DOI: 10.5433/1679-0375.2016v37n1p107

Application of the multiresponse optimization simplex method to the biodiesel B100 obtaining process

Aplicação da otimização multirresposta através do método simplex no processo de obtenção do biodiesel B100

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Abstract

The process of obtaining B100 biodiesel from vegetable oil and animal fat mixtures by transesterification under basic conditions was optimized using the super-modified simplex method. For simultaneous optimization, yield, cost, oxidative stability and Cold Filter Plugging Point (CFPP), were used as responses, and the limits were established according to the experimental data and the conformity parameters established by legislations. Based on the predictive equations obtained from the simplex-centroid design-coupled functions, the multi-response optimization showed an optimal formulation containing 38.84 % soybean oil, 21.90 % beef tallow and 39.25 % poultry fat, resulting in reaction yield of 94.94 %, 8.99 h for oxidative stability at 110 °C, 2.83 °C of CFPP and cost US$ 864.60. The validation showed that there are no significant differences between the predicted and experimental values. The simplex-centroid mixture design and simplex optimization methods were effective tools in obtaining biodiesel B100, using a mixture of different raw materials.

Keywords: Cold Filter Plugging Point. Desirability Functions. Oxidation Stability. Multi-response Optimization.

Resumo

O processo de obtenção de biodiesel B100, a partir da transesterificação em meio básico, de uma mistura de óleo vegetal e gordura animal foi otimizado utilizando o método simplex supermodificado. Para otimização simultânea foram usados como respostas o rendimento, custo, estabilidade oxidativa e ponto de entupimento de filtro a frio (CFPP), e os limites foram estabelecidos de acordo com os dados experimentais e os parâmetros de conformidade estabelecidos pela legislação. A otimização multirresposta utilizando as equações preditivas, obtidas a partir do delineamento simplex-centroide acopladas às funções de desejabilidade, apresentou uma formulação ótima contendo 38,84% de óleo de soja, 21,90 % de sebo bovino e 39,25 % de gordura de ave com rendimento de 94,94 %, estabilidade oxidativa a 110 ºC de 8,99 horas, CFPP de 2,83 ºC e custo de US$ 864,60. A validação mostrou não haver diferença significativa entre os valores preditos e os valores experimentais. O delineamento de mistura e a otimização simplex-centroide se mostraram metodologias eficazes na obtenção de biodiesel B100, usando uma mistura de diferentes matérias-primas.

Palavras-chave: Ponto de Entupimento de Filtro a Frio. Funções de Desejabilidade. Estabilidade Oxidativa. Otimização multirresposta.

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Introduction

The processes in biodiesel production and the raw materials used depend on the region, and the possibilities of employment generation as well as social, economic and environmental differences, which generate distinct regional motivations for its production and consumption, should be taken into account (BALAT, 2011; ORIVES et al., 2014). The use of vegetable oils, such as soybean oil, can harm the food and chemical sectors due to the large demand required by the biodiesel industry. For this reason, various raw materials, including any available vegetable oil, used frying oils, animal fats such as beef tallow, pork and chicken fat, among others, have been widely studied (DABDOUB, BRONZEL; RAMPIN, 2009; CUNHA et al., 2013). The high availability on and low price of animal fat are getting attention from industry, as its use in conjunction with soybean oil for biodiesel production can decrease the production costs, although it can cause problems in the product (ORIVES et al., 2014; BORSATO et al., 2010b). The recent use of tallow in biodiesel production is a new environmentally friendly application. It contributes to problems of waste management because the extra fats that are not used by the soap industry, when they are overwhelmed, end up being incinerated or disposed in landfills (MATA et al., 2011; GHAZAVI; FALLAHIPANAH; JESHVAGHANI, 2013). Brazil is the third largest producer of poultry meat, and most of the fat obtained is used either in the cosmetic industry or in animal feed production. However, about 500,000 tons of poultry fat are usually rejected (CENTENARO, FURLAN; SOUZA-SOARES, 2008; RAMALHO et al., 2011).

