APPLICATION OF FACTORIAL PLANNING AND RESPONSE SURFACE METHODOLOGY IN THE PRODUCTION OF BIODIESEL FROM COTTONSEED OIL (*Gossipium hisutum* L.)

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ABSTRACT

In this work the synthesis of biodiesel from cottonseed oil (*Gossipium hisutum* L.) via the methyl route was carried out using a homogeneous commercial catalyst, Na-Methylat[®]. By means of a 2³ experimental planning methodology, it was possible to assess the influence of some parameters in the process, such as oil/alcohol molar ratio, % of catalyst and temperature. The best operation conditions that must be used in actual processes, typically a 1:8 oil/alcohol molar ratio, 40 °C and 1% of catalyst, were determined by gas chromatography, reaching 96.79 % in conversion, therefore above the level established by European regulations (96.50 %). The analysis of regression showed that the only significant effect, at a confidence level of 95 %, was the changeable temperature. The biodiesel samples were analyzed by infra-red spectroscopy, identifying strong methyl ester bands that correspond to the C=O axial deformation. Physicochemical analysis indicated conformity with the specifications of Brazilian Agency of Petroleum, Gas and Biofuels, which, together with the thermal and rheological analyses, demonstrated that the biodiesel produced from cottonseed oil can be used as an advantageous alternative in substitution of diesel.

KEYWORDS

biodiesel; factorial planning; surface response; commercial catalyst; Na-methylat[®]

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1. INTRODUCTION

The serious worldwide energy crisis of the 1970s, caused by the reduced supply and sharp increase in oil prices, led the main industrial countries to invest in alternative fuels (Knothe et al., 2005). This crisis showed the need for alternative energy sources and, since then, studies aimed at decreasing dependence on oil and its derivatives, or actually substituting it entirely, have been conducted throughout the world, given that this energy source is becoming increasingly scarce and in danger of running out in the future.

During the crisis, developing countries such as Brazil were severely affected. The Brazilian government tried to diminish its impacts by implementing the National Program of Alcohol, PROALCOOL (Pousa et al., 2007), but this program was not sufficient, given that large vehicles, such as those used in public transport and for heavy loads, as well as industrial machines, run on diesel fuel. In a new departure, in the early 1980s vegetable oils were proposed as a renewable alternative to compete with fossil diesel fuel, but difficulties were encountered due to their high viscosity and low ignition power (Agarwal et al., 2008).

In addition, besides the growing demand for energy, it is important to consider the environmental question. The impacts caused by the emissions of pollutants have increased with time, inflicting serious damage on the environment. The marked environmental imbalance caused by the emission of carbon and its oxide derivatives is related to global warming. This has led to the emergence of biodiesel, a very promising renewable energy source derived from vegetable oils and animal fats. This fuel may partially or totally substitute fossil diesel, given its similar physicochemical characteristics and ecological correctness.

The motivation to produce biodiesel and to conduct research in this area or on any other renewable energy source is that it is always associated with the concept of sustainable development, producing clean, renewable, responsible energy with social, economic and environmental benefits. In the semiarid region of Northeastern Brazil, millions of underprivileged families could benefit from incentive programs to produce seeds with oleaginous potential. The

purpose of this study was to produce biodiesel via the methyl route using cottonseed oil and a commercial catalyst (Na-Methylat[®]). The study was conducted with the Statistica[®] 7.0 software, an extremely important tool to investigate the optimization of the transesterification process, using factorial planning and response surface analysis.

2. MATERIALS AND METHODS

2.1 Raw material

The semi-refined cottonseed oil used in the transesterification reaction was supplied by Agrovigna Import and Export Ltda. (Brazil), Rancharia (SP, Brazil) and by Icofort Agroindustrial Ltda. (Juazeiro, BA, Brazil).

The characterization of oil and biodiesel was performed using physicochemical techniques recommended by ANP (Brazilian Agency of Petroleum, Gas and Biofuels) and by DGF standard method (DGF-Einheitsmethoden, 2002; Moretto and Alves, 1986). Gas chromatography analyses were also carried out to identify the components present in the oil and their corresponding amounts. The column used was a DB-5HT model, with helium as carrier gas at a flow rate of 3 mL·min⁻¹; the volume of sample injected was 1 µL and the MS detector temperature was 250 °C.

