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RESEARCH ARTICLE

PRODUCTION OF RENEWABLE HYDROCARBONS IN THE RANGE OF AVIATION BIOKEROSENE FROM *BABASSU OIL*

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ABSTRACT

In this work, babassu oil was selected as a raw material potentially capable of producing renewable hydrocarbons in the biokerosene range by hydrodeoxygenation (HDO), in the presence of the NiMo / γ-Al_2O_3 catalyst. According to gas chromatography, practically 70 % of the fatty acids constituent of babassu oil had carbon chains containing between 10 and 16 carbon atoms, with a predominance of saturated and monounsaturated fatty acids with 12 carbon atoms (44.58 %). A full factorial design 2^3 with a central point was carried out in order to investigate the individual and interaction effects on the selectivity to hydrocarbons of the following factors: reaction time, temperature, and H_2 pressure. The liquid reaction products were characterized by gas chromatography (CG-FID) and the experimental results were adjusted by a mathematical model. According to Analysis of Variance (ANOVA), the parameters temperature, reaction time, and H_2 pressure were significant. Temperature was the variable with the greatest influence on selectivity to hydrocarbons. The interaction factors reaction time - temperature and temperature - H_2 pressure were also significant. The best selectivity result was achieved at a temperature of 340 ºC and 70 bar of H_2, in which 98.41 % of hydrocarbons were obtained, in a time of 5 h. Under the conditions evaluated in this work, it was possible to obtain a high selectivity to renewable hydrocarbons in the range of aviation biokerosene by hydrodeoxygenation (HDO) from babassu oil. Babassu oil has proved to be a potential raw material for obtaining this biofuel.

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INTRODUCTION

The extensive use of fossil fuels is associated with sharp increases in greenhouse gas emissions, responsible for global warming.[1] The aviation sector is responsible for about 2 % of global CO_2 emissions, a percentage that tends to increase due to the expected growth by air services.[2] Faced with this perspective, the aviation industry has set a group of goals, including the reduction of CO_2 emissions by 50 % by 2050, compared to 2005 levels, in addition to carbon neutral growth from 2020.[3] The use of biokerosene ("drop-in") was the main solution chosen by civil aviation worldwide to achieve these goals.[2,3] The hydrodeoxygenation process (HDO) of oils and fats is a suitable technology for the conversion of triglycerides into hydrocarbons, making it possible to obtain green paraffinic fuels.[1,4-6] Through this process, oxygen is removed in the form of water (H_2O) or carbon oxides (CO_x), which can occur through three distinct and simultaneous routes: decarboxylation, decarbonylation and hydrogenation (or dehydration).[7] Babassu is one of the most representative palm trees of Brazilian plant extractivism, of wide natural occurrence in the North and Northeast regions of Brazil.[8] The incentive to use babassu as a raw material for the production of biofuels allows the reduction of carbon emissions by avoiding the deforestation of babassu palms, in addition to valuing national raw materials. [9,10] Its fruits contain high oil content (60 – 65 %)[11] and stand out as a potential raw material for the production of aviation biokerosene due mainly to its composition in fatty acids. According to the literature,[12] the main fatty acids found in babassu oil are saturated fatty acids, with a predominance of lauric acid (C 12:0) (50 %), followed by 11 – 27 % of myristic acid (C 14:0), and 9 – 20 % of oleic acid (C 18:1).In the HDO process, mainly paraffinic hydrocarbons are obtained, with carbon chains of equal number or lower in one unit compared to the precursor fatty acid.[7,13] Thus, after being hydrodeoxygenated, the constituent fatty acids of babassu oil should form, mainly, alkanes in the aviation biokerosene range (C9 - C15). Therefore, this work was carried out with the objective of obtaining results of the conversion of babassu oil into renewable hydrocarbons, in the aviation biokerosene range (C9 - C15), by HDO, in the presence of the commercial catalyst NiMo/γ-Al_2O_3, under different conditions of H_2 pressure, temperature and reaction time. Thus, it was possible to evaluate the influence of the reactional parameters on the composition of the final product and determine the conditions that provide greater hydrocarbon selectivities in the desired range.

EXPERIMENTAL

Feedstock and Catalyst: Refined babassu oil of commercial origin, supplied by Destilaria Bauru Ltda, was used as feedstock for HDO reactions. As a catalyst, nickel and molybdenum supported on γ-alumina (NiMo/γ-Al_2O_3), of commercial origin, supplied by CENPES (Centro de Pesquisas Leopoldo Américo Miguez de Mello) were used. This solid is currently used in petroleum refineries in the hydrotreatment of aviation kerosene and diesel fractions, mainly for the removal of sulfur, nitrogenous and oxygenated contaminants.

Determination of the Fatty Acids Profile of Babassu Oil: Babassu oil was characterized according to its composition in fatty acids, using the gas chromatography technique. For this, in a first step, samples of the oil were reacted, producing methylated compounds. To obtain fatty acid methyl esters (FAME), saponification was performed, reacting 300 mg of the oil with 2 ml of potassium hydroxide solution in methanol (0.5 mol/L); followed by an esterification with 2 mL of a solution of hydrochloric acid in methanol (5 % v/v). The reactions were performed in a closed environment, in a water bath (75 ºC), for 10 min. After the addition of 2 ml of distilled water and 2 ml of hexane P.A. in a separatory funnel, the organic phase with hexane was sent to a second step. In this step, the produced FAMEs were analyzed in a gas chromatograph (Shimadzu GC-2014) with flame ionization detector (FID), split/splitless injector and Carbowax 20M capillary column (30 m x 0.25 mm x 0.25 µm). The carrier gas used was H_2 (26.5 cm/s). The temperature programming used was: 60 °C for 2 min; 60 °C to 200 °C (gradient of 10 °C/min); 200 °C to 240 °C (gradient of 5 °C/min), remaining at this temperature for 15 min. The FAMEs were identified by comparing their retention times with those of a mixture of 37 external standards (C 4:0 to C 24:0) from Sigma. The composition was determined by the area normalization method.