It is of paramount importance that the raw material chosen is of good quality and it does not compromise the final product. The use of poor-quality biodiesel in engines can cause damage to pumps and any system that comes in contact with the fuel (PAULA et al., 2011). There is great concern for the characterization and quality of biofuel, because it must conform to specifications determined by the Brazilian National Petroleum Agency in order to be a marketable product in the country (PAULA et al., 2011; GALVAN et al., 2013).

Among these requirements is the cold filter plugging point (CFPP), which is important when the fuel runs at low temperatures, as this directly influences the operation of the engine (CUNHA et al., 2009). Another parameter of great importance for quality control is the oxidative stability of biodiesel. This parameter is expressed by the induction period (IP), that is, the oxidation resistance of the sample (GALVAN et al., 2014). These specifications are directly related to the chemical structures present in the feedstock; saturated chains exhibit a greater stability during auto-oxidation and, in contrast, unsaturated chains have a lower tendency to solidify at lower temperatures (DABDOUB, BRONZEL; RAMPIN, 2009; GALVAN et al., 2014).

Experimental designs have been employed when modelling the systems to be optimized, especially when there is a lack of knowledge about the behaviour of the variables involved and, moreover, when the systems are seen as a technology to achieve quality excellence of a product.

Among the various designs (MARCHI et al., 2010), highlights the mixtures, where two or more components are mixed in various proportions and the characteristics of the resulting products are registered. The responses are independent of the physical states, depending only on the proportions of the ingredients in the mixtures (BREITKREITZ; JARDIM; BRUNS, 2009; CINI et al., 2013). Recently, the mathematical-model application, new numerical algorithms for solving optimization problems, use of statistical methods and easy access to computers have enabled the rapid development of new products with cost minimisation and quality improvement (BORSATO et al., 2010b).

One proposal, known as the simplex method, was presented by Spendley, Himsworth e Hext (1962). Simplex is a regular figure moving on a surface to prevent unsatisfactory response regions.

In the *n*-dimensional simplex, there is a polyhedron with flat faces having $n + 1$ vertices, where n is the number of independent variables (continuous or discrete). The method is a recursive procedure, which tends to lead the simplex to a great value through reflection of specific points. Once in the vicinity of the optimum value, the simplex can undergo contraction in order to determine a more precise position (GAO; HAN, 2012; BREA et al., 2013). The simplex is easy to implement in automated processes. Its application is relatively easy and fast, and allows, with a good safety margin, the location of the optimal region, despite not being able to provide clear information regarding the behaviour of variables (CARNEIRO et al., 2005; GAO; HAN, 2012; KONSTANTINIDIS et al., 2012). According to Carneiro et al. (2005), simplex optimization is an automatable procedure for sequential experimental design. Once the parameters for the initial condition have been established, the algorithm suggests new experimental sequences. Thus, all experiments can automatically be oriented towards the optimum point. This study aimed to optimise, using the simplex method with constraints, B100 biodiesel production using a ternary mixture of soybean oil, poultry fat and beef tallow.

Material and methods

Biodiesel

The following were used as the raw materials: beef tallow (Frigorífico Frambov: Rolândia, Paraná, Brazil), poultry fat (Big Frango: Rolândia, Paraná, Brazil) and non-transgenic soybean oil that was free of antioxidants (Cooperativa Imcopa: Cambé, Paraná, Brazil). The transesterification reaction was carried out following the methyl route, using sodium methoxide (95 %, Sigma–Aldrich, USA) as the catalyst and methanol (PA grade: 99.8%, Fmaia, Brazil); the proportions of raw materials were established by mixture design. The mixtures were subjected to slow agitation while heating under reflux at 60 °C for 2 h (Borsato et al., 2010a). Then, the biodiesel was separated from glycerol by decantation, washed with a solution of acetic acid (0.01 mol L^{-1}) until a neutral pH was achieved and then dehumidified with anhydrous sodium sulfate (PA grade: 99 %, Anidrol, Brazil).

Yield

The percentage yield was determined according to the stoichiometry of the transesterification reaction, taking into account the total mass and the mass of biodiesel obtained from the raw materials, based on the calculation of the molar mass of oleic acid.

Oxidative Stability

Samples were subjected to accelerated heating according to EN 14112, using Rancimat equipment Model: 873 (Metrohm, Switzerland) according to EN 14214.