2.2 Experimental apparatus

The experimental apparatus used consists of a 3-spouted 1-L jacketed Pyrex glass reactor equipped with a temperature gauge and a 45-cm spiral condenser, coupled to a mechanical agitator adapted from a FB 13 Somar drill press, controlled by a CFW 08 WEG frequency inverter, where agitation was maintained at 300 rpm, and a TE-184 TECNAL water bath.

2.3 Operational procedure

The methyl route was implemented and the operational conditions adopted were based on literature studies with different oils, including cottonseed (Ferella et al., 2010; Patil and Deng, 2009; Souza et al., 2007). For the transesterification reaction, the amount of oil was fixed at 100 grams, while the amount of methanol and catalyst (Na-methylat[®]) followed experimental

planning values, according to the study interval of the variables. The oil was placed in the reactor under agitation until the main operation condition of the system was stabilized (desired temperature). Once the temperature of interest was reached, the other reagents were introduced and the reaction time was recorded (fixed at 60 minutes). After the reaction time, the biphasic mixture was transferred to a separation funnel and each phase was collected.

The biodiesel was then submitted to a purification process whereby methyl esters were washed out with hot distilled water (80 °C) to extract any remaining oil and catalyst residues. After each washing, the water with impurities, as well as any soaps that might be formed, were separated by decantation and then discarded. The washing stage was stopped when the pH of the washing water was neutral. Then, the drying process was carried out in a stove at 100 °C for 20 minutes.

2.4 Experimental planning

An experimental planning methodology was conducted considering three factors and two levels with triplicate at the central point, to obtain a maximum of useful information about the best

conversion rates. The following operation variables were analyzed: temperature of the reaction system, amount of catalyst and oil/alcohol molar ratio. The intervals for all variables are presented in Table 1, and the experimental matrix of the factorial planning is shown in Table 2.

2.5 Thermal study

Thermogravimetry and Derivative Thermogravimetry (TG/DTG) were used to determine the thermal stability of biodiesel. Differential Scanning Calorimetry (DSC) was used with the purpose of evaluating the enthalpy transitions of biodiesel. The thermogravimetric curves were obtained using a Shimadzu DTG 60 thermal analyzer in a synthetic air atmosphere, with a flow rate of 50 mL·min⁻¹, at a heating rate of 10 °C·min⁻¹. A 10-mg sample was accommodated in an aluminum crucible and the temperature was set to 700 °C.

The calorimetric curves were obtained using a TA DSC 2920 thermal analyzer in a synthetic air atmosphere, also with a flow rate of 50 mL·min⁻¹ and a heating rate of 10 °C·min⁻¹. In these assays, 6-mg samples were accommodated in an aluminum crucible and the temperature was set to 500 °C.

Table 1. Operation conditions and study intervals of the variables.

Variable	Range	Central Point
Oil/Alcohol molar ratio [O/A MR]	1:6 – 1:8	1:7
Temperature [T] (°C)	40 – 60	50
Catalyst amount (% cat)	0.5 – 1.0	0.75
Fixed reaction time: t = 60 min		

Table 2. Experimental matrix of the factorial planning.

Assay	O/A MR	T (°C)	Catalyst (%)
1	1:6 / -1	40 / -1	0.5 / -1
2	1:8 / +1	40 / -1	0.5 / -1
3	1:6 / -1	60 / +1	0.5 / -1
4	1:8 / +1	60 / +1	0.5 / -1
5	1:6 / -1	40 / -1	1.0 / +1
6	1:8 / +1	40 / -1	1.0 / +1
7	1:6 / -1	60 / +1	1.0 / +1
8	1:8 / +1	60 / +1	1.0 / +1
9	1:7 / 0	50 / 0	0.75 / 0
10	1:7 / 0	50 / 0	0.75 / 0
11	1:7 / 0	50 / 0	0.75 / 0

2.6 Absorption spectroscopy in the infrared region

The absorption spectra in the infrared region were obtained using a BOMEN MB-102 spectrometer, employing the KBr disk technique, within the 4000–400 cm^{-1} range.

2.7 Rheological study

The rheological parameters were obtained with the coaxial cylinder system, whereby the sample is sheared between the cylinder walls. The assays were carried out at a temperature of 40 °C for the cottonseed oil and the biodiesel using a bath coupled to a Mars rheometer.

matrix of independent variables, with the response of the 2^3 factorial planning with triplicate at the central point (standard matrix). These data were submitted to linear regression using the Statistica® 7.0 software, by means of which it was possible to propose a significant mathematical model from the statistical viewpoint (Equation 1). In addition, the influence of each variable on the process was assessed at a 95 % confidence level.

