A Química nas Áreas Natural, Tecnológica e Sustentável

3

Érica de Melo Azevedo
(Organizadora)

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APRESENTAÇÃO

A Coleção "A Química nas Áreas Natural, Tecnológica e Sustentável" apresenta artigos de pesquisa na área de química e que envolvem conceitos de sustentabilidade, tecnologia, ensino e ciências naturais. A obra contem 69 artigos, que estão distribuídos em 3 volumes. No volume 1 são apresentados 29 capítulos sobre aplicações e desenvolvimentos de materiais adsorventes sustentáveis e polímeros biodegradáveis; o volume 2 reúne 20 capítulos sobre o desenvolvimento de materiais alternativos para tratamento de água e efluentes e propostas didáticas para ensino das temáticas em questão. No volume 3 estão compilados 20 capítulos que incluem artigos sobre óleos essenciais, produtos naturais e diferentes tipos de combustíveis.

Os objetivos principais da presente coleção são apresentar aos leitores diferentes aspectos das aplicações e pesquisas de química e de suas áreas correlatas no desenvolvimento de tecnologias e materiais que promovam a sustentabilidade e o ensino de química de forma transversal e lúdica.

Os artigos constituintes da coleção podem ser utilizados para o desenvolvimento de projetos de pesquisa, para o ensino dos temas abordados e até mesmo para a atualização do estado da arte nas áreas de adsorventes, polímeros, análise e tratamento de água e efluentes, propostas didáticas para ensino de química, óleos essenciais, produtos naturais e combustíveis.

Após esta apresentação, convido os leitores a apreciarem e consultarem, sempre que necessário, a coleção "A Química nas áreas natural, tecnológica e Sustentável". Desejo uma excelente leitura!

Érica de Melo Azevedo

SUMÁRIO

CAPÍTULO 18

OPTIMIZATION SYNTHESIS OF BIODIESEL FROM MACAUBA OIL (*ACROCOMIA ACULEATA*) USING EXPERIMENTAL DESIGN TECHNIQUE

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ABSTRACT: This study aimed to evaluate the synthesis of methyl esters, having as raw material macauba almond oil (*Acrocomia aculeata mart.)* from the transesterification reaction using p-toluenesulfonic acid as catalyst. The planning conducted for the transesterification trials was the Rotatable Central Composite Design, with a factor 2^2, which originated the experimental mathematical model. The evaluation of the content of methyl esters was performed by thermogravimetry, and the best condition found for the percentage yield of methyl esters was obtained employing 11,5% catalyst, molar ratio of oil: methanol 1:6, 65°C temperature, 200 rpm stirring and reaction time of 4.25 hours, achieving a yield of 99%. From the generated mathematical model was demonstrated the validity of the experimental conditions.
KEYWORDS: Biofuel, Oil Macaúba almond, Transesterification, Thermogravimetry, Mathematical Model.

RESUMO: Este estudo teve como objetivo avaliar a síntese de ésteres metílicos, tendo como matéria-prima o óleo da amêndoa de macaúba (*Acrocomia aculeata mart.)*, a partir da reação de transesterificação empregando o ácido p-toluenossulfônico. O planejamento realizado para os ensaios de transesterificação foi o Delineamento do Composto Central com fatorial de 2^2 sendo a avaliação do teor de ésteres metílicos obtida por termogravimetria. A melhor condição encontrada foi obtida empregando-se 11,5% de catalisador, razão molar óleo:metanol de 1:6, temperatura 65 °C, agitação de 200 rpm e tempo de reação de 4,25 horas, obtendo-se um

rendimento de 99%. A partir do modelo matemático gerado, foi comprovada a validade deste para as condições experimentais.

PALAVRAS-CHAVE: Biocombustível, Óleo da Amêndoa de Macaúba, Transesterificação, Termogravimetria, Modelo Matemático.

1 I INTRODUCTION

World politics has given relevance to new technologies that work together to build an ecologically sustainable and less polluted world. Due to limited oil reserves and the consequent increase in oil prices, renewable energy sources, biofuel, has been the subject of intense investigations [1–5].

A major advantage of the use of renewable energy sources (particularly those of vegetable origin) is in the fact of producing less polluting compounds [6,7] and lower environmental impact in their burning processes, besides being part of the carbon mass naturally processed by plants.

