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Application of the simplex-centroid design with process variable in the optimization of production conditions of B100 biodiesel from sunflower oil

Gabriel Henrique Dias, Carmen Luisa Barbosa Guedes, Elisangela Tavares da Silva, Karina Gomes Angilelli, Rodolfo Lopes Coppo and Dionisio Borsato*

*Departamento de Química, Universidade Estadual de Londrina, Rodovia Celso Garcia Cid, PR-445, km 380, Cx. Postal 10011, 86057-970, Londrina, Paraná, Brazil.*Author for correspondence. E-mail: dborsato@uel.br*

ABSTRACT. A simplex-centroid design was applied to optimize conditions for obtaining B100 biodiesel from sunflower oil using different catalysts with methanol and ethanol as process variable. Sodium methoxide was indicated as the best catalyst in the transesterification reaction with methanol at a 98.30% yield. Reaction yield was optimized only to 89.65% when ethanol as process variable and KOH as catalyst were employed. Tests with the obtained products, in optimal conditions, indicated that they were within the parameters established by Brazilian legislation and by the European Union.

Keywords: transesterification, mixture design, fatty acids.

Aplicação do delineamento simplex-centroide com variável processo na otimização das condições de produção do biodiesel B100 de óleo de girassol

RESUMO. O delineamento simplex-centroide foi aplicado para otimizar as condições de obtenção de biodiesel B100 de óleo de girassol, utilizando diferentes catalisadores, com metanol e etanol como variável de processo. A reação de transesterificação, usando metanol, indicou o metóxido de sódio como o melhor catalisador com rendimento de 98,30%. Usando etanol como variável de processo e KOH como catalisador, o rendimento da reação foi de somente 89,50%. Os ensaios com os produtos obtidos, nas condições ótimas, indicaram que eles estavam de acordo com os parâmetros estabelecidos pela legislação brasileira e pela União Europeia.

Palavras-chave: transesterificação, delineamento de mistura, ácidos graxos.

Introduction

Although biodiesel yields about 10% less energy than petroleum diesel, engine performance is almost the same when power and torque are taken into account. Due to its higher viscosity, biodiesel delivers more increased lubricity than petroleum diesel, with a consequent wear reduction of the engine´s moving parts. Moreover, biodiesel has simpler molecular structures than its precursor, triglycerides, coupled to higher burning efficiency, which significantly reduces waste disposal in the engine´s internal parts (LÔBO et al., 2009).

Several researches have been performed to optimize conditions for obtaining biodiesel using methanol (RASHID et al., 2008; MORADI et al., 2013) or ethanol (ENCINAR et al., 2007; KUCEK et al., 2007) as a transesterification agent. However, as far as is currently known, there are no studies on the use of the simplex-centroid mixture design to compare process variables with mathematical algorithms to optimize conditions for obtaining biodiesel from vegetable oil.

Mixture designs are employed in various experiments for product development. In these trials, two or more ingredients or components are mixed in different proportions and characteristics of the resulting products are recorded. Responses depend only on the proportions of components in the mixture rather than on their absolute amount (CORNELL, 1990; MAIA et al., 2011).

Corroborating studies by Scheffé (CINI et al., 2013), others have been produced using mixture design. More recently, Borsato et al. (2010) presented an analysis of B100 biodiesel oxidation kinetics applying the simplex-centroid design. Maia et al. (2011) used the same design and studied the efficiency of synthetic antioxidants when added to soybean oil-derived B100 biodiesel.

In addition to the components of mixtures, some types of problems involve process variables. Factors such as pH, temperature and reactant concentrations are typical examples of process variables. Changes in variables´ levels may affect experimental results through their individual effects and interaction with other variables in the mixture, although their levels may be independently varied (BORSATO et al., 2010). Scheffé presented studies involving mixture designs with process variables (MAIA et al., 2011). Cornell (1990) combined mixtures of ingredients with process variables in food experiments, whereas Coppo et al. (2013) developed experiments involving mixture components with process variables in the study of FAME storage time. Cini et al. (2013) also applied process variable in the study of B100 biodiesel in mixture with synthetic antioxidants to assess two methods of accelerated oxidation.