After optimization, the model equation for the conversion rate as a function of the main process variables was obtained (equation 1).

$$X (\%) = 93.165 - 3.33 \cdot T + 0.836 \cdot MR + 0.151 \cdot MR \cdot Cat - 0.359 T \cdot Cat \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Cottonseed oil characterization

The main physicochemical properties of the semi-refined cottonseed oil are shown in Table 3.

3.2 Factorial planning and response surface

The conversion data obtained experimentally using transesterification are listed in Table 4 as a

Where:

X = conversion (%)

T = temperature (°C)

MR = oil/alcohol molar ratio

Cat = percentage of catalyst with respect to the mass of oil

Table 3. Physicochemical properties of cottonseed oil.

Property	Value	Property	Value
Acidity index (mg KOH/g)	0.2	Moisture (ppm)	980
Calorific power (kcal/kg)	9,490.27	Density (g/cm^3)	0.9193
Saponification index (mg KOH/g)	194.42	Free glycerol content (%)	N/A(*)
Surface tension (dyn/cm)	28.0	Flash point (°C)	163
Kinematic viscosity ($\text{mm}^2 \cdot \text{s}^{-1}$)	35.35	Free fatty acids (%)	0.22
Dynamic viscosity (cP)	32.50	Ash content (g/100 g)	traces

(*) Not available

Table 4. Standard matrix of the 2^3 factorial planning with triplicate at the central point.

Assay	O/A MR	T / °C	Catalyst / %	Conversion / %
1	1:6	40	0.50	94.88
2	1:8	40	0.50	96.66
3	1:6	60	0.50	89.36
4	1:8	60	0.50	90.32
5	1:6	40	1.00	95.77
6	1:8	40	1.00	96.80
7	1:6	60	1.00	87.42
8	1:8	60	1.00	90.34
9	1:7	50	0.75	92.52
10	1:7	50	0.75	94.92
11	1:7	50	0.75	95.85

Figure 1. Response surface as a function of temperature and amount of catalyst.

Figure 1 shows the response surface, plotted as a function of the variables that were most significant in the process, namely temperature and amount of catalyst.

It can be observed that the response surface (conversion) shows a marked tendency towards its maximum (optimal) point with decreasing process temperature and increasing amount of catalyst, indicating the best path to follow in order to obtain maximum conversion in the process.

Figure 2. TG/DTG curves of the cottonseed oil.

Figure 3. TG/DTG curves of the biodiesel samples.

Statistical significance was determined using analysis of variance, showing that the proposed model fitted well the experimental results. According to **Barros Neto et al. (1996)**, such a model is statistically significant according to the F-test, but is not predictive within the predetermined intervals for each variable. However, in order to propose a model that is predictive, it would be necessary to increase the operating range of the variables chosen for the process.

3.3 Thermal Study

In Figure 2, the TG/DTG curves of the cottonseed oil showed three stages of mass loss, which were attributed to volatility and/or decomposition of the triacylglycerides.

The first stage occurred between 252 and 393 °C, with mass loss of 55.5 %. The second stage occurred between 393 and 458 °C, with mass loss of 31.3 %, and the third stage was observed between 458 and 581 °C, with mass loss of 13.1 %.

In Figure 3, the TG/DTG curves of the cottonseed oil methyl biodiesel showed two stages of mass loss, attributed to volatility and/or decomposition of methyl esters, mainly linoleate and methyl palmitate. The first stage occurred between 130 and 250 °C, with mass loss of 91.8 %, and the second stage was detected between 251 and 502 °C, with mass loss of 6 %.

Methyl biodiesel was thermally less stable than cottonseed oil, the former exhibiting more volatility due to the breakdown of triacylglyceride molecules in the oil which occurred during the transesterification reaction. This could also be evidenced by the DSC curves, as shown in Figure 4a, which depicts the DSC curve of the cottonseed oil, where four exothermal transitions, attributed to triacylglyceride combustion, can be seen. The first transition occurred between 317 and 366 °C, with enthalpy of 422 J/g; the second transition was observed between 366 and 426 °C, with enthalpy of 249 J/g; the third transition was detected between 426 and 474 °C, with enthalpy of 82 J/g; and the fourth transition occurred between 474 and 483 °C, with enthalpy of 50 J/g. Also, in Figure 4b, the DSC curve of the biodiesel showed three exothermal transitions, which were attributed to methyl ester combustion. In this case, the first transition occurred between 228 and 300 °C, with

enthalpy of 158 J/g; the second transition was detected between 300 and 370 °C, with enthalpy of 39 J/g; and the third transition took place between 370 and 400 °C, with enthalpy of 5.8 J/g.