Among the main renewable fuels stand out ethanol, vegetable oils and biodiesel [8]. The use of vegetable oils for biodiesel production, from the transesterification process has been object of recent research, attracting huge worldwide attention as an alternative fuel. Thus, the exploitation of native oilseeds need specific research to their encompassing in the energy matrix in a sustainable way [5,9,10].

In this context, the fruit of macauba palm (*Acrocomia aculeata mart.*) appears as a promising raw material for obtaining vegetable oils, mainly due to their high oil content in the pulp (60% to 70% on a dry basis) and in the nuts (40% to 50% on a dry basis), besides its high productivity (about 6.5 tons of oil per hectare) [11–14]economically important species of palm tree found in the Brazilian state of Mato Grosso do Sul. In this work, the general physicochemical characteristics and fatty acid composition of the fruit (bocai\u00fava. It features wide dispersion in Brazil and neighboring countries such as Colombia, Bolivia and Paraguay. In Brazil, this palm is native in Minas Gerais, Ceará, Mato Grosso and Mato Grosso do Sul, being more abundant in the Cerrado region, where their exploitation is carried out in an extractive way, taking advantage of the occurrence of large populations in these regions [14].

There are several studies on the use of macauba as raw material in the manufacture of oil for food purposes, the manufacture of soaps and burning for lighting and heating purposes. This palmácea excels in producing biodiesel for its oil production potential per unit area, adaptation (benefiting disadvantaged regions to commercial agriculture), plus the ability to use in agrossilvipastoris systems and viability in small plantations or associated with familiar agriculture [15,16].

The main way to obtain biodiesel is via transesterification reaction between a triglyceride, from vegetable oil, alcohol and a catalyst under appropriate conditions of temperature and agitation. The reaction is processed in the presence of a catalyst and generates methyl/ethyl esters (biodiesel) and glycerol by-product, commonly called glycerin [17–19].

Currently, the production of biodiesel is performed by transesterification of vegetable oil triglycerides using methanol and an alkali catalyst, usually NaOH or KOH [20–22]alkaline bases are used to catalyze the reaction. These catalysts require anhydrous conditions and feedstocks with low levels of free fatty acids (FFAs. The reaction is usually carried out at 60-80 °C and the glycerol and methyl ester are separated by sedimentation after neutralization of the catalyst [23,24].

The catalysts used are given special attention for its potential reduction of time and production costs, besides direct influence in the final product purity level [25–27]. In this context, p-toluenesulfonic acid (APTS) is a strong non-oxidizing acid having desirable characteristics for use as catalyst in transesterification processes. Due to peculiar features, this catalyst has highlighted as a catalyst in organic reactions. However, few studies in the literature report the utilization of APTS as catalyst for transesterefication[28–30]. The research employing the APTS use a product with high purity. Sulfonac ATS 95 (p-toluenesulfonic acid 95%) is a product marketed in Brazil having wide applicability as catalyst in industrial processes. Its cost is about 3 to 4% of the p-toluenesulfonic acid 98% commercialized for chemical companies.

Within this context, the aim of this study is to evaluate the synthesis of methyl esters derived from macauba almond oil from the transesterification reaction employing the Sulfonac ATS 95 (p-toluenesulfonic acid) as a catalyst.

2 | MATERIALS AND METHODS

2.1 Materials and Reagents

The macauba almond oil was purchased from Cooperativa Central do Cerrado. The used catalyst, p-toluenesulfonic acid 95% (Sulfonac ATS 95), was supplied by Sisterquímica S/A. Methyl alcohol 99.8% was obtained from Alphatec. All reagents were utilized without previous physical-chemical treatment.

2.2 Transesterification Reaction of oil

On a 250 mL volumetric flask attached to a reflux condenser, 10g of oil was added until reaching the reaction temperature (65°C). The catalyst solution and methyl alcohol was separately prepared and added to the preheated oil. The computation time started with the sealing of the balloon and initiation of constant stirring (200 rpm). The amounts of catalyst and reaction time employees obeyed the predetermined experimental design. After the reaction period, the flask contents were transferred to a separatory funnel. The bottom layer containing glycerol and impurities was drained. The top layer underwent a washing process using 40 mL (2 x 20 mL) of distilled water at 50°C. Subsequent to washing, the samples were heated for 30 minutes to remove any traces of water and methanol. The samples obtained in this process were stored in amber vials at room temperature (25°C).