Optimization methods have been applied in the chemical, thermal industry and cost-saving management (MAIA et al., 2011). Mixture design may simultaneously generate multiple responses which may impair the search for an optimal solution to obtain optimal formulations (MAIA et al., 2011). Derringer and Suich (1980) suggested a method to determine the best combination of responses with multiple restrictions. They proposed a compromise function which defines the desired intervals. This approach is considered a non-linear programming method for an optimal solution from a simultaneous combination of models with restrictions.

Current study forwards a detailed analysis of conditions to obtain biodiesel from the transesterification reaction of sunflower oil with methanol or ethanol as the process variable, while examining the influence of different types of catalysts in the reaction yield by employing mixture design.

Material and methods

Transesterification reaction

Triglycerides of refined sunflower oil (100 mL, Salada®) were transesterified with analytical grade absolute ethanol (99.3% purity, provided by F Maia) and methanol (99.8 % purity, F Maia), with an alkali catalyst at 70 and 60°C, respectively, and slow stirring.

Catalysts

Catalysts employed were analytical grade potassium hydroxide (85% purity, Vetec), sodium hydroxide (97% purity, F Maia), sodium methoxide (NaMet – 97% purity, Fluka) and sodium ethoxide (NaEt – 95% purity, Fluka). Proportions were established by mixture design and added directly into the methyl alcohol and ethyl alcohol at a concentration of 0.8 g 50 mL^{-1} alcohol.

Yield

Yield was calculated according to transesterification reaction stoichiometry, using the mass of sunflower oil and the mass of biodiesel obtained, being as a basis for calculating oleic acid.

Compliance analysis

B100 biodiesel density was determined according to ASTM D4052 (2002); flash point according to ASTM D93 (2001); acid value by ASTM D664 (2001); glycerin content, mono-, di- and triglycerides by ASTM D6584 (2003); alcohol content and esters by EN 14110 (CEN, 2003); and water content by EN 12937 (CEN, 2000).

Chromatographic analysis

A GC-17A chromatograph with a Shimadzu QP5000 mass detector was used. Data were collected by software Shimadzu CLASS-CR10 mass spectrometer operated within the 45 to 700 m/z range with 0.5s scan rate by electron impact. A fused silicon capillary column DB1 (RESTEK) – 100% polymethylsiloxane, with 30 m length x 0.25 mm internal diameter x 0.25 μm film thickness, was employed. Split injector and detector temperature were gauged at 340°C. The heating ramp was maintained initially at 50°C for 2 min. and henceforth heated at the rate of 10°C $min.^{-1}$ until 180°C, and kept at this temperature for 2 min.; it was then heated at the rate of 15°C $min.^{-1}$ until 340°C, and kept at this temperature for 10 min. Flow gas N_2 was 1.5 mL $min.^{-1}$ and the injection volume 2.0 μL, with split ratio 10.

Mixture experimental design (STATSOFT, 2009)

A simplex-centroid design for three components was used, with two replications at the central point, with 2^q-1 mixture combinations, where q is the number of independent variables whose sum is 1 or 100%.

Mathematical model for the mixture design

The function used was

$$Y(\mathrm{x}) = \sum_{1\le i\le q}^{q} \beta_i \mathrm{x}_i + \sum_{1\le i\le j\le q}^{q} \beta_{ij}\mathrm{x}_i\mathrm{x}_j + \beta_{123}\mathrm{x}_1\mathrm{x}_2\mathrm{x}_3 \qquad (1)$$

where:

Y (x) represents the response function of the experimental data;

x_1, x_2 and x_3 are independent variables and correspond to the percentage of NaOH, KOH and sodium methoxide or sodium ethoxide in the mixture, respectively;

β comprises the estimated parameters (CORNELL, 1990; STATSOFT, 2009).

Combined mathematical model

The combined model containing three components and the process variable, which represents the transesterification agent, was adjusted to the combination $(2^q - 1)x2^n$ where n is the number of process variables, in this case represented in equation (2) by z that was encoded for $z = +1$, the reaction indicating the presence of methanol; and $z = -1$, the presence of ethanol. Regression coefficients were obtained by equation $\gamma = (X'X)^{-1}X'Y$, where X is the design matrix including the process variable and Y is the responses vector.

$$Y(x,z) = \sum_{1\le i\le q} \gamma_i^{\circ} x_i + \sum_{1\le i\le q} \gamma_i^{1} x_i z + \sum_{1\le i\le j\le q} \gamma_{ij}^{\circ} x_i x_j + \sum_{1\le i\le j\le q} \gamma_{ij}^{1} x_i x_j z + \gamma_{123}^{\circ} x_1 x_2 x_3 + \gamma_{123}^{1} x_1 x_2 x_3 z \qquad (2)$$

In equation (2), γ° represents the estimated parameters for the terms without the process variable and γ^{1} represents those estimated for the terms with the process variable (CORNELL, 1990).