Catalytic Tests

Experimental Design and Statistical Analysis of Data: For the realization of HDO reactions of babassu oil, a complete factorial design was adopted, composed of three variables, each tested at two levels (2^3), with three repetitions at the central point. The selected factors were: reaction time, temperature and H_2 pressure, represented by the coded variables A, B and C, respectively. Selectivity to hydrocarbons was considered as the response variable. The factor levels were coded (- 1, 0, + 1) according to Equation 1.[14]

$$x_i = \frac{X_i - \bar{X}}{\delta} \qquad (1)$$

Where, x_i = coded value of the variable X_i; X_i = real value of the variable; $\bar{X}$ = mean value of the variable; δ = value of the X_i variation range. The tests were performed in random order and without replicates, with the exception of those carried out at the central point. Table 1 shows the real and coded values (- 1, 0, + 1) of the levels of each factor investigated.

Table 1. Real and coded levels of the variables studied in factorial design 2^3 with central point

Factors		Levels		
		Minimum	Central Point	Maximum
		(- 1)	(0)	(+ 1)
A	Reaction time (h)	5	6	7
B	Temperature (ºC)	300	320	340
C	H_2 pressure (bar)	30	50	70

Table 2. Planning matrix of the factorial design 2^3 with central point, containing the real and normalized levels of the factors

Assay		Reaction time (h)		Temperature (ºC)		H_2 pressure (bar)	
Standard order	Real order	Real	Normalized	Real	Normalized	Real	Normalized
1	8	5	- 1	300	- 1	30	- 1
2	3	7	+ 1	300	- 1	30	- 1
3	2	5	- 1	340	+ 1	30	- 1
4	9	7	+ 1	340	+ 1	30	- 1
5	6	5	- 1	300	- 1	70	+ 1
6	11	7	+ 1	300	- 1	70	+ 1
7	4	5	- 1	340	+ 1	70	+ 1
8	5	7	+ 1	340	+ 1	70	+ 1
9	10	6	0	320	0	50	0
10	1	6	0	320	0	50	0
11	7	6	0	320	0	50	0

The planning matrix, containing all possible combinations of the chosen levels, plus the tests at the central point, is shown in Table 2. From the experimental results obtained, a mathematical model capable of describing the functional relationship between the dependent variable (selectivity to hydrocarbons, y) and the independent variables (reaction time, temperature and pressure of H_2) was determined. The statistical tool used in the treatment of the data was the Analysis of Variance (ANOVA), with the objective of verifying the significance and quality of the model's adjustment, besides determining which factors produce significant (main and interaction) effects on the system's response. The statistical study was performed with the Design Expert 9.06 software, using a 95 % confidence interval ($\alpha = 0.05$).

HDO Reactions of Babassu Oil: The HDO reactions were performed in a high pressure reactor (Parr Instrument Company 4848), of 300 mL capacity, in a simple batch system, with temperature and pressure control. Before each reaction, the NiMo/γ-Al_2O_3 catalyst was reduced by flow of H_2 (50 mL/min), at 425 ºC for 4 h, in a tubular oven. The reduction conditions were defined based on a previous temperature programmed reduction (TPR) analysis. A 3 % (w/w) catalyst/babassu oil ratio was used. After cooling to room temperature inside the oven, the catalyst was quickly transferred to the reactor, already containing the raw material. The reactor was pressurized with H_2 and heated to the reaction temperature. The reactions were processed under agitation (1200 rpm) and the pressure was kept constant by injection of hydrogen.

Characterization of the Products: In the characterization of liquid fraction products, a gas chromatograph (Shimadzu GC-2010) was used, with flame ionization detector (FID), split/splitless injector and DB 23 column (J & W Scientific). The samples were previously diluted in n-heptane (99.9 % v/v), in a proportion of 0.05 g of sample to 1.5 mL of solvent. The identification of the products was carried out by comparing their retention times with those of hydrocarbon standards (C9 to C22), in addition to standards of fatty alcohols, wax esters, fatty acids and fatty acid esters. In this work, the products of the gas fraction were not analyzed. The conversion of babassu oil (C) was defined in terms of triglycerides converted into other products (intermediates and hydrocarbons) and calculated according to Equation 2.

$$C = 100\ \% - \frac{A_{trg}}{A_{total}} \cdot 100\ \% \tag{2}$$

Where, C = conversion of triglycerides; A_{trg} = sum of the triglyceride peak areas; A_{total} = sum of the peak areas of triglycerides and products. The selectivity (mass percentage) to each of the products (S_i) was calculated according to Equation 3.

$$S_i = \frac{A_i}{A_{total\ products}} \cdot 100\ \% \tag{3}$$

Where, S_i = selectivity to product i; A_i = area of the peaks of compound i; $A_{total\ products}$ = sum of the peak areas of all products formed.

RESULTS AND DISCUSSION

Determination of the Fatty Acids Profile of Babassu Oil: The fatty acid composition of babassu oil is presented in Table 3. The predominance of the fatty acids with 12 carbon atoms lauric (C 12:0) and lauroleic (C 12:1) is observed, totaling 44.58 %. It is also noted that 69.7 % of the fatty acids in this oil have carbon chains containing between 10 and 16 carbon atoms, thus falling within the fraction with the potential to generate hydrocarbons in the aviation biokerosene range (C9 - C15) by HDO.

Table 3. Fatty Acids Profile of Babassu Oil

Nomenclature	Structure	Fatty Acids Profile (%)
Caproic Acid	C 6:0	1,34
Caprylic Acid	C 8:0	1,21
Capric Acid	C 10:0	1,45
Lauric Acid	C 12:0	18,54
Lauroleic Acid	C 12:1	26,04
Myristic Acid	C 14:0	6,23
Miristoleic Acid	C 14:1	9,35
Palmitic Acid	C 16:0	3,09
Palmitoleic Acid	C 16:1	4,99
Stearic Acid	C 18:0	7,66
Oleic Acid	C 18:1	18,45
Linoleic Acid	C 18:2	1,65
Saturated (%)		39,52
Monounsaturated (%)		58,83
Polyunsaturated (%)		1,65