Cold Filter Plugging Point

The CFPP analyses were performed by the company CHRONION Chemical Analysis and Trade Ltd. (Quatro Barras, Paraná, Brazil) using the method NBR 14747 and by following ANP specification No. 14 (from march 11th, 2012).

Chromatographic Analysis

A gas chromatograph (model GC-17A) was used with a flame-ionisation detector (Shimadzu, Japan) and a DB1 column (J & W Scientific, UK) with 100% polydimethylsiloxane and 30 m length x 0.25 mm internal diameter x 0.25 μm film thickness. Data were collected through Shimadzu CLASS-CR10 software.

Conformity Analysis

Analyses of the acidity value of the feedstock were performed according to NBR 14448. Biodiesel compliance analyses were carried out according to ASTM D93 for the flash point, ASTM D664 for the acidity value, EN14111 for the iodine value, ASTM D4052 for the specific mass and ASTM D6584 for the free and total glycerin content, mono-, di- and triglycerides. The alcohol content was obtained by EN 14110 and ester content by EN 14103.

Experimental Design

The simplex-centroid design was applied, with three replications at the central point, and with $2^q - 1$ mixtures that are combinations of q number of components that equal 1 or 100 % (HILL & LEWICKI, 2006).

Simplex Optimization

The application was developed in a Microsoft Excel spreadsheet according to the method proposed by Bona et al. (2000).

Mathematical Model

The function used was as follows:

$$Y_n(x) = \sum_{1\le i\le q}^{q} \beta_i\, x_i + \sum_{1\le i\le j\le q}^{q} \beta_{ij}x_ix_j + \beta_{123}x_1x_2x_3 \qquad (1)$$

in which Y_n is the response function of the experimental data (yield, cost, IP and CFPP); x_1, x_2 and x_3 are the independent variables that correspond to the percentage of soybean oil, beef tallow and poultry fat used, respectively, and β is the estimated parameter (STATISTICA, 2009).

Optimization

The search was performed using an optimal multi-response computer program that combined equation 1 with the method of super-modified simplex optimization coupled with the Derringer desirability functions developed by Derringer and Suich (1980). These functions involve the transformation of each dependent variable at a value of desirability d_n, where $0 \le d_n \le 1$. The normalisation of the responses follows the expression:

$$d_n = \left(\frac{Y-a}{b-a}\right)^s \qquad (2)$$

$d_n = 0$ for $Y_n \le a$ (lower limit)

$0 < d_n < 1$ for $a < Y_n < b$

$d_n = 1$ for $Y_n \ge b$ (upper limit)

On maximising, a is the lower limit and b is the upper limit, whereas, on minimising, these limits were reversed, which represents a complement $(1 - d_i)$. The exponent s is related to the degree of importance of the variable subjective weight parameter, which is specified by the user. The function of the convenience-combined response is defined as the geometric mean of the individual functions:

$$D = (d_1 . d_2 \ldots\ldots d_n)^{\frac{1}{n}} \qquad (3)$$

A null value for d_n indicates that the contribution of D is zero, representing an unsatisfactory answer. On the other hand, if the value of the function is the maximum convenience ($D = 1$), the overall contribution is achieved, which allows further optimization.

Statistical Analysis

The regression coefficients and analysis of variance were calculated using Statistica software v.9.0 (Statistica, 2009).

Results and Discussion

In order to evaluate the oxidative stability, B100 biodiesel was subjected to accelerated oxidation testing at 110 °C (EN 14112).

The simplex-centroid mixture design, consisting of seven tests with three repetitions at the central point, to evaluate the error variance (Table 1). The mixture experimental design was applied to assess the effect of soybean oil (x_1), beef tallow (x_2) and poultry fat (x_3) in the B100 biodiesel that was produced. The responses for the yield, IP, clogging point and cost, for all tests, are presented in Table 1.