Results and discussion

Transesterification with methanol

The transesterification reaction was conducted with catalysts previously dissolved in methanol. Excess methanol displaced the reaction towards the formation of biodiesel. After the separation of glycerin, the biodiesel obtained was washed with acidified water and dehumidified in an oven. Reaction yield was determined.

Table 1 shows the simplex-centroid design used and the average experimental yields obtained, in triplicate, with the different catalysts with methanol as the transesterification reagent.

Table 1. Experimental design and yields with methanol.

Treatment	1	2	3	4	5	6	7
Design*	(1;0;0)	(0;1;0)	(0;0;1)	(1/2;1/2;0)	(1/2;0;1/2)	(0;1/2;1/2)	(1/3;1/3;1/3)
Yield (%)	87.93	94.86	98.30	92.00	92.88	95.26	92.50

*(%NaOH; %KOH; %NaMet)

The experimental design consisted of different proportions of the catalysts used, ranging from 0 to 100%, with sodium hydroxide represented by x_1, potassium hydroxide by x_2 and sodium methoxide by x_3. The canonical equation (3), adjusted to the experimental data, where $Y(x,+1)$, represents the reaction yield when using methanol as transesterification agent for the three components. Terms with an asterisk were significant at 5%. In addition, linear terms and the binary mixture of sodium hydroxide and potassium hydroxide had positive coefficients which indicated that they positively influenced the reaction yield.

$$Y_1 = 87.93^* x_1 + 94.86^* x_2 + 98.30^* x_3 + 2.42 x_1 x_2 - 0.94 x_1 x_3 - 5.28 x_2 x_3 - 20.82 x_1 x_2 x_3 \qquad (3)$$

Analysis of variance showed that the model and the linear terms were significant at 5% level. Further, since adjusted R^2 was 91% and lack of fit was not significant ($p = 47.99\%$), the model might be used for predictive purposes.

Tukey´s test, applied to averages at 5% level, only showed a significant difference between treatment 1 and 2, 3, 5, 6, 7; and treatment 3 and 4, 5, 7, indicating that the three catalysts used had different effects on the reaction to obtain B100 biodiesel. Moreover, according to Levene test, the hypothesis of homogeneity of variances at 5% level was accepted since p-value was 54.91% (STATSOFT, 2009).

The region between the ternary combination of the independent variables x_1, x_2 and x_3 may be observed by contours shown in Figure 1. In fact, Figure 1 shows the contour of the surface response regions for the dependent variable, reaction yield, obtained by the mathematical model when methanol is used. Figure 1 shows that the best performance was obtained by sodium methoxide as catalyst.

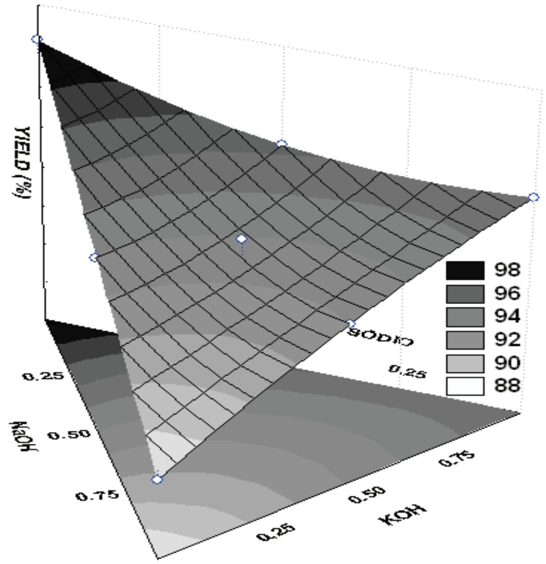

Figure 1. Combination region among variables for the reaction yield with methanol.

Figure 2 shows the optimization of reaction yield by the predictive equation. A 98.30% yield was obtained with 100% sodium methoxide.