2.3 Analytical Methodology

2.3.1 Analysis of fatty acid methyl esters

For determination of the fatty acid methyl esters profile, the lipids were by Hartman and Lago method (1973). The fatty acid methyl esters were analyzed on gas chromatograph (Perkin Elmer 680, USA) equipped with a flame ionization detector (FID) and fused silica capillary column (30 m x 0.25 mm x 0.25 μm, Elite Wax, Varian). The column temperature was programmed to started with 65 ºC, heating rate 15ºC min^{-1} up to 170ºC, followed by heating rate 6ºC min^{-1} up 220ºC. The sample split ratio used was 50:1 and sample volumes of 1 mL were injected. Ultrapure helium (White Martins), 1.30 mL min^{-1}, was used. The detector and injector temperatures were maintained at 220 ºC and 230 ºC, respectively. The fatty acids were identified by comparison of the retention times with those of fatty acid methyl ester standard (Supelco 23, Sigma–Aldrich).

2.3.2 Characterization of the almond oil and methyl ester

Macauba almond oil was characterized by acidity index (AOCS, 1998[30]), peroxide index (AOCS, 1998[30]), iodine index (AOCS, 1997[32]),humidity (AOCS, 1997[32]), density and viscosity measurements. Viscosity measurements were obtained using a basic rheometer (Brookfield DV-III) at 25º C temperature with rotational speed 100 rpm. The density was calculated using a 25mL pycnometer at 20 ° C temperature.

The amount of methyl esters present in transesterified samples of macauba almond oil was estimated using thermogravimetric analysis performed on a PerkinElmer thermo analyzer, model STA 6000, expressed as a weight loss percentage. The employed experimental condition for thermogravimetric analysis was heating about 6 mg of sample from 50°C to 600°C, with 10°C min^{-1} heating rate in nitrogen atmosphere with a flow of 20 mL min^{-1} using a platinum sampler.

Furthermore, the functional groups of biodiesel samples were investigated using absorption spectroscopy in the infrared - FTIR, acting in the range between 4000 cm^{-1} and 400 cm^{-1} with resolution of 2 cm^{-1} and number of accumulations of 16 spectra. A FTIR Perkin Spectrum100 spectrophotometer was used in order to obtain the spectrum samples in attenuated total reflectance UATR mode.

2.4 Experimental Planning

A Rotatable Central Composite Design (RCCD) was used, based on Response Surface Methodology. The independent variables were the concentration of APTS and time. The dependent variable was the concentration of methyl esters defined by thermogravimetric analysis.

For the RCCD experimental design 2^2 factorial trials were performed with 5 repetitions at the central point and 4 trials in the axial points, totaling 13 trials. Statistical tests were performed by Statistic 7.0 statistical software, where the main effects of the factors and their interactions on the response variable were calculated. The molar ratio of oil:methanol 1:6, 65°C temperature and agitation of 200 rpm were set.

In Table 1, the conditions provided can be seen as well as the intervals of the study design variables. The choice of these experimental groups was based on results from preliminary tests.

	-1.41	-1	0	1	+1.41
Time (h)	1.59	2	3	4	4.41
Catalyst (%)	6.6	8	11.5	15	16.4

Table 1. Real values corresponding to the coded

A quadratic model was fitted to fatty acid methyl ester concentration (FAME) response due to the factors: reaction time and catalyst concentration, according to Equation 1.

$$CEM = \alpha_1 + \alpha_2 t^2 + \alpha_3 t + \alpha_4 C^2 + \alpha_5 C + \alpha_6 t.C \qquad \text{(Equation 1)}$$

Where:

FAME = Fatty Acid Methyl Ester (%);

α_i = Model regression coefficients.

t = Reaction time (encoded value, dimensionless).

C = Catalyst Concentration (encoded value, dimensionless).

3 I RESULTS AND DISCUSSION

A. Characterization of the almond oil

The values of acidity index, peroxide index, iodine index, humidity, density and viscosity are given in Table 2. These analyzes indicate that the oil used in this study has suitable characteristics for biodiesel production. The acid index value was higher than expected, however, there are several factors that influence the oil acidity, such as how the harvest is done, ripening, storage and realization of fruit drying processes, as well as forms of oil extraction. Thus, these factors may explain the different values for the acid value reported in the literature.