Table 1. Yield, oxidative stability, CFPP and cost values obtained by simplex-centroid mixture design

Assay	Mixture *	Responses			
		Yield (%) $_{w/w}$	P. I. (h)	CFPP (ºC)	Cost (US$)
1	$(1;0;0)$	98.85	3.76	-5	1,036.04
2	$(0;1;0)$	95.01	9.57	16	495.50
3	$(0;0;1)$	91.96	9.77	0	900.90
4	$(\frac{1}{2};\frac{1}{2};0)$	97.62	8.19	7	765.77
5	$(\frac{1}{2};0;\frac{1}{2})$	93.32	7.92	-2	968.47
6	$(0;\frac{1}{2};\frac{1}{2})$	94.39	12.92	10	698.20
7	$(\frac{1}{3};\frac{1}{3};\frac{1}{3})$	95.80	10.04	5	810.81
7	$(\frac{1}{3};\frac{1}{3};\frac{1}{3})$	95.67	9.27	6	810.81
7	$(\frac{1}{3};\frac{1}{3};\frac{1}{3})$	95.22	10.07	5	810.81
7	$(\frac{1}{3};\frac{1}{3};\frac{1}{3})$	95.63	9.35	5	810.81

* Proportion of soybean oil, beef tallow and poultry fat.

Source: author

The biodiesel obtained using 100% poultry fat presented the lowest yield (91.96 % $_{w/w}$) and that obtained with only soybean oil had highest yield (98.85 % $_{w/w}$), whereas the biodiesel obtained with beef tallow showed an intermediate value of 95.01 % $_{w/w}$. However, the raw material with the highest yield had the highest associated cost and lowest IP and CFPP values.

The specification established by the test method EN 14112 indicates that the oxidative stability at 110 °C must be maintained for at least 6 h. According to Table 1, for this temperature, only the B100 biodiesel produced from soybean oil showed a lower stability than the minimum IP (BRAZIL, 2012).

As expected, biodiesel with 100% soybean oil showed the lowest value for CFPP (–5 °C), due to the high degree of unsaturation, whereas the biodiesel made with 100% beef tallow resulted in a higher value (16 °C) and 100% poultry fat, with the intermediate degree of saturation, has a CFPP of 0 °C. The binary and ternary mixtures were effective in reducing this parameter, especially when the product was obtained in the presence of soybean oil, thus proving the dependence of CFPP on the properties comprising the esters of biodiesel (KNOTHE, 2005; IMAHARA; MINAMI; SAKA, 2006).

Typically, raw materials with higher amounts of saturated fatty acids have lower costs, as in the case of beef tallow (US$ 495.50 ton^{-1}), whereas vegetable oils such as soybean have a higher cost (US$ 1,036.03 ton^{-1}). Poultry fat has an intermediate cost value (US$ 900.90 ton^{-1}), compared to soybean oil and beef tallow.

Employing a single constituent in the production of biodiesel may cause problems in the final product. As soybean oil is more susceptible to oxidation, owing to the abundance of unsaturated fatty in its composition, it has better physicochemical properties at low temperatures, whereas, in beef tallow, predominantly saturated fatty acids occur, giving it greater stability oxidation and lower performance at low temperatures (YANG et al., 2013).

Given the distinct characteristics of each raw material, the use of mixture designs becomes critical in optimising the conditions for obtaining B100 biodiesel, because through them we can see the interactions between the components and we can see if there is an optimal formulation in which the desirable characteristics of each individual subject are maintained and the harmful ones are reduced.

By simplex-centroid mixture design, models containing only significant terms at 5%, represented by equations (4)–(7), were obtained for the yield of the reaction (Y_1), oxidative stability at 110 °C (Y_2), CFPP (Y_3) and cost (Y_4). The coefficients of determination (R^2) ranged from ($0.94 \leq p \leq 1.00$) and the adjusted coefficients (R^2) for the equations ranged from ($0.92 \leq p \leq 1.00$) (STATISTICA, 2009).

$$Y_1 = 98.7867x_1 + 94.9447x_2 + 91.8937x_3 + 4.0736x_1x_2 - 7.0204x_1x_3 + 4.9356x_2x_3 \tag{4}$$

$$Y_2 = 4.6032x_1 + 10.0447x_2 + 10.0967x_3 + 12{,}0643x_2x_3 \tag{5}$$

$$Y_3 = -4.8344x_1 + 16.0015x_2 + 0.1657x_3 + 5.6412x_1x_2 + 7.6412x_2x_3 \tag{6}$$

$$Y_4 = 1{,}036.03x_1 + 495.50x_2 + 900.90x_3 \tag{7}$$

The quality of the fitted equations was proven by analysis of variance measurement, which indicated statistically significant models at 5 % ($1x10^{-6} \leq p \leq 9x10^{-4}$), with the lack of fit not significant ($0.11 \leq p \leq 0.74$) at the same level of variation. Therefore, the coefficients for the determination were higher than 0.90, with no significant deviation from the regression at 5 %, and significant mathematical models that can be used for predictive purposes.