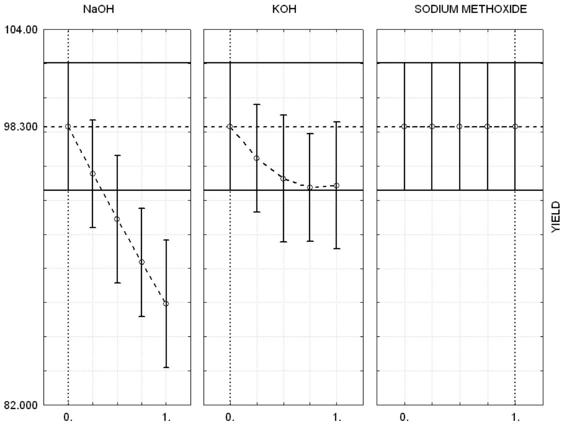

Figure 2. Optimum conditions for variables studied in the reaction with methanol.

The reaction for obtaining B100 biodiesel using the optimal conditions, in triplicate, yielded 98.42%. The *t* test showed that there was no significant difference (p = 48.30%) between this value and estimated yield (98.30%). Thereby, the predictive equation obtained was validated.

Figure 3 shows the chromatogram of B100 biodiesel obtained with optimum conditions shown in Figure 2.

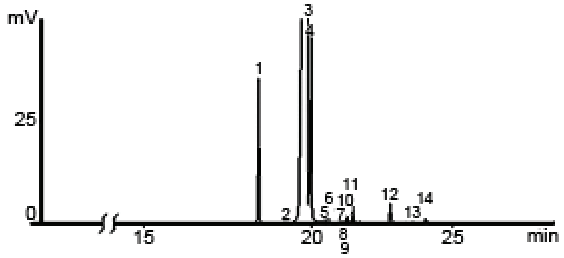

Figure 3. Chromatographic profile of the sample B100 Biodiesel obtained in optimal conditions with methanol.

The ester content in biodiesel is a parameter set out in EN 14214 (CEN, 2003); required minimum ester percentage is 96.5% mass to be determined by the chromatographic method EN ISO 14103 (LÔBO et al., 2009; CEN, 2003).

Chromatographic analysis (Figure 3) showed that biodiesel obtained under optimal conditions indicated in Figure 4 consisted mainly of palmitic acid methyl esters, methyl oleate, methyl linoleate, methyl linolenate and other methyl esters whose composition range between C16:0 and C22:0.

Peaks 1 and 2 correspond to C16 esters representing 7.71% of the biodiesel sample. Peaks 3, 4 and 5, with retention time around 20 minutes, represent a mixture of methyl oleate, methyl linoleate and methyl stearate, totalizing 89.77%. The other peaks represent higher molecular weight esters that added together 2.38%. Therefore, these esters were 99.86% of the substances present in the B100 biodiesel obtained and were therefore in accordance with the European Union specification which state that the content of free fatty acids, alcohol, glycerin and water should be minimized so that the biodiesel purity may be higher than 96.5% (KARAOSMANOGLU; BECKER, 1996). These results were consistent with the percentage distribution of fatty acids from sunflower oil, obtained by Canakci and Gerpen (2001), or rather, 8% for C16 and approximately 90% for C18.

To ensure biodiesel quality, it is necessary to establish quality standards, aiming to set levels of contaminant components limits which will not impair the quality of the burning issues, as well as the performance, safety and integrity of the motor transport and handling. Possible degradations of the product during storage should also be monitored (LÔBO et al., 2009). Table 2 shows the main parameters of the B100 biodiesel conformity limits obtained with methanol, the optimum conditions established by the predictive model.

Table 2. Analyses of samples of biodiesel B100 derived from sunflower oil with methanol.

Property	Method	Unit	Limit	Result
Specific gravity at 20°C	ASTM D4052 (ASTM, 2002)	kg m^{-3}	850-900	880.6
Flash Point	ASTM D93 (ASTM, 2001)	°C	Min. 100	165.5
Acid Number	ASTM D664 (ASTM, 2001)	mg KOH g^{-1}	Max. 0.50	0.48
Free Glycerin	ASTM D6584 (ASTM, 2003)	% m m^{-1}	Max. 0.02	0.001
Total Glycerin	ASTM D6584 (ASTM, 2003)	% m m^{-1}	Max. 0.25	0.005
Monoglyceride	ASTM D6584 (ASTM, 2003)	% m m^{-1}	0.80	0.01
Diglyceride	ASTM D6584 (ASTM, 2003)	% m m^{-1}	0.20	N.D.
Triglyceride	ASTM D6584 (ASTM, 2003)	% m m^{-1}	0.20	N.D.
Methanol	EN 14110 (CEN, 2003)	% m m^{-1}	Max. 0.20	0.07
Ester content	EN 14110 (CEN, 2003)	% m m^{-1}	Min. 96.5	99.86
Water content	EN 12937 (CEN, 2000)	mg kg^{-1}	Min. 200	absent