Analysis	**Value**
Acidity index (mgKOH g^{-1})	3.9 ± 0.25
Peroxide index (meqK g^{-1})	5.9 ± 0.21
Iodine index (gI_{2}/100)	26.69 ± 1.48
Density (gm L^{-1})	0.91 ± 0.01
Humidity (%)	0.22 ± 0.01
Viscosity (cSt)	40.66 ± 1.29

Table 2 - Characterization of the macauba almond oil

The fatty acid methyl esters profile of macauba almond oil consists of unsaturated and saturated fatty acids. Oleic acid is predominant, about 38.59%, 43.49% of the total unsaturated fatty acids as can be seen in Table 3.

Retention (min)	**Fatty acid (%)**	**MM**	**Value Found (%)**
14.973	Lauric acid (C12:0)	200.32	27.9
19.423	Myristic acid (C14:0)	228.37	10.77
25.640	Palmitic acid (C16:0)	256.43	10.65
30.163	Stearic Acid (C18:0)	284.48	5.47
30.666	Oleic acid (C18:1n-9)	282.46	38.59
31.501	Linoleic acid (C18:2n-6)	288.44	4.12
	Outros		2.50

Table 3 - Fatty acid composition of macauba almond oil sample.

B. Thermogravimetric Analysis applied to biodiesel

The transesterification reactions of the macauba almond oil were performed using variable concentration of APTS and time, the molar ratio oil:methanol 1:6, 65°C temperature and constant stirring of 200 rpm defined using literature searches and preliminary testing. To set the response variable, concentration of methyl esters, thermogravimetric analysis was employed for the monitoring of transesterification reactions and observation of thermodegradation stages of biodiesel and oil [31].

Thus, based on thermodegradation temperature range for macauba almond oil and its methyl esters and in the identification of bands present in the thermogravimetric profile of the sample it was possible to determine the percentage conversion of the biodiesel produced.

In Table 4, it is possible to view the conditions provided by the experimental design for execution of the reactions as well as the percentage concentration of methyl esters, evaluated by thermogravimetric analysis (TGA).

Run	t (h)	C (%)	FAME (%)
1	4 (+1)	8 (-1)	91
2	2 (-1)	8 (-1)	80
3	4 (+1)	15 (+1)	98
4	2 (-1)	15 (+1)	93
5	3 (0)	11.5 (0)	94
6	3 (0)	11.5 (0)	93
7	3 (0)	11.5 (0)	94
8	3 (0)	11.5 (0)	95
9	3 (0)	11.5 (0)	93
10	4.25 (+1.41)	11.5 (0)	99
11	1.35 (-1.41)	11.5 (0)	88
12	3 (0)	16.4 (+1.41)	98
13	3 (0)	6.6 (-1.41)	79

Table 4. Results for the response variable, concentration of fatty acid methyl esters (FAME) for RCCD with a factor 2^2.

t: time; C: catalyst; FAME = Fatty acid methyl ester concentration;

It was found that the content of methyl esters had a variation of 79% to 99%, increasing with the increase in time and percentage of catalyst used in the testing and it was possible to achieve a minimum percentage of esters needed for the transesterified oil. Biodiesel can be considered, over 96.5%, as determined by the Agência Nacional de Petróleo, Gás Natural e Biocombustíveis - ANP, Brazil. [32].

The three best results (3, 10 and 12) ranged from 3 to 4.25h and 11.5 to 16.4% catalyst. It was observed that the amount of catalyst used was inversely proportional to the reaction time.

The best conditions found, where a transesterified ester content of 99% was obtained, was reached at an axial point, using 11.5% catalyst, 4.25 h reaction time, molar ratio oil:methanol 1:6, 200 rpm stirring and 65°C temperature.

Based on the levels of methyl esters obtained (93% to 95%) to the central points, trials 5 to 9 can confirm the repeatability of the tests.

The thermogravimetric profiles of macauba almond methyl biodiesel oil of tests 3, 10 and 13, where the highest and lowest yield were noted, along with the macauba almond oil are illustrated in Figure 1.