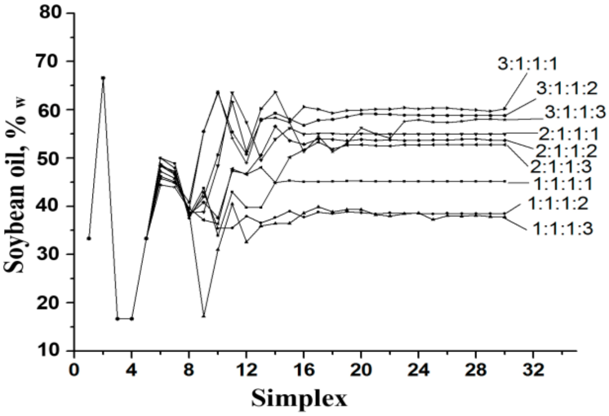
In simultaneous optimization, the limits used for the yield ($92\ \%_{w/w} \leq Y_1 \leq 100\ \%_{w/w}$) and the cost (US\$ $698.20 \leq Y_4 \leq$ US\$ 1,036.03) were estimated from experimental data (Table 1); for oxidative stability (6 h $\leq Y_2 \leq$ 12 h) and CFPP (–5 °C $\leq Y_3 \leq$ 5 °C), the limits were established from the conformities of parameters established by ANP (Brazil, 2012). These limits were coded to values between 0 and 1 [Eq. (2)] to standardise the responses.

The four equations were optimized simultaneously using the super-modified simplex method coupled to the functions of Derringer and Suich (1980). Maximum and minimum values of the restrictions for the answers can be applied when seeking a formulation in which the answers have limits established by standards. Therefore, the need for multi-response optimization, as in this case, is due to the legislation establishing compliance parameters for B100 biodiesel. Thus, for the oxidative stability at 110 °C, there is a minimum of 6 h, so equation 5 must be maximised and for CFPP and equation 6 must be minimised to a limit of 5 °C. In addition, the reaction yield was maximised and the costs were minimised.

The importance degree was defined as *s*=1 for oxidative stability at 110 ºC and the CFPP, because they have been established by legislation, and the values of importance range from 1 to 3 for the yield and the cost, respectively (Eq. 2).

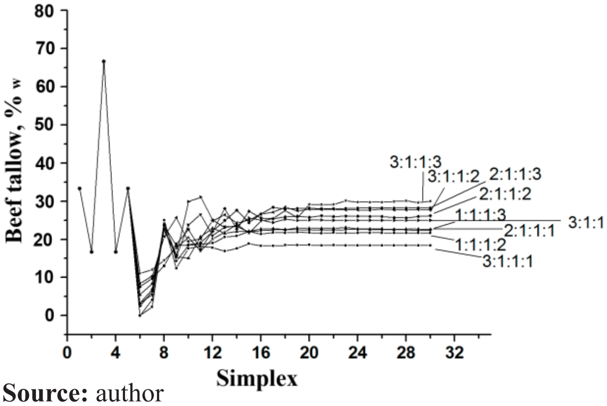
Figures 1, 2 and 3 show, for different importance degrees, the convergence and stability of the mixture variables corresponding to the contents of soybean oil, beef tallow and poultry fat.

Figure 1. Stabilization of the percentage values of soybean oil during the application of the simplex method.