Also according to Table 3, the percentage of saturated fatty acids obtained for babassu oil was close to 40 %, higher than most other vegetable oils, such as canola (6 %), sunflower (11 %), soybean (15 %) and olive (14 %),[11] and among unsaturated fatty acids, the polyunsaturated content (1.65 %) is quite low. The high content of saturated fatty acids present in this oil is advantageous, since the presence of unsaturations favors the occurrence of secondary cracking reactions of HDO products of triglycerides. Statistical Analysis and Catalytic Evaluation of Babassu Oil HDO: The HDO reactions of babassu oil were conducted according to the complete factorial design (Table 2). The results obtained are presented in Table 4, which shows the conversion and selectivity values to the different products of the liquid fraction obtained. Table 4 shows that, in addition to the compounds of interest, fatty acids, fatty alcohols, wax esters and fatty acid esters (methyl and ethyl) were obtained as by-products. The $NiMo/\gamma\text{-}Al_2O_3$ catalyst showed satisfactory catalytic activity in the HDO process, providing a conversion of 100 % of the triglycerides into products under all conditions employed. In addition, the catalyst was able to produce hydrocarbons with high selectivities (> 80 %) when associated with more favorable experimental conditions, obtaining mainly C11 and C12 alkanes. The combination of high temperature (340 ºC) and high H_2 pressure (70 bar) yielded the best result, in which hydrocarbons were produced with a selectivity of 98.41 %, in a reaction time of 5 h. Under these conditions (340 ºC and 70 bar of H_2), the increase in reaction time from 5 h to 7 h did not produce significant effects on the selectivity to hydrocarbons obtained, which went from 98.41 % to 98.6 %. In contrast, hydrocarbon selectivities below 50 % were obtained in reactions carried out at low temperature (300 ºC). The worst result (10.7 %) was observed when low temperature (300 ºC) was associated with low H_2 pressure (30 bar) and low reaction time (5 h). The combination of low temperature (300 ºC) with high H_2 pressure (70 bar) and high reaction time (7 h) was able to increase the hydrocarbon selectivity obtained to only 43.19 %. A more in-depth discussion about the effects of temperature levels, H_2 pressure and reaction time on the selectivities to hydrocarbons and by-products obtained can be found in item 3.2.2 (Catalytic Evaluation).

Table 4. Results of factorial design 2^3 with central point for the HDO reactions of babassu oil

	Factors			Selectivity (%)					
	1	2	3						
Assay	Reaction Time (h)	Temperature (ºC)	H_2 Pressure (bar)	Conversion (%)	Hydrocarbons	Fatty Alcohols	Wax Esters	Fatty Acids	Fatty Acid Esters
1	5	300	30	100	10,70	8,60	28,06	52,58	0
2	7	300	30	100	19,49	1,48	27,4	44,62	7,01
3	5	340	30	100	38,43	1,07	10,3	4,56	3,64
4	7	340	30	100	83,04	1	9,69	1,27	5
5	5	300	70	100	16,19	7,14	36,68	19,39	20,6
6	7	300	70	100	43,19	9,1	30,3	10,5	6,2
7	5	340	70	100	98,41	0,1	0	1,29	0,2
8	7	340	70	100	98,60	0,1	0	1,2	0,1
9	6	320	50	100	78,36	0,68	6,75	12,15	2,06
10	6	320	50	100	76,82	0,57	5,15	15,62	1,84
11	6	320	50	100	78,01	0,81	7,09	12,11	1,98

Analysis of Variance: Table 5 shows the results of ANOVA, performed using the Design Expert 9.06 software.

Table 5. Analysis of Variance (ANOVA) of hydrocarbon selectivity in HDO reactions of babassu oil

Source of Variation	SS	DF	MS	F_{calc}	p-value
Linear Regression	$6{,}36 \cdot 10^{-3}$	6	$1{,}06 \cdot 10^{-3}$	233,59	0,0004
Reaction Time (A)	$1{,}12 \cdot 10^{-3}$	1	$1{,}12 \cdot 10^{-3}$	247,32	0,0006
Temperature (B)	$3{,}67 \cdot 10^{-3}$	1	$3{,}67 \cdot 10^{-3}$	808,37	< 0,0001
H_2 Pressure (C)	$7{,}53 \cdot 10^{-4}$	1	$7{,}53 \cdot 10^{-4}$	165,88	0,0010
AB	$5{,}57 \cdot 10^{-4}$	1	$5{,}57 \cdot 10^{-4}$	122,77	0,0016
AC	$3{,}83 \cdot 10^{-5}$	1	$3{,}83 \cdot 10^{-5}$	8,43	0,062
BC	$2{,}21 \cdot 10^{-4}$	1	$2{,}21 \cdot 10^{-4}$	48,78	0,0060
Residuals	$1{,}36 \cdot 10^{-5}$	3	$4{,}54 \cdot 10^{-6}$	-	-
Lack of Fit	$1{,}36 \cdot 10^{-5}$	1	$1{,}36 \cdot 10^{-5}$	753,30	0,0013
Pure Error	$3{,}61 \cdot 10^{-8}$	2	$1{,}8 \cdot 10^{-8}$	-	-
Corrected Total	$7{,}54 \cdot 10^{-3}$	10	-	-	-
% of Explained Variation (R^2) : 99,79 %					
Maximum % of Explained Variation: 100,0 %					
Adjusted R^2	99,36 %				
Predicted R^2	88,48 %				

Legend: Source of Variation: source of variation; SS: sum of squares; DF: number of degrees of freedom; MS: mean squares; F_{calc}: calculated value of F; p-value: p-value.