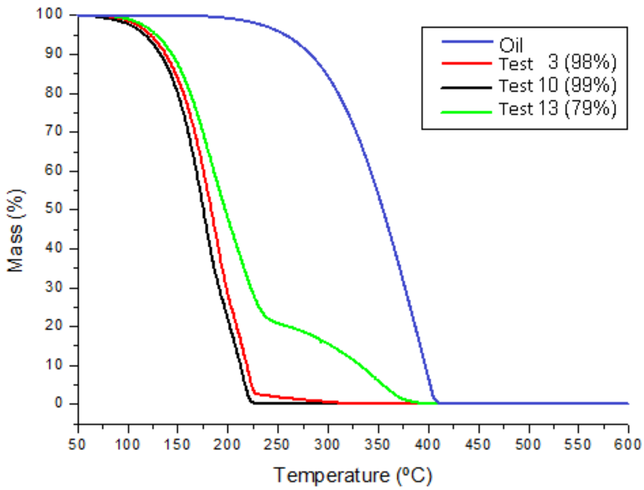

Figure 1. Thermogram of tests 3, 10 and 13.

For the analysis of the percentage of methyl esters obtained in the reaction was first performed the thermogravimetric profile of the oil, which showed a single degradation step (220 to 420ºC), as can be seen in Figure 2. This parameter was used as a reference for other analyzes.

The curves for tests illustrate that biodiesel has two steps of volatilization. The larger mass losses thresholds that are observed until an approximate temperature of 225°C can be attributed to the methyl esters, the other step is associated with the carbonization of the sample.

In the spectrum of the methyl biodiesel of the macauba almond oil resulting from test 10 (Figure 2a), where the highest yield was obtained, absorption bands of the functional group C=O (carbonyl) can be verified, and an axial average absorption of the functional group C=O–C–O (ester) in the region of 1750 cm^{-1} to 1220 cm^{-1} respectively. The methylene groups $(CH_2)_n$ of the carbon chain of esters were confirmed by the bands in the region of 3000 cm^{-1} and 720 cm^{-1}.

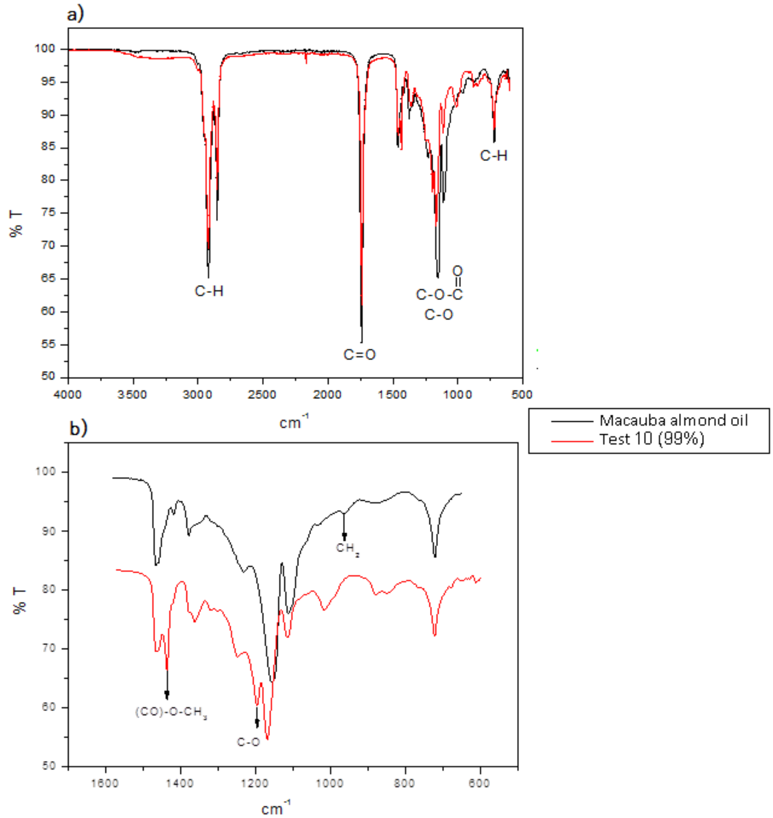

Figure 2. a) Infrared spectrum of biodiesel (99%) of test 10 and macauba almond oil. b) Absorption bands in region the 660 cm^{-1} to 1600 cm^{-1}.

Comparing the spectrum of the methyl esters of the test 10 with the macauba almond oil (Figure 2b), it was possible to observe differences in displacements and in the intensity of absorption bands in region the 660 cm^{-1} to 1600 cm^{-1}. In the region in 1168 cm^{-1} which identifies one of the major changes present in methyl esters, this band in the oil appears as a strong signal at 1159 cm^{-1} after transesterification this signal is divided into two on biodiesel, that they are visible in 1168 and 1195 cm^{-1}, the latter being equivalent to CO stretching band of an ester.