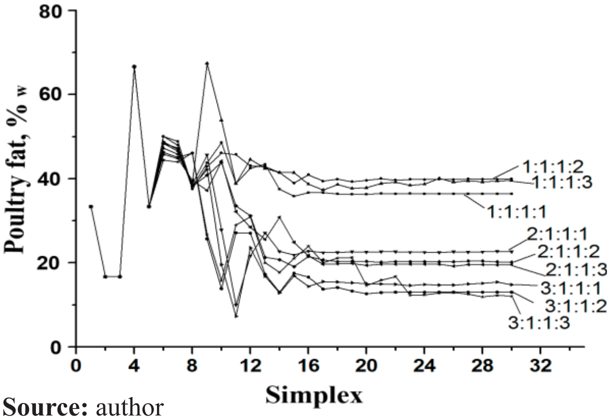
Source: author

Figure 2. Stabilization of the percentage values of beef tallow during the application of the simplex method.



Source: author

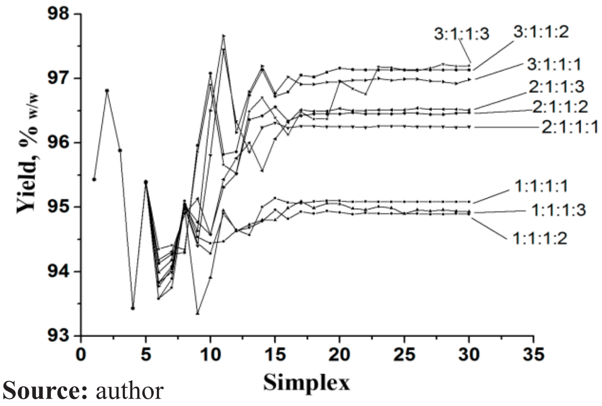
Figure 3. Stabilization of the percentage values of poultry fat during the application of the simplex method.



Source: author

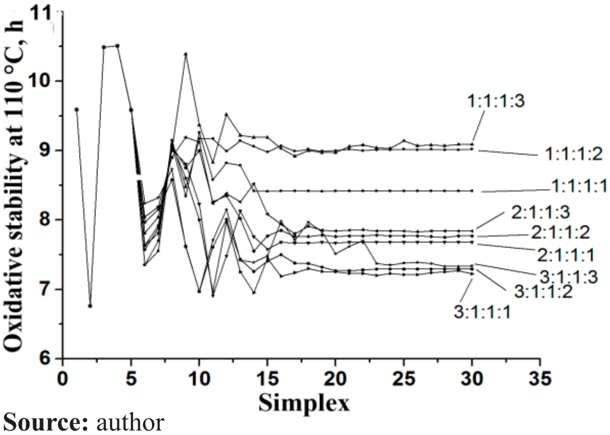
Figures 4, 5, 6 and 7 show the behaviour of responses used in the joint optimization, the reaction yield, the oxidative stability at 110 ºC, the CFPP and associated costs, each having its respective degree of importance.

Figure 4. Stabilization of the yield values during the application of the simplex method.



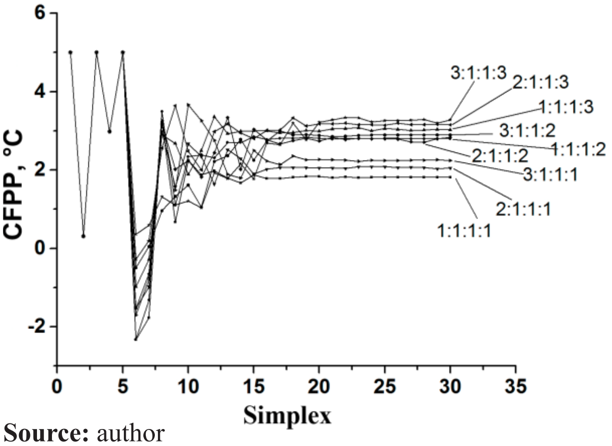
Source: author

Figure 5. Stabilization of the oxidative stability values during the application of the simplex method.