3.4 Absorption spectroscopy in the infrared region

The cottonseed oil spectrum (Figure 5) shows a strong intensity band at 1740 cm^{-1} corresponding to stretching of the carbonyl group ($\text{C}=\text{O}$), and a medium intensity band at 1165 cm^{-1} corresponding to C-O axial deformation. The IR spectrum of the biodiesel sample is also shown in Figure 5. A strong band caused by the stretching of the carbonyl group ($\text{C}=\text{O}$) with regard to ester is seen between 1735.8 and 1743.5 cm^{-1} , and two medium bands are observed at 1172 and 1196 cm^{-1} related to the axial deformation of the C-O bond, characteristic of esters. In addition, a weak band was observed at 1126 cm^{-1} and was attributed to asymmetric stretching vibration of the O-C-C moiety, in accordance with reports by Monteiro et al. (2008) and Nabi et al. (2009).

3.5 Physicochemical characterization of the biodiesel

Table 5 shows that all the physicochemical parameters of cottonseed oil methyl biodiesel are within the limits established by technical regulation N°. 1/2008), by ANP.

3.6 Rheological study

The rheological study of cottonseed oil and methyl biodiesel was conducted by determining a number of parameters such as viscosity and rheological behavior. A sharp drop in viscosity after

oil transesterification could be observed, from 32.91 cp for cottonseed oil to 4.81 cp for biodiesel (dynamic viscosity at 40°C), confirming the breakdown of triacylglyceride molecules. Experimental analyses showed that the oil and biodiesel samples exhibit Newtonian rheological behavior, since the viscosity remains constant with an increase in shear rate, as is the case of fossil diesel.

(a)

(b)

Figure 4. DSC curves of the cottonseed oil (a) and biodiesel (b).

Table 5. Physicochemical properties of biodiesel.

Property	Biodiesel	ANP
Acid content (mg KOH/g)	0.27	Max. 0.5
Moisture (ppm)	463	Max. 500
Density (g/cm^3)	0.8796	0.85 – 0.90
Flash point (°C)	144	Min. 100 °C
Sulfur content (mg/kg)	0	Max. 50
Cold filter plug point (°C)	4	Max. 19
Calorific power (kcal/kg)	9,638.48	—
Surface tension (dyn/cm)	21.4	—
Kinematic viscosity at 40 °C (mm^2/s)	5.28	3.0 – 6.0
Flow point (°C)	4	—
Ester content (%)	96.79	Min. 96.5
Cloud point (°C)	5	—

Figure 5. Infrared spectra of the cottonseed oil and biodiesel.

4. CONCLUSIONS

The physicochemical characterization of cottonseed oil demonstrated that its properties are within the ideal limits for obtaining biodiesel, showing a low acid index, low moisture and fatty acid content. These are the essential characteristics of viable transesterification reactions, thereby decreasing the likelihood of parallel reactions of saponification. The experimental planning showed that the best conversion rate occurred under the following conditions: oil/alcohol molar ratio (1:8), temperature of 40 °C and 1 % of catalyst, with a yield in biodiesel as high as 96.79 %. Temperature was the most significant parameter, and the model proposed by the software showed a good fit for the factorial planning with statistical significance. The thermogravimetric profile of cottonseed oil proved that it is more thermally stable than biodiesel, given that its initial decomposition temperature was higher than that of biodiesel, thereby confirming the higher volatility of biodiesel. The DSC curves showed that the cottonseed oil exhibited higher combustion temperatures than those of biodiesel, confirming their enhanced volatility, due to the breakdown of triacylglyceride molecules during the transesterification reaction. The rheological study proved that both cottonseed oil and biodiesel showed Newtonian fluid behavior. All the physicochemical parameters of biodiesel are in accordance with technical regulations of the Brazilian Agency of Petroleum, Natural Gas and Biofuels (ANP), thereby corroborating the potential use of this biodiesel as an alternative fuel in actual applications and industrial operations.

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