The region of 960 cm^{-1} was observed in the oil, which relates to symmetric vibration out of the plane of this in CH_2 triglyceride and the band in 1435 cm^{-1} in the biodiesel, which is related to deformation vibration of the methyl ester group.

C. Statistical Analysis and Validation of the Experimental Model

In Figure 3 is observed the Pareto diagram for the parameters studied. This diagram allows you to check the effect of each parameter monitored, as well as which terms are statistically significant. Considering the 95% confidence interval, the quadratic term of the catalyst, the linear term of the catalyst and time, as well as the interaction between them, it was verified that were significant as the concentration of methyl esters.

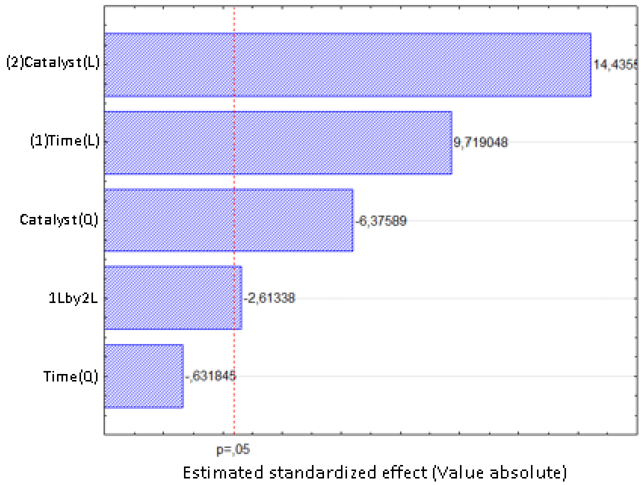

Figure 3. Pareto diagram for the yield content of esters, at a confidence level of 95%

Using the results obtained, the regression coefficients shown in Table 5 were calculated.

	Effects	Coefficients	Standard Error	p - value
Mean		93.8	0.5133	3.8824E-14
T	7.8890	3.9445	0.4058	2.5807E-05
I(t^2)	-0.55	-0.275	0.4352	0.5475
C	11.7175	5.8587	0.4058	1.8242E-06
I(C^2)	-5.55	-2.775	0.4352	0.0003
t:C	-3	-1.5	0.5739	0.0347

Table 5. Regression coefficients applied to the yield as a percentage of esters

t: time; C: catalyst

To perform the test of hypothesis (F test) and subsequent validation of the mathematical model is required to analyze the variance (ANOVA) for yield answer content of methyl esters, as can be seen in Table 6. This analysis model is the most used to numerically evaluate the quality of the adjustment of a model, doing an analysis of waste. Despite the quadratic term of time not being significant in the range worked, it was decided to keep it in the mathematical model.

Source of Variation	Degrees of freedom	Sum of Squares	Mean Squares	$F_{calculed}$	$F_{tabulated}$ $F_{5; 7; 0.05}$	p-value
Regression	5	461.699	92.340	70.013	3.972	7.9771E-06
Residual	7	9.224	1.318			
Total	12					

Table 6. Analysis of variance for the concentration-response esters (95% confidence interval)

According to Table 6 the value of Fcalculated (70.013) is greater than Ftabulated (3.972) determining the validity of the model with 95% confidence, that can also be observed because the p-value is smaller than 0.05.

The quadratic model adjusted for the response Fatty Acid Methyl Ester Concentration (FAME) showed a coefficient of determination equal to 98.04%, confirming that the mathematical model satisfactorily explains the relation between the treatments used and observations.

From the model, it was possible to generate the surface response graphics and contour curves for the variable concentrations of methyl esters. In Figure 4 it is presented the response graphic in function of the variables time and percentage of catalyst.

The contour curves chart (Figure 5) shows a great region for the catalyst, approximately 0.1 to 1.2 in coded values, and a growing trend for the time, reaching 100% of the theoretical yield. However, in practice, because it is a reversible reaction, time values that exceed the range applied from 2 h to 4 h, can compromise the performance as a percentage of methyl esters.