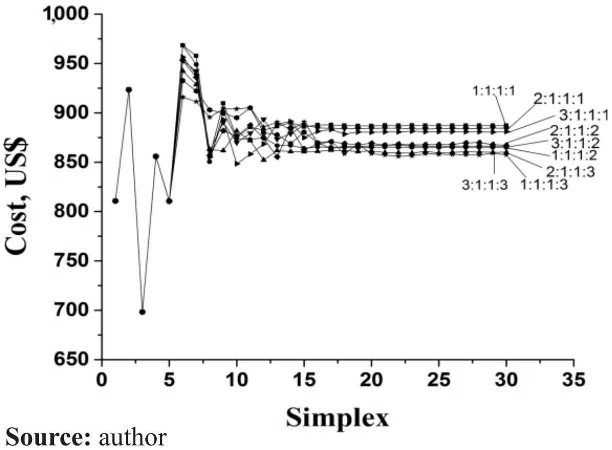
Source: author

Figure 6. Stabilization of the CFPP values during the application of the simplex method.



Source: author

Figure 7. Stabilization of the cost values during the application of the simplex method.



Source: author

The presented conditions for the third simplex resulted in a yield of 95.88 % $_{w/w}$ (Figure 4), oxidative stability after 10.49 h (Figure 5), a CFPP of 11.36 ºC (Figure 6) and a cost of US$ 653.18 (Figure 7). This lower cost does not indicate the best conditions, because the value of the point of clogging was very high, exceeding the maximum value of 5 ºC set as a constraint. In simultaneous optimizations, when the value is found to be outside the restrictions conditions, it is replaced by the minimum or maximum value established. Therefore, the conditions presented in Figures 4–7 for this simplex, were not chosen, because the biodiesel thus obtained would not meet the standards of marketing. The convergence criteria used were achieved when the response ceased to grow less than 10^{-3}, three consecutive times, for each condition-established importance degree.

Table 2 shows the ratio of components, which was considered by the simplex convergence criterion as well as the estimated models, by different importance degrees to the yield and cost responses. Among the trials with an importance value of 1 for the yield and by varying the importance of the cost, it was found that the 1:2 test showed no significant differences between the yield values, but it did show the lowest cost. Using the same criteria, testing for 2:2 and 3:1 were chosen.

Table 2. Relative importance, proportion and responses obtained by simplex when used as convergence criteria.

R. I.*	Components proportions			Responses			
Y_4	Soybean oil $x_{1\,w}$	Beef tallow $x_{2\,w}$	Poultry fat $x_{3\,w}$	Yield (%) $_{w/w}$	I.P. (h)	CFPP (ºC)	Cost (US$)
1	0.4463	0.1908	0.3630	94.96	8.56	1.93	884.35
2	0.3884	0.2190	0.3925	94.94	8.99	2.83	864.60
3	0.3568	0.1877	0.4554	94.48	9.16	2.39	873.01
1	0.5550	0.1731	0.2719	95.81	7.61	1.03	905.72
2	0.4734	0.2247	0.3019	95.61	8.30	2.47	873.79
3	0.5966	0.2905	0.2143	95.69	8.15	2.26	878.72
1	0.6036	0.2089	0.1875	96.60	7.24	1.47	897.78
2	0.5974	0.1952	0.2074	96.41	7.29	1.24	902.49
3	0.5966	0.1881	0.2153	96.00	7.54	1.17	903.14

* Relative importance
Source: author

Table 3 presents the validation of assays in triplicate 1:2, 2:2 and 3:1, and the values obtained by statistical tests used to compare the averages. The Tukey test showed no significant differences between the mean values of the responses used in the validation of the optimized values for the three cases highlighted. Furthermore, the Levenes test, applied to all cases presented in Table 3, proved to be insignificant, indicating that the assumption of homogeneity of variance can be accepted.

Table 3. Values from the statistical testing used to compare the means of the chosen tests.

