. Sprules, D. Price, Production of fatty esters. US Patent 2,366–494, 1950
- [24] Y. Tanaka, A. Okabe, S. Ando, Method for the preparation of a lower alkyl ester of fatty acids. US Patent 4,303–590, 1981.
- [25] G.F. Silva, M.S. Castro, J.S. Silva, J.S. Mendes, A.L.O. Ferreira, Simulation and optimization of biodiesel production by soybean oil transesterification in non-ideal continuous stirred-tank reactor, *Int. J. Chem. Reactor Eng.* 8 (A34) (2010) 1–20.
- [26] R. Fillieres, B. Benjelloun-Mlayeh, M. Delmas, Ethanolsis of rapeseed oil—quantitation of ethyl-esters, monoglycerides, diglycerides, and triglycerides and glycerol by high-performance size-exclusion chromatography, *J. Am. Oil Chem. Soc.* 72 (1995) 427–432.
- [27] A.V. Tomasevic, S.S. Marinkovic, Methanolysis of used frying oils, *Fuel Process. Technol.* 81 (2003) 1–6.
- [28] Freedman B., Pryde E.H., Fatty esters from vegetable oils for use as diesel fuel, *Proceedings Book of International Conference on Plant and Vegetable Oils as Fuel*, ASAE, Fargo, 1982, p. 117.
- [29] B. Freedman, R.O. Butterfield, E.H. Pryde, Variables affecting the yields of fatty esters from transesterified vegetable oils, *J. Am. Oil Chem. Soc.* 61 (1984) 1638–1643.
- [30] S.V. Ghadge, H. Raheman, Process optimization for biodiesel production from mahua (*Madhuca indica*) oil using response surface methodology, *Bioresour. Technol.* 97 (2006) 379–384.
- [31] J.M. Encinar, J.F. Gonzalez, J.J. Rodriguez, A. Tejedor, Biodiesel fuels from vegetable oils: transesterification of *Cynara cardunculus* L. oils with ethanol, *Energy Fuels* 16 (2002) 443–450.
- [32] S.M.P. Meneghetti, M.R. Meneghetti, C.R. Wolf, E.C. Silva, G.E.S. Lima, L.L. Silva, T.M. Serra, F. Cauduro, L.G. Oliveira, Biodiesel from castor oil: a comparison of ethanolsis versus methanolysis, *Energy Fuels* 20 (2006) 2262–2265.