The validation of the experimental model was performed under conditions of 0.3 (12.5%) for the catalyst and 1.2 (4.12h) for time in coded values. These conditions were established considering the optimal region provided by the surface response graph and contour curves, which propitiates values greater than those established by the Agência Nacional de Petróleo, Gás Natural e Biocombustíveis [33], in the matter of esters percentage, which is 96.5%, using reactants and the smallest possible power levels.

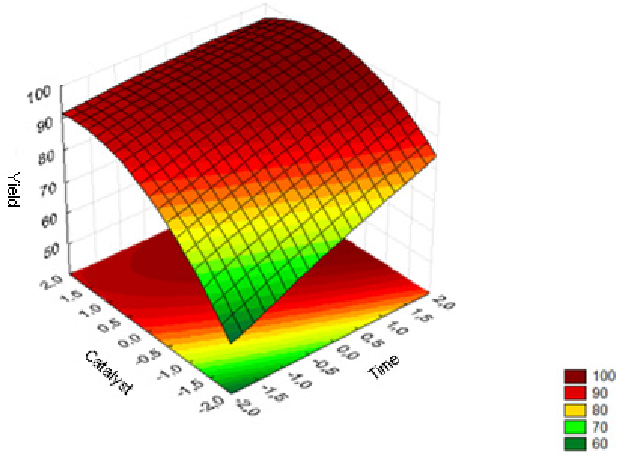

Figure 4. Surface response graph for the parameter concentration of esters in function of time and percentage of catalyst

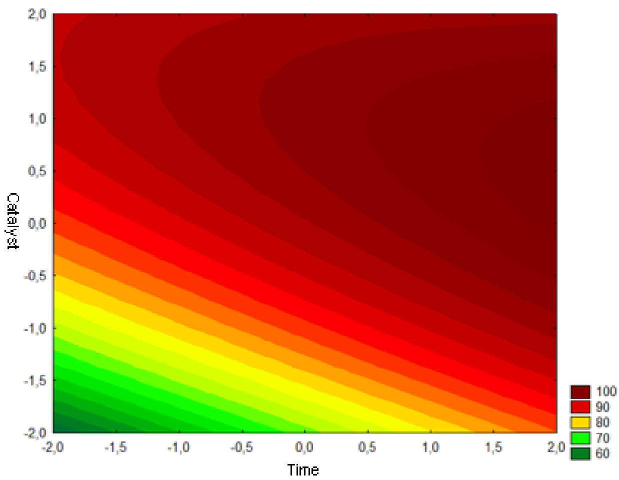

Figure 5. Graph contour curves for the concentration of esters parameter as a function of time and percentage of catalyst

Under such conditions, the value of the concentration of methyl esters predicted by the mathematical model was 99%. Thus, the model validated experimentally confirmed to obtain the esters, taking into account the optimal region obtained. In Table 7 there is the average of the concentrations achieved for validation tests.

Run	Time (h)	Catalyst (%)	FAME (%)
14	4.12 (1.2)	12.5 (0.3)	99
15	4.12 (1.2)	12.5 (0.3)	97
16	4.12 (1.2)	12.5 (0.3)	98
Mean			98

Table 7. Results of the validation of the experimental conditions, performed in triplicate, the temperature of 65°C, molar ratio oil:methanol 1:6 and 200 rpm stirring

In Figure 6, can be seen the thermogravimetric profiles of tests 14, 15 and 16, analyzed in an atmosphere of nitrogen.

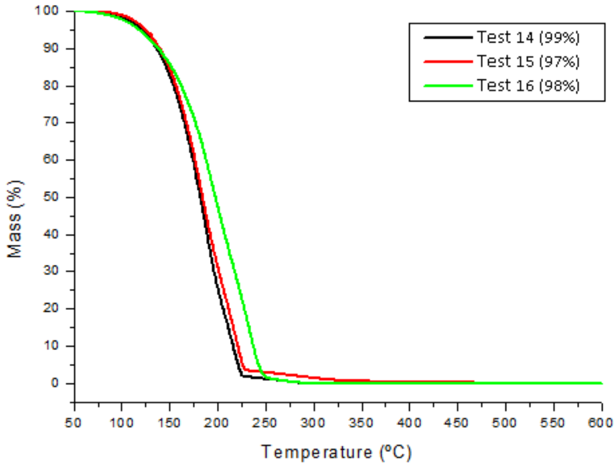

Figure 6. Thermogram of validation tests 39, 40 and 41 (C= 12.5%, R = 1:6 R and t = 4.12 h).