The flash point is the lowest temperature corrected to a barometric pressure of 101.3 kPa, at which the application of an ignition source causes the vapors of the sample to ignite under specific test conditions (BORSATO et al., 2009). In the case of biodiesel, the specification indicates that the flash point should be at least 100°C. However, flash point values are considerably higher than those found for diesel fuel which must be at least 38°C. In the case of biodiesel, flash point value is close to 170°C, but the presence of minute amounts of alcohol causes a very significant decrease in this rate (LÔBO et al., 2009).

Free and total glycerin contents were 5mg 100^{-1} g and 1 mg 100^{-1} g, respectively. Values were lower than those suggested by Brazilian law with maximum total of 0.25% glycerin (w / w) and free 0.02% (m / m) (BRASIL, 2012).

The determination of residual glycerin serves as a parameter to assess the efficiency of biodiesel purification. High glycerin concentrations in biodiesel cause storage problems because glycerin separates in storage tanks when the biodiesel is blended with petroleum diesel. Problems such as deposit formation, engine nozzle clogging and aldehyde emissions are also related to high glycerin concentration in the biodiesel (LÔBO et al., 1999). Moreover, values for density, flash point, acid value, methanol and water content were consistent with current legislation (BRASIL, 2012).

Transesterification with ethanol

Table 3 shows the simplex-centroid design used and the average experimental yields obtained in triplicate with the different catalysts previously dissolved in ethanol to excess. After separating the glycerin, the biodiesel obtained was washed with acidified water and dehumidified in an oven.

Table 3. Experimental design and yields with ethanol.

Treatment	1	2	3	4	5	6	7
Design*	(1; 0; 0)	(0; 1; 0)	(0; 0; 1)	(1/2; 1/2; 0)	(1/2; 0; 1/2)	(0; 1/2; 1/2)	(1/3; 1/3; 1/3)
Yield(%)	78.99	89.65	80.5	86.77	85.74	87.85	87.82

*(%NaOH; %KOH; %NaEt)

The experimental area consisted of different proportions of the catalysts used, ranging between 0 and 100%, where sodium hydroxide was represented by x_1, potassium hydroxide by x_2 and sodium ethoxide by x_3. The canonical equation (4), adjusted to the experimental data, Y(x,-1), represented the yield of the reaction when ethanol is used as the transesterification agent for the three components. Terms with an asterisk were significant at 5% and all the linear and binary terms showed positive coefficients, indicating that they influenced positively the reaction yield.

$$Y_2 = 78.99 * x_1 + 89.65 * x_2 + 80.5 * x_3 + 9.8 x_1 x_2 + \\ + 23.98 * x_1 x_3 + 11.10 x_2 x_3 - 5.85 x_1 x_2 x_3 \tag{4}$$

The analysis of variance showed that the model and the linear and quadratic terms were significant at 5% level. In addition, the adjusted R^2 was 94.17% and the lack of fit was not significant (p = 92.22%), which indicated that the model may be used for predictive purposes.

Tukey´s test applied to the medium only showed significant difference between treatments 1 and 2 at 5% level of significance. The above indicated that only sodium hydroxide and potassium had different yields. The other catalysts used had a similar effect in obtaining the B100 biodiesel´s reaction. Levene´s test showed that the p-value test (p = 54.26%) was higher than the 5% significance level. Consequently, the hypothesis of homogeneity of variances was not rejected (STATSOFT, 2009).

The region between the ternary combination of the independent variables x_1, x_2 and x_3 may be observed by the contours in Figure 4 which shows surface response regions for the dependent variable yield of the reaction with ethanol, obtained by the mathematical model. Figure 4 shows that better performance was obtained with only potassium hydroxide as catalyst.