R.I.	Y_1^{a} (%)$_{w/w}$	Y_1^{b} (%)$_{w/w}$	Y_2^{a} (h)	Y_2^{b} (h)	Y_3^{a} (°C)	Y_3^{b} (°C)	Y_4^{a} (US$)	Y_4^{b} (US$)
1:2	$(0.42)^{c}$	95.33	$(0.37)^{c}$	8.2	$(0.42)^{c}$	3.5	864.59	864.59
	94.94	97.22	8.99	10.79	2.83	3.0		
	$(0.77)^{d}$	93.38	$(0.21)^{d}$	11.29	$(0.62)^{d}$	2.5		
Media		95.31						
2:2	$(0.19)^{c}$	97.65	$(0.31)^{c}$	7.81	$(0.18)^{c}$	2.0	869.14	869.14
	96.45	97.44	7.76	6.9	2.74	4.0		
	$(0.12)^{d}$	99.59	$(0.30)^{d}$	7.5	$(0.92)^{d}$	2.0		
Media		96.45						
3:1	$(0.35)^{c}$	97.7	$(0.39)^{c}$	6.97	$(0.18)^{c}$	4.0	880.31	880.31
	96.95	98.42	7.25	7.86	2.27	2.0		
Media	$(0.36)^{d}$	99.13	$(0.19)^{d}$	8.45	$(0.61)^{d}$	2.0		

^{a} Theorical value; ^{b} Pratical value; ^{c} *p* for Levene's test; ^{d} *p* for *t* test

Source: author

For the three assays, the *t*-test showed no significant differences between the estimated optimal values or the average of the experimental values, because the statistical *p*-values ranged from $0.12 \leq p \leq 0.92$. As the three trials showed average values without significant differences, the 1:2 test with the lowest cost was chosen for the test of conformity.

Table 4 lists the main parameters of conformity in the biodiesels, and each sample had values in accordance with the current legislation.

Table 4. Conformity parameters of the optimized biodiesel.

Characteristics	Method	Units	Limit	Result
Specific mass at 20 °C	ASTM D4052	Kg m^{-3}	850–900	868
Flash point *	ASTM D93	°C	Min. 100	147
Acidity value	ASTM D664	$mg_{KOH}\ g^{-1}$	Max. 0.50	0.45
Iodine value	EN 14111	$g_{I_2} 100g^{-1}$	Note	45.60
Oxidative stability at 110 °C	EN 14112	h	Min. 6	10.79
CFPP **	NBR 14747	°C	Max. 5–14	3
Free glycerine	ASTM D6584	% w	Max. 0.02	0.005
Total glycerine	ASTM D6584	% w	Max. 0.25	0.09
Monoglycerides	ASTM D6584	% w	0.8	0.41
Diglycerides	ASTM D6584	% w	0.2	0.18
Triglycerides	ASTM D6584	% w	0.2	0.07
Methanol	EN 14110	% w	Max. 0.20	*ND*
Total Esters	EN 14103	% w	Min. 96.5	97.4

*When flash point is higher than 130 ºC, it is not needed to analyse the methanol content.

** Depends on the season.

ND: Not detected.

Source: author

Chromatographic analysis of biodiesel obtained under optimum conditions by simplex showed that it was composed mainly of methyl esters ranging from C_8 to C_{24}. These esters account for 97.40 $\%_w$ of substances present in the B100 biodiesel and, therefore, it was not in accordance with the specification of the European Union. Moreover, the levels of mono-, di- and triglycerides totalled 0.66 $\%_w$, and the content of free glycerol was 0.005 $\%_w$, that is, it is lower than that established by Brazilian law, which provides a maximum free glycerin content of 0.02 $\%_w$. The biodiesel also presented a flash point of 147 °C, a density at 20 °C of 868 kg m^{-3}, an acidity value of 0.45 g mg^{-1}_{KOH} and oxidative stability for 10.79 h, which meets with the Resolution ANP. The maximum CFPP depends on the unity of the federation and the month that it is marketed, ranging from 5 ºC for the coldest and 14 ºC for warmest, according to the table set out in that resolution months.

Conclusions

The simplex-centroid mixture design and simplex optimization methods were effective tools in obtaining biodiesel B100, using a mixture of different raw materials. The validation of the results of three chosen tests showed no significant differences between the estimated values and the average of the results obtained experimentally. Multi-response optimization with constraints, applying relative importance, allowed us to formulate a biodiesel within compliance parameters established by ANP 2012 and EN 14112, without the need for additives, and to reduce the final cost of the product. The simplex optimization multi-response application developed herein was proven to be friendly and portable, and it can be used for various systems and process optimizations.

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Recebido em 4 Maio 2015- Received on May 4, 2015.
Aceito em 8 Junho, 2015 - Accepted on June 8, 2015.