Among the possible models presented in the Design Expert 9.06 software, the inverse linear proved to be the most suitable to relate the dependent variable (hydrocarbon selectivity) and the independent variables (temperature, H_2 pressure and reaction time). The exchange of the variable selectivity to hydrocarbons for its inverse, through a linearizing transformation, allowed to obtain a simpler model, which fit to the experimental data set. Thus, a polynomial model (Equation 4)[15] was adjusted to the data of Table 4, with the coefficients determined by the method of least squares, in a linear regression and 95 % confidence level.

$$\hat{y} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 + e \qquad (4)$$

Where, $\hat{y}$ = values of the response variable predicted by the model; β_i = model parameters; x_1, x_2 and x_3 = coded independent variables (reaction time, A; temperature, B; and H_2 pressure, C); e = random error associated with the model. The regression equation obtained can be expressed in coded and uncoded units, according to the levels in Table 1. The adjusted model obtained with the coded values of the factors time, temperature and H_2 pressure is described by Equation 5.

$$\frac{1}{Y} = 0.036 - 0.012\,A - 0.021\,B - 9.70 \cdot 10^{-3}\,C + 8.35 \cdot 10^{-3}\,AB + 2.19 \cdot 10^{-3} AC + 5.26 \cdot 10^{-3}\,BC \qquad (5)$$

Where, Y = hydrocarbon selectivity (%); A = reaction time (h); B = temperature (ºC); C = H_2 pressure (bar). The model generated with the values of the original variables is described by Equation 6.

$$\frac{1}{Y} = 1.52 - 0.15 \cdot Time - 4.23 \cdot 10^{-3} \cdot Temperature - 5.35 \cdot 10^{-3} \cdot Pressure + 4.17 \cdot 10^{-4} \cdot Time \cdot Temperature + 1.09 \cdot 10^{-4}\,Time \cdot Pressure + 1.32 \cdot 10^{-5} \cdot Temperature \cdot Pressure \qquad (6)$$

Where, Y = hydrocarbon selectivity (%); $Time$ = reaction time (h); $Temperature$ = temperature (ºC); $Pressure$ = H_2 pressure (bar). Initially, the statistical significance of the obtained model was evaluated using the F-test. Comparing the tabulated value of F (F_{tab} = F(1;3;5 %) = 10.13)[16] to the calculated F (F_{calc} = 233.59) (Table 5), it is found that F_{calc} is much larger than F_{tab}, indicating that the null hypothesis (H_0), that the factors together have no effect, should be rejected. Similarly, it is observed that the p-value of the model (p-value = 0.0004) is much lower than the 5 % significance level set for the test ($\alpha = 0.05$), confirming that the null hypothesis should be discarded, that is, the model is statistically significant.

Subsequently, the statistical significance of the main and interaction effects of the factors under study on hydrocarbon selectivity was evaluated based on the p-value associated with each effect. ANOVA shows that A (reaction time), B (temperature) and C (H_2 pressure) factors, as well as interactions between factors AB (reaction time and temperature) and BC (temperature and pressure of H_2) are statistically significant parameters ($p < 0.05$), unlike the AC interaction (reaction time and H_2 pressure), which is not within the 95 % confidence interval. In particular, it appears that the main effect of the temperature was highly significant ($p < 0.0001$), a criterion presented by Rodrigues and Iemma[16]. The AC interaction was maintained in the model, although it did not show statistical significance, in contrast to the 3rd order ABC interaction (reaction time, temperature and H_2 pressure), excluded in the model adjustment so that it became valid within the confidence interval. The lack of fit test was applied to assess the adequacy of the model to the data distribution. According to ANOVA, the p-value of the lack of fit (p-value = 0.0013) is less than the 5 % significance level set for the test ($\alpha = 0.05$) and, thus, the null hypothesis, H_0, which proposes that the line equation is adequate to describe the data, should be rejected. However, the other analyzes of model adequacy must also be considered to confirm if there is indeed a lack of fit. In addition, as the sum of squares for the pure error was much lower than that of the lack of fit, the F_{calc} of the test may be overestimated, as also verified by Garcia[17]. According to Garcia[17], since pure error is obtained only from the variation between the results of the central points, a very low value of this parameter, despite indicating a good repeatability of the analyses, may end up overestimating the deviations due to the lack of fit. In this case, as the quadratic sum of the pure error is very low in relation to the lack of fit, a very high value of F_{calc} is obtained in the hypothesis test, higher than F_{tab}, indicating a "false" lack of fit of the model. In this case, the deviation between the experimental data and the data predicted by the model should be calculated and evaluated. Thus, to check the quality of the model's fit to the data distribution, a graph of experimental results versus results predicted by the adjusted model was also constructed (Figure 1).

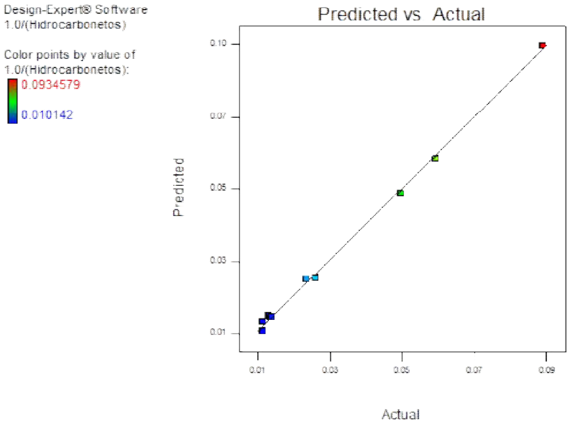

Figure 1. Graph of experimental values versus values predicted by the adjusted model of 1 / hydrocarbon selectivity for each test

In Figure 1, the percentages of hydrocarbons observed experimentally are quite close to the best line, indicating an adequate adjustment of the statistical model to the experimental data. The determination coefficient (R^2) obtained (R^2 = 99.79 %), very close to 1, attests the quality of the fit of the regression line to the set of experimental points. The result indicates that 99.79 % of the total variation in selectivity to hydrocarbons around the average is explained by the regression, and only 0.21 % is attributed to the residuals (influences other than those exerted by the variables under study).