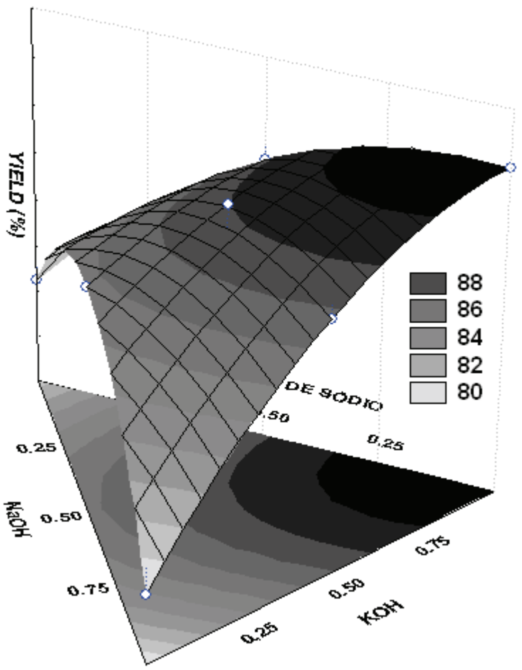

Figure 4. Combination region among variables for the reaction yield with ethanol.

The optimization of reaction yield by the predictive equation is provided in Figure 5. An 89.65% yield was obtained only when using potassium hydroxide as catalyst.

The reaction for obtaining B100 biodiesel under optimal conditions provided by the optimization had an average yield of 91.97%. Since the application of t test showed that there was no significant difference (p = 37.85) between this value and the estimated yield (89.65%), the predictive equation obtained was validated.

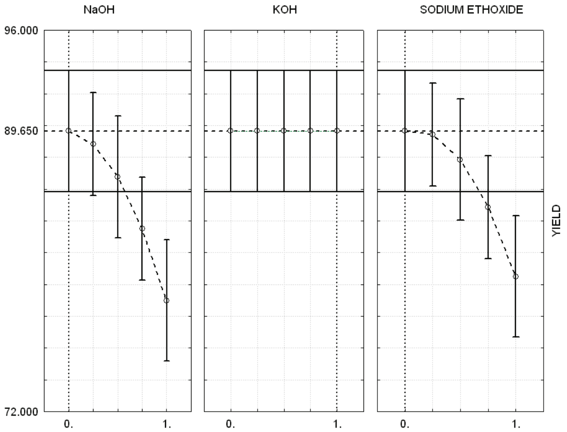

Figure 5. Optimum conditions for variables studied in the reaction with ethanol.

Figure 6 shows the chromatogram of B100 biodiesel obtained with optimum conditions shown in Figure 5.

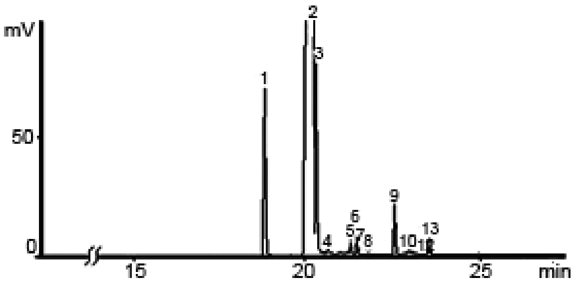

Figure 6. Chromatographic profile of the sample B100 Biodiesel obtained in optimal conditions with ethanol.

Chromatographic analysis (Figure 6) showed that biodiesel obtained under the optimum conditions shown in Figure 5 mainly consisted of palmitic acid ethyl esters, ethyl oleate, ethyl linoleate, ethyl linolenatoethyl ester and others whose composition ranged between C16: 0 and C22: 0.

The first peak corresponded to the ethyl palmitate with 12.91% of the biodiesel sample. Peaks 2, 3 and 4, with retention time around 20 minutes, respectively represent ethyloleate, ethyl octadecanoate and 9, 12-ethyl octadecanoate, totaling 79.15%. The other peaks represented molecular weight esters of higher percentage total, namely 5.27%. Therefore, these esters together comprised 97.33% of the substances present in the B100 biodiesel obtained and were therefore in accordance with the European Union specification where the content of free fatty acids, alcohol, glycerin and water should be minimized so that the biodiesel purity may be higher than 96.5% (KARAOSMANOGLU; BECKER, 1996). Table 4 shows the main conformity parameters of the B100 biodiesel obtained using ethanol, or rather, the optimum conditions established by the predictive model.

Table 4. Analyses of samples of biodiesel B100 from sunflower oil with ethanol.