It can be seen that the concentration values of methyl esters found in validation tests ranged from 97% to 99%, which are very close values to the predicted by the model. Also, the average percentage error between the value predicted by the model for the selected condition and value observed in tests was validated by 1%, considered satisfactory value. Thus, it proved the validity of the mathematical model to the experimental conditions.

Because of the optimum range of weather conditions and catalyst percentage for the concentration of methyl esters above 96.5%, the analyzed conditions and reagents have great potential for industrial development, since small variations in the process do not result in major impacts on yield end.

A test was conducted without the presence of a catalyst employing the same reaction conditions used in the test 10. However, it was not observed the formation of fatty acid methyl esters. The results obtained by some studies using macauba oil to obtain biodiesel are reported in Table 8. It is observed that the reaction conditions and catalysts employed have not exhibited superior results (except 37 reference employing more complex catalysts and higher amounts of solvent and temperature) that obtained with p-toluenesulfonic acid, which produced biodiesel with 99% FAME.

Catalyst (wt%)	Temperature (ºC)	Time (min)	Oil:alcohol ratio	FAME (%)	Reference
Supercritical 15MPa	375	90	1:30 methanol (5wt% water)	78	34
Supercritical 15MPa	325	90	1:30 ethanol (5wt% water)	69.6	34
Sodium Methoxide (1)	Reflux	70	1:6 methanol	92.1	35
H_2SO_4 (1.3)	113.9	120	1:10.3 ethanol	93.9	36
Nb_2O_5/SO_4 (30)	250	240	1:120 ethanol	99.2	37
Supercritical 20MPa	325	45	1:50 methyl acetate	83	38
Enzyme CALB (6)	40% 5Hz (ultrasound)	30	1:6 methanol	93.3	39
Enzyme Novozym 435 (20)	65 ultrasound	30	1:9 ethanol	70	40
Enzyme Rhizomucor miehei (15.1)	40	480	1:3 ethanol	91	41

Table 8. Works using macauba oil for biodiesel production

The conditions employed in this work compared to other catalysts and systems employed in Table 8, it appears that the advantage of this process occur in a single step and cost of the catalyst (APTS 95 %) is very low, compared to the others catalysts.

Comparing this work to others that also used p-toluenesulfonic acid as catalyst, there is the lack of optimization studies applying this catalyst in transesterification reactions of vegetable oils to biodiesel production, furthermore all have employed APTS with high purity.

Reis *et al* [28] employed p-toluenesulfonic acid (homogeneous catalysis) in the esterification of free fatty acids as compared to A35 resin (heterogeneous catalysis), obtaining the best results for oleic and palmitic acids.

Encinar [29]diethyl ether (DEE, studied the application of p-toluenesulfonic acid in the pre-esterification of fats for later application basic catalysis. By applying just p-toluenesulfonic acid not obtained methyl ester yield.

It may be noted that the macauba almond oil has a great potential for biodiesel production processes as well as the catalyst applied, p-toluenesulfonic acid 95%, in addition to even present a great economic viability because of its low cost of ownership compared to traditional catalysts applied as well as its pure compound.

4 I CONCLUSION

In the transesterification process of the macauba almond oil catalyzed by p-toluenesulfonic acid, the quantities were critical to high concentrations of methyl esters. For the applied planning, values equal or greater than 11.5% were needed for the yield, as the percentage of esters was higher than that required by the legislation of the Agência Nacional de Petróleo, Gás Natural e Biocombustíveis [33] to be considered biodiesel, which is 96.5%. Also, due to the acid character of the catalyst, it was found that reaction times of 2 hours are sufficient for the process to occur in its entirety.

Within the range applied in studying, the best condition found for the percentage yield of methyl esters was processed using 11.5% catalyst (p-toluenesulfonic acid) molar ratio oil:methanol 1:6, 65°C temperature, 200 rpm stirring and reaction time of 4.25 hours, achieving a yield of 99%;

Using the regression coefficients resulting of data of the experimental design, a mathematical model was generated. The validation of this was performed by means of an assay in triplicate, where it was observed an average percentage error of 1%, proving the validity of the mathematical model to the experimental conditions employed.

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ÍNDICE REMISSIVO

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