The residual quadratic sum, which represents the part of the variation of the responses around the mean that the model cannot reproduce, was only $1.36 \cdot 10^{-5}$. The model generated an adjusted R^2 value greater than 0.9 (adjusted R^2 = 0.9936), confirming a good fit and adequacy to the data. In addition, the calculated value of predicted R^2 (predicted R^2 = 0.8848) was very close to 0.9, indicating that the model obtained is able not only to explain the experimental data, but also to predict new data. To verify whether the residuals left by the model are normally distributed, a necessary condition for the use of the F-test,[14] a probability-probability graph (P-P plot) was used (Figure 2), which presents the values of the empirical cumulative distribution function versus the values of the theoretical cumulative distribution function.[18]

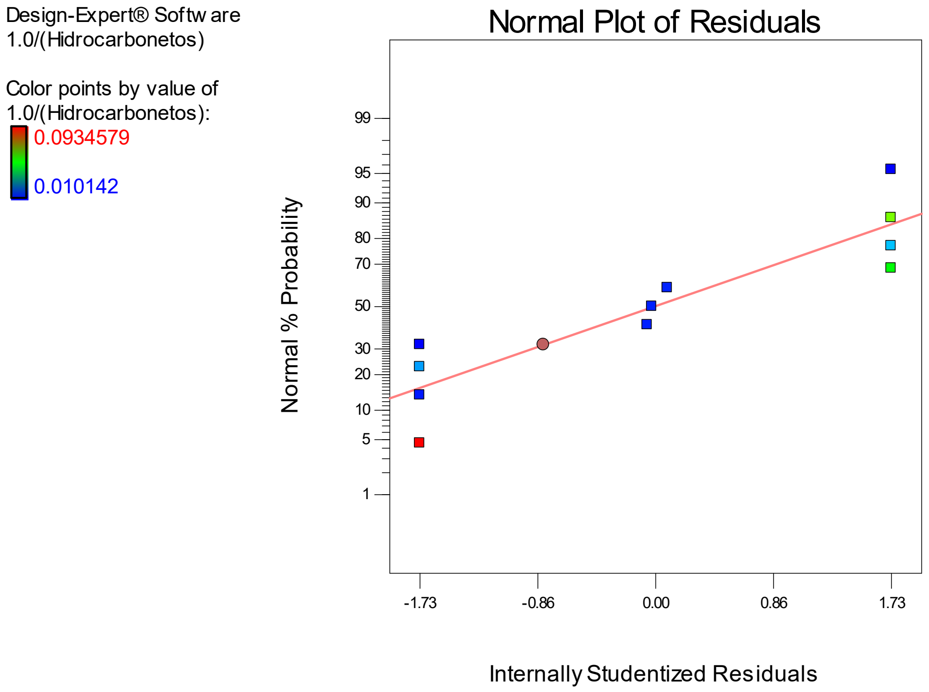

Figure 2 . Normal P-P plot of residuals

In the interpretation of the P-P plot, the location of the points on the diagonal line indicates that the two distributions are identical, while the observation of points situated strictly above or below the line indicates that one distribution dominates the other.[19] In Figure 2, although the points present are not on the straight line, they tend to concentrate around it. Thus, there is no evidence of absence of residuals normality. Given the above, although the lack of fit test indicates a significant lack of fit of the model to the experimental data, it was adopted since the other tests showed good results. Finally, a comparison was made among the absolute values of the coefficients of the regression equation based on coded units (Equation 5), which makes it possible to determine which factor has the greatest influence on the response.[14]

It is observed that the factor B (temperature), which presents the associated parameter with the highest absolute value, is the variable that exerts the greatest influence on selectivity to hydrocarbons individually. Among the interaction effects, the importance of the temperature factor is observed again, since it is present in the synergism among the factors that obtained the greatest effects on the response: the interaction between reaction time (factor A) and temperature (factor B), and the interaction between temperature (factor B) and H_2 pressure (factor C). These results confirm what had already been verified based on the p-value numbers.

Catalytic Evaluation: In this topic, the influence of the variables under study on selectivity to hydrocarbons and by-products was discussed.

Influence of Reaction Time: Figures 3a and 3b show the variations in the selectivity to hydrocarbons produced as a function of the reaction time, evaluated at the minimum (5 h) and maximum (7 h) levels of this variable, under different temperatures (300 ºC and 340 ºC) and pressures of H_2 (30 bar and 70 bar).

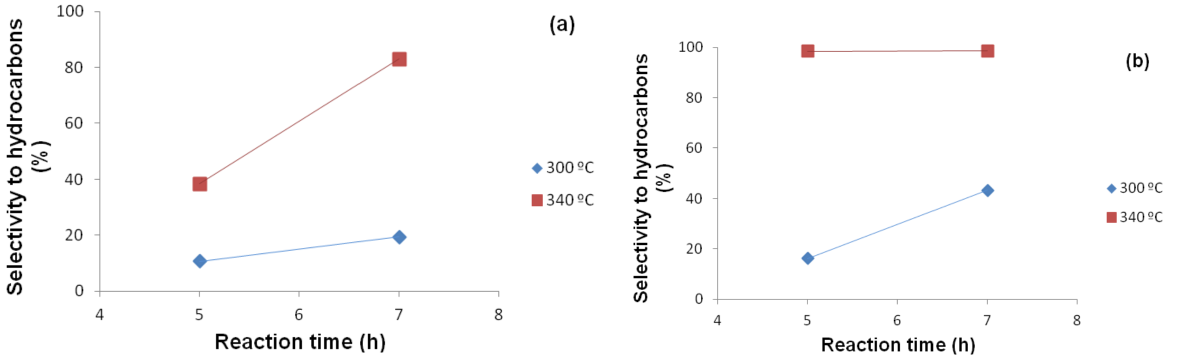

Figure 3. Selectivity to hydrocarbons as a function of reaction time: a H_2 pressure of 30 bar; b H_2 pressure of 70 bar

From Figure 3, it can be seen that the selectivity to hydrocarbons increased with the contact time for practically all temperatures and pressures used, with the exception of the tests performed at 340 ºC and 70 bar of H_2 (Figure 3b), in which the percentages of hydrocarbons obtained in 5 h (98.41 %) and 7 h (98.60 %) were practically identical.

Thus, in general, the increase in reaction time, from 5 h to 7 h, favored the production of hydrocarbons at the expense of the obtaining of by-products, which had their selectivities reduced by up to 44.61 % (at 340 ºC and 30 bar of H_2), according to Table 4. On the other hand, under conditions of high temperature (340 ºC) and pressure (70 bar of H_2), the increase in reaction time reduced the selectivity to by-products by only 0.19 %. The tendency to obtain higher hydrocarbon yields as a result of the increase in reaction time was also verified by Zuo and collaborators,[20] in the HDO of methyl palmitate ester.