Property	Method	Unit	Limit	Result
Specific gravity at 20°C	ASTM D4052 (ASTM, 2002)	kg m^{-3}	850-900	879.3
Flash Point	ASTM D93 (ASTM, 2001)	°C	Min. 100	145.5
Acid Number	ASTM D664 (ASTM, 2001)	mgKOH g^{-1}	Max. 0.50	0.42
Free Glycerin	ASTM D6584 (ASTM, 2003)	% m m^{-1}	Max. 0.02	0.0085
Total Glycerin	ASTM D6584 (ASTM, 2003)	% m m^{-1}	Max. 0.25	0.22
Monoglyceride	ASTM D6584 (ASTM, 2003)	% m m^{-1}	0.80	0.17
Diglyceride	ASTM D6584 (ASTM, 2003)	% m m^{-1}	0.20	0.07
Triglyceride	ASTM D6584 (ASTM, 2003)	% m m^{-1}	0.20	N.D.
Ethanol	EN 14110 (CEN, 2003)	% m m^{-1}	Max. 0.20	0.07
Ester content	EN 14110 (CEN, 2003)	% m m^{-1}	Min. 96.5	97.33
Water content	EN 12937 (CEN, 2000)	mg kg^{-1}	Min. 200	absent

Combined model

The polynomial model (Equation 5) was developed as proposed by Cornell (1990) who combined the components mixed with the process variable (Equation 2). They showed that it was possible to measure not only how the components of the mixture, alone or together, produced different effects on responses, but also how changes in process conditions might influence the behavior of mixtures of these components. The process variables (*z*) and mixture (*x*) are present in the formulations and the ability to study both may lead to better understanding of the system as a whole. The simplex-centroid mixture design was associated with a polynomial where the test was conducted with methanol coded for $z=+1$ and with ethanol coded for $z=-1$.

$$\begin{aligned} Y(x,z) = {} & 83.46x_1 + 4.47x_1z \\ & + 92.255x_2 + 2.605x_2z + 89.4x_3 \\ & + 8.9x_3z + 6.09x_1x_2 - 3.67x_1x_2z \\ & + 11.52x_1x_3 - 12.46x_1x_3z + 2.91x_2x_3 \\ & - 8.19x_2x_3z - 13.275x_1x_2x_3 - 7.635x_1x_2x_3z \end{aligned} \tag{5}$$

By applying *t* test for parameters containing the process variable, it was found that the linear terms and the binary mixture of NaOH and methoxide or ethoxide were significant at 5% significance level.

Comparison of the treatment with methanol and ethanol showed a significant difference when employing *t* test at the 5% level between the products produced using NaOH, KOH and sodium methoxide or ethoxide as catalysts alone. There was also a significant difference between treatments with the binary mixture NaOH and sodium methoxide or ethoxide.

Tukey´s test showed significant difference at 5% level among the treatments performed with methanol and ethanol. Further, Levene test showed that the hypothesis of homogeneity of variance could be accepted (p = 46.08%).

Equation analysis showed that the lowest yields were obtained with ethanol as transesterification agent, i.e., with $z=-1$. The lowest yield was with the transesterification reaction with methanol since ethanol promoted a greater spread of glycerin and monoesters in the biodiesel, making phase separation difficult. This represents higher industrial costs in the purification step and results in greater liabilities, with lower yield in the process. However, ethanol is less toxic, it is renewable and produces biodiesel with more lubricity and cetane number (LÔBO et al., 2009). Studies have shown that methyl esters produced from sunflower oil have better oxidation stability than ethyl esters (LIANG et al., 2006).

Applying the equation jointly to optimized values of the catalyst concentration (Figures 2 and 5) the same yield values were obtained, that is, 98.3 and 89.65%, when using methanol and ethanol, respectively. The above showed that the equation, which indicated the process variable, may be used for predictive purposes.

Conclusion

The ethylic route in biodiesel production from sunflower oil showed no significant difference between treatments. When compared to the methyl route, it proved to be inferior in reaction yield. Similar to the alcoholic route, the methyl route showed no significant difference between the different treatments both of which produced B100 biodiesel within the specifications set by Brazilian legislation and the European Union.

The simplex-centroid mixture design proved to be a suitable tool to optimize the conditions for obtaining B100 biodiesel from sunflower oil using different catalysts with methanol and ethanol as the process variable.

Acknowledgements

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