Influence of Temperature: The results of selectivity to hydrocarbons produced from babassu oil as a function of the reaction temperature, evaluated at the minimum (300 ºC) and maximum (340 ºC) levels of this variable, under different times (5 h and 7 h) and pressures of H_2 (30 bar and 70 bar), are shown graphically in Figures 4a and 4b.

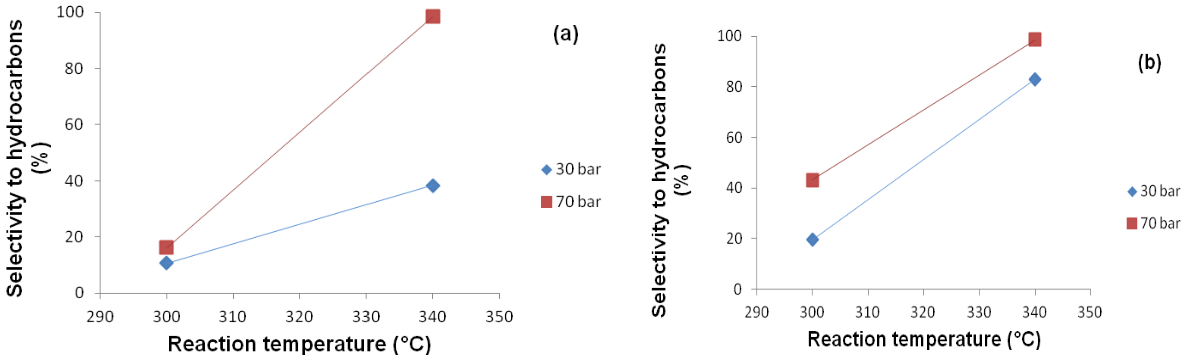

Figure 3. Selectivity to hydrocarbons as a function of reaction temperature: a reaction time of 5 h; b reaction time of 7 h

From Figure 4, it can be noted that at the lowest temperature of 300 ºC, HDO occurred slowly, producing a low proportion of hydrocarbons (less than 50 %) even under high pressures of H_2 (70 bar) and long reaction times (7 h). On the other hand, at high temperature (340 ºC), proportions of hydrocarbons higher than those of the other compounds were obtained in general, with selectivities above 80 % for all conditions of pressure and reaction time investigated, with the exception of the process performed at low pressure (30 bar), which required a longer reaction time (7 h) to obtain a satisfactory result.

Therefore, the rise in temperature, from 300 ºC to 340 ºC, favored HDO reactions, resulting in an increase in selectivity to hydrocarbons and, consequently, in a reduction in selectivity to by-products, for all H_2 pressures and reaction times evaluated.

According to Table 4, the selectivity to by-products decreased by at least 27.73 % (at 30 bar of H_2 and 5 h), reaching a reduction of up to 82.22 % (at 70 bar of H_2 and 5 h) with the increase in temperature in the aforementioned range. The increase in yield of alkanes produced by HDO following the increase in temperature has been reported in the literature for vegetable oils,[21,22] microalgae oils[23] and associated model molecules, such as fatty acid esters.[24,25]

Influence of H_2 Pressure: The H_2 pressure not only affects the yield of the products, but also consists of a limiting economic factor of great importance in hydrotreating.[26] Figures 5a and 5b show the selectivity to hydrocarbons obtained at the minimum (30 bar) and maximum (70 bar) levels of this variable, under different reaction times (5 h and 7 h) and temperatures (300 ºC and 340 ºC).

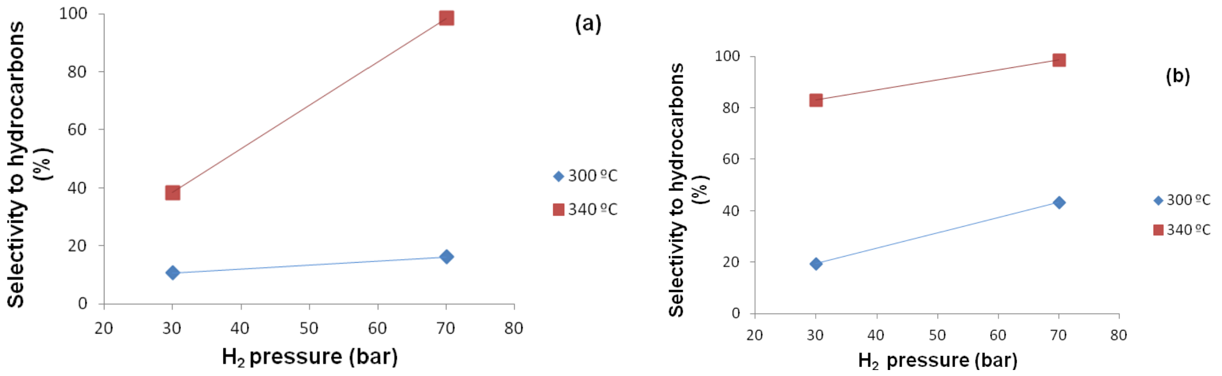

Figure 5. Selectivity to hydrocarbons as a function of H_2 pressure: a reaction time of 5 h; b reaction time of 7 h

The analysis of Figure 5 shows that the increase in H_2 pressure favored the formation of hydrocarbons, increasing their selectivity values. The combination of high pressure (70 bar) with higher temperatures (340 ºC) made it possible to obtain a selectivity to hydrocarbons greater than 98 % in a minimum time (5 h). On the other hand, under reduced H_2 pressures, HDO occurred more slowly, demanding longer contact times of the reactional mixture in the reactor to obtain an efficient HDO. The use of a lower pressure of 30 bar, in general, was insufficient to achieve a selectivity to hydrocarbons of more than 40 % under all temperature and reaction time conditions tested. At the pressure of 30 bar, a selectivity to hydrocarbons greater than 80 % was obtained only at high temperature (340 ºC) and long reaction time (7 h). According to Kubicka, Simácek and Zilková,[27] the decrease in the pressure of H_2 limits the mass transfer of H_2 through the liquid film on the surface of the catalyst particle, thus reducing the availability of H_2 at the active sites and, consequently, decreasing deoxygenation rates and hydrocarbon production. In addition, the pressure of H_2 is a parameter known to influence the reaction path.[28] As reported in Peng *et al.*,[23] the increase in H_2 pressure may benefit the fatty acid hydrogenation step, which determines the HDO rate, thus increasing the overall HDO rate, as well as the selectivity to hydrogenation products. In relation to the obtained by-products, according to Table 4, the increase in H_2 pressure from 30 to 70 bar reduced the selectivity to these compounds for all temperatures and reaction times used, with the exception of wax esters. The selectivity to by-products was reduced by at least 5.49 % (at 300 ºC and 5 h) and by up to 59.98 % (at 340 ºC and 5 h), due to the increase in H_2 pressure. The tendency to reduce the selectivity to oxygenated by-products accompanied by the increase in H_2 pressure suggests that these compounds act as intermediates in the conversion of triglycerides, and that higher H_2 pressures benefited the subsequent HDO reactions of these intermediates, producing hydrocarbons as final products, as also reported in Kubicka, Simácek and Zilková.[27] Table 4 shows that the low temperature (300 ºC) favored the formation of wax esters, which presented high percentages, above 27 %, in all pressures and times employed. At this temperature, particularly, the increase in H_2 pressure, from 30 to 70 bar, led to an increase in selectivity to this class of by-products. The reduction in selectivity to oxygenated intermediates (fatty acids, fatty alcohols and wax esters) during HDO of vegetable oils, as a result of the increase in H_2 pressure and temperature, was also observed by Kubicka, Simácek and Zilková[27] and Anand and Sinha.[29]

Interaction among Variables: In this topic, the 2nd order interaction effects between the variables under study were graphically analyzed. Whenever the interaction effects are statistically significant in an analysis, it is not possible to interpret the main effects in isolation, without considering the interaction effects.[Error! Reference source not found.] As all the factors studied are involved in significant 2nd order interactions, only the interaction effects were evaluated, according to Figures 6, 7 and 8. In these graphs, since the response variable is the inverse of the selectivity to hydrocarbons, as one walks along the y axis "from top to bottom", the selectivity values increase. The graphs lead to conclude that, in all the evaluated interactions, a greater response is obtained when working simultaneously at the upper level (+1) of the two variables involved.

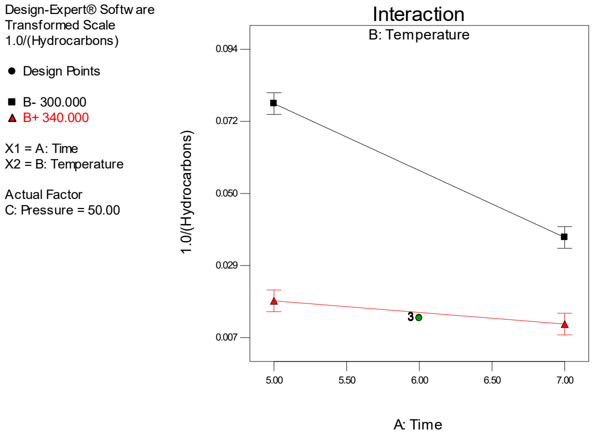

Figure 6. Graph of the interaction effects between time (A) and temperature (B) on selectivity to hydrocarbons

In Figure 6, the lines are not parallel. This indicates that the effect caused by the change in the level of factor A (time) in the response (selectivity to hydrocarbons) depends on the level of factor B (temperature) and, therefore, there is an interaction between factors A and B.

This result corroborates that obtained in the statistical analysis, according to which the AB interaction is significant ($p < 0.05$). As shown in the graph in Figure 6, the selectivity to hydrocarbons increases with the reaction time and with the temperature, being minimum (≈ 13 %) for the conditions of 5 h and 300 ºC and maximum (≈ 80 %) in 7 h and 340 ºC. It is observed that the lower the temperature, the greater the increase in selectivity caused by increases in reaction time.

The possibility of obtaining hydrocarbon percentages close to 80 %, even if intermediate H_2 pressures (50 bar) are employed, reaffirms the significance of the AB interaction effect. In addition, the steep slope of the upper straight line shows that, for the temperature of 300 ºC, the increase in reaction time increases significantly the selectivity obtained, while the gentle slope of the lower straight line indicates that, for the temperature of 340 ºC, the selectivity obtained with 5 h is already above 60 % (≈ 67 %), improving even more with the increase of the reaction time. The distance between the upper and lower straight lines reaffirms that temperature is a factor of high influence on selectivity to hydrocarbons so that the increase of this variable, from 300 ºC to 340 ºC, provided much higher selectivity values, regardless of the reaction time employed.

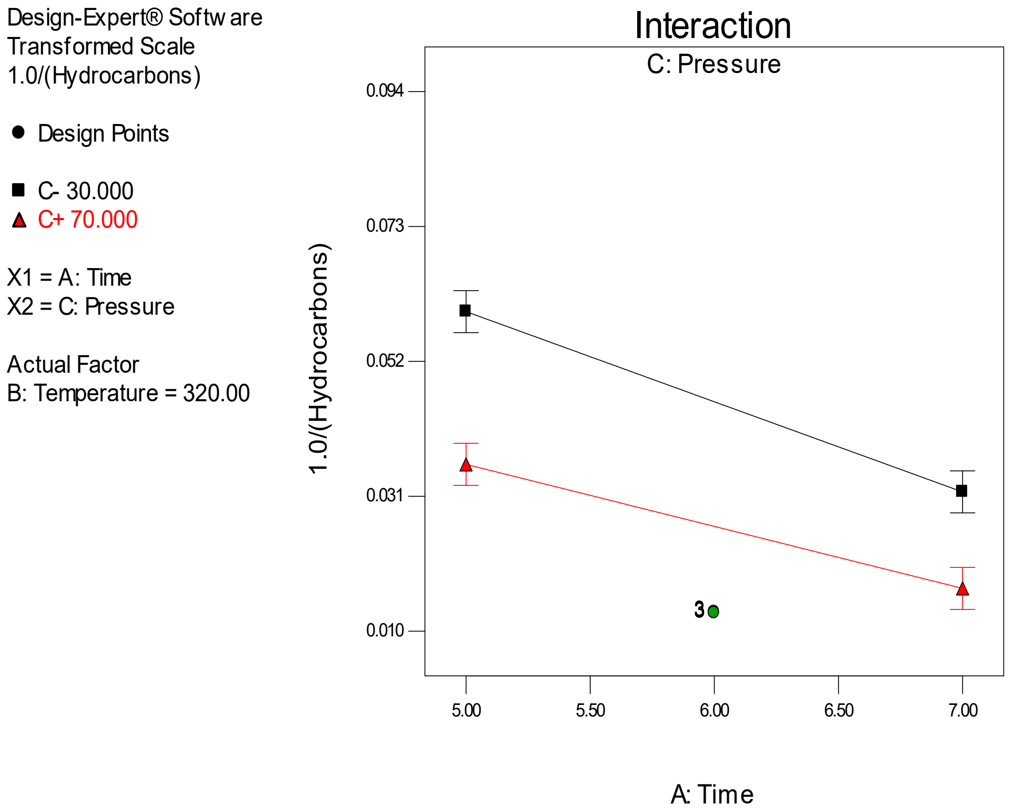

Figure 7. Graph of the interaction effects between time (A) and H_2 pressure (C) on selectivity to hydrocarbons

The position of the two straight lines in Figure 7, practically parallel, demonstrates that the effect caused by the change in factor A level (time) on the response (selectivity to hydrocarbons) is independent of factor C (H_2 pressure) and that, therefore, there is no significant interaction effect between such factors. This result confirms that the effect of AC interaction is not statistically significant ($p > 0.05$). According to the graph, at 320 ºC, the selectivity to hydrocarbons is minimal (≈ 17 %) under conditions of 5 h and 30 bar, and increments in the reaction time and in the pressure of H_2 increase the selectivity to hydrocarbons obtained.

The analysis of Figure 7 attests to the prominent influence of the temperature variable in obtaining the desired products. The performance of babassu oil HDO at an average temperature (320 ºC) provided a maximum hydrocarbon selectivity below 70 % (≈ 65 %), a result obtained when a high pressure of H_2 (70 bar) was combined with a long reaction time (7 h). Such observation also confirms the results already discussed in previous topics, in which it was verified that, based on the parameter of the associated model equation, the interaction term between the reaction time (A) and H_2 pressure (C) factors has the least significant contribution to hydrocarbon selectivity.

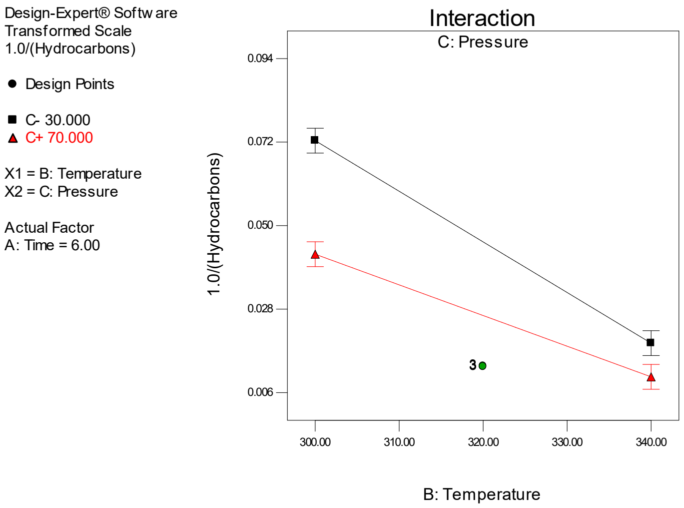

Figure 8. Graph of the interaction effects between temperature (B) and H_2 pressure (C) on selectivity to hydrocarbons

In Figure 8, the straight lines are not parallel, indicating that the effect caused by the change in the level of factor B (temperature) on the response (selectivity to hydrocarbons) depends on the level of factor C (pressure) and, therefore, there is interaction between factors B and C. In addition, ANOVA showed that the interaction effect between factors B and C is statistically significant ($p < 0.05$). The graph shows that increases in temperature and pressure lead to higher hydrocarbon selectivities, and the lower the pressure, the greater the gain in selectivity caused by increases in temperature. It is also noted that, in the studied intervals, with a reaction time of 6 h, the selectivity to hydrocarbons is minimal (≈ 14 %) under conditions of 300 ºC and 30 bar and maximum (≈ 90 %) at 340 ºC and 70 bar.

CONCLUSION

The fatty acids profile showed that babassu oil has triglycerides predominantly formed by saturated and monounsaturated fatty acids with 12 carbon atoms (44.58 %). Approximately 70 % of the fatty acids that make up the oil correspond to the fraction with the potential to produce hydrocarbons in the aviation biokerosene range (C9 - C15). The HDO reactions of babassu oil, in the presence of the NiMo/γ-Al_2O_3 catalyst, led to the production of the compounds of interest (hydrocarbons), also generating fatty acids, fatty alcohols, wax esters and fatty acid esters as by-products. The best result was obtained in the conditions of 340 ºC and 70 bar of H_2, in which a selectivity to hydrocarbons of 98.41 % was achieved, in a reaction time of 5 h. ANOVA showed that the model obtained is statistically significant and fits properly with the experimental data. According to the model, both the temperature, the pressure of H_2 and the reaction time significantly affected the selectivity to hydrocarbons ($p < 0.05$), with the temperature being the variable of greatest influence among the three studied ($p < 0,0001$). Attesting the importance of the temperature factor on the response, ANOVA showed that it was present in synergism between the factors that obtained statistically significant effects ($p < 0.05$): the reaction time - temperature interaction and the temperature - H_2 pressure interaction. Higher selectivities could be obtained when working simultaneously at the upper level (+ 1) of the two variables involved in an interaction, that is, 7 h of reaction, 340 ºC and 70 bar of H_2. The results obtained in this work point out the potential of using babassu oil as raw material for the production of renewable hydrocarbons in the aviation biokerosene range (C9 - C15), through the HDO process, and demonstrate the influence of reaction time, temperature and H_2 pressure conditions on obtaining such products.

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