RESEARCH ARTICLE **OPEN ACCESS**

HYDROLYSIS REACTION OF BRAZILIAN MACAUBA OIL USING USY ZEOLITE AND PHOSPHATED NIOBIA AS CATALYSTS

Yordanka Reyes Cruz[1], Vinicius Rossa[*1,2], Gisel Chenard Díaz[1], Darlis Adriana Varón Cárdenas[1], Germildo Juvenal Muchave[1], Winny Rego Cardoso[1] and Donato Alexandre Gomes Aranda[1]

[1]LaboratórioGreenTec, UFRJ, Av. Horácio Macedo, 2030, CEP: 21941-909. Rio de Janeiro, RJ, Brasil; [2]Grupo de Catálise e Biomassa, UFF, R. São João Batista, 2-188, CEP. 24020-141. Niterói, RJ, Brasil

---

ABSTRACT

The commercial use of macauba oil feasible and make it a desirable species, where the hydrolysis process of trilglycerides is a promising alternative for obtaining fatty acids. After hydrolysis, glycerin is removed and the fatty acids generated later can be used for the production of biodiesel. This research also innovates due to the challenge of using heterogeneous catalysts based on niobium oxide impregnated with phosphoric acid, which presented superior results in the hydrolysis process when compared with H-USY zeolite. It should be noted that the best catalytic performance has a straight relationship with the increase in acid characteristics acquired by such catalysts in the hydrolysis reaction, where it had conversions higher than 90%. In the conditions used in this work, we can conclude that the introduction of phosphoric acid in the reaction medium of Nb_2O_5 positively influences acidic, textural properties such as pore diameter and catalytic properties even at temperatures above 500°C, in addition to presenting high activity, selectivity. It is noteworthy that the phosphating process of niobic acid ($Nb_2O_5.nH_2O$) generated a much more active catalyst, H_3PO_4/Nb_2O_5.

INTRODUÇÃO

Macauba (Acrocomia aculeata) is a palm tree native to tropical forests. It is widely dispersed in Brazil and in neighboring countries such as Colombia, Bolivia and Paraguay. In Brazil, they occur widely spread over the Cerrado areas[1,2]. The fruit of macauba for the extraction of vegetable oil is the most important part of this palm, mainly for the productive potential that it has although all of it can be used: bark, pulp and almond[3,4]. Macauba oil is increasingly being valued by the national and international markets, as it presents high oil production. It is estimated that macaúba has productivity of 4,000kg of oil per hectare, which compares favorably with the productivity of palm oil, 6,500kg of oil per hectare[5]. Table 1 shows the average fatty acid composition present in the almond and in the pulp of macauba oil reported in the literature[6-8]. Currently, several projects are being developed with the objective of making the commercial use of viable macauba, making it even more attractive for the industrial sector. Current research includes: surveying the occurrence of native macauba clusters, using sustainable extraction practices to prevent rapid depletion of the energy source, and developing production systems with rational planting, genetic improvement, fertilization and spacing between plants[9-13].

Oleochemistry is the science that studies oils and fats and their possible modifications through chemical reactions, in products of higher added value. Oils and fats have long been used by humankind in soap and paint formulations, in candle making, in public and residential lighting, among others. However, recently, oleochemistry has been recovering its space as an excellent alternative to replace petroleum products in various sectors, such as polymers, fuels, printing inks, lubricants, cosmetics, among others[14]. Vegetable oils are composed of triglyceride molecules (TG), these molecules are esters formed from fatty acids and glycerol and correspond to 98% of the chemical composition of the oils. Each triglyceride contains three fatty acid chains attached to a glycerol molecule. These fatty acid chains can be saturated, monounsaturated and polyunsaturated. The acyl units, corresponding to fatty acids, represent approximately 95% of the molecular weight of triglycerides. The remaining portion consists of mono (MG) and diglycerides (DG), free fatty acids (AGL), phosphatides and lipid substances, such as sterols, carotenoids and waxes[15-25]. Triglycerides when hydrolysed generate compounds of high added value and of great interest to the cosmetics industry: monoglycerides, diglycerides, fatty acids and glycerol. The hydrolysis process of vegetable oils is of great importance for the oleochemical industry. The process can be carried out thermally as a liquid-liquid

(or gas-liquid) reaction or using a suitable catalyst[15]. The triglycerides hydrolysis is a reversible reaction, of the first order, that occurs in the oily phase. With three moles of water, one mole of triglyceride is divided into three moles of free fatty acids and one mole of glycerol. The reaction proceeds in three stages, which occur simultaneously, but at different speeds[16]. Initially, triglycerides (TG) are converted into diglycerides (DG) and free fatty acids (AGL), followed by monoglycerides (MG) and AGL and, finally, into AGL and glycerol[17].

Table 1. Average fatty acid composition of macauba parts

Fatty acids	Pulp	Almond
Caprylic	0.45	6.20
Capric	0.27	5.30
Lauric	1.97	43.6
Myristic	0.45	8.50
Palmitic	18.7	5.30
Palmitoleic	4.00	2.29
Stearic	2.80	2.40
Oleic	53.4	25.5
Linoleic	17.7	3.30
Linolenic	1.50	1.92
Saturated fatty acids	24.6	71.2
Unsaturated fatty acids	75.4	28.8

Adapted from [6-8].

The reaction temperature and the water-oil ratio are the two main parameters for optimizing the hydrolysis process[17]. The solubility of water in the oil phase[20], the concentration of glycerol in the aqueous phase[18] and the type of catalyst[16], are other important parameters that should receive greater attention during the hydrolysis reaction. Increasing the reaction temperature not only increases the rate of water diffusion in triglycerides but also increases the speed, leading to equilibrium. At temperatures close to 180°C, the water solubility in the oil phase is very low. In the range of 230-250°C, the oil phase may contain between 10-20% of dissolved water, which is sufficient for the reaction to occur[18]. The conventional hydrolysis process is usually carried out at temperatures between 100-280°C and pressures between 1-70bar, with water: oil ratio of 0.1 to 1.5 (w/w), with or without an acid catalyst. The process lasts from 2 to 48h and can be carried out with oils and/or fats in any content of fatty acids and moisture, as already mentioned, in addition to industrial and domestic waste[15,23]. The use of catalysts tends to considerably accelerate the hydrolysis reaction, in addition to allowing the process to be carried out under moderate conditions of temperature and pressure. The catalyst promotes higher solubilization of water in oil, in addition to more significant contact between reagents.

A smaller amount of fission occurs due to the action of water dissolved in the oil phase[21]. The characteristics of catalysts play an important role during the reaction, in general. The use of homogeneous catalysts presents, as the main disadvantages, the difficulty of separating the reaction medium and the impossibility of reuse, in most cases. Also, these catalysts can often be toxic and corrosive. One way of improvement would be through the use of heterogeneous catalysts. These materials have the advantage of significantly reducing the product purification stage, in addition to the possibility of reuse[22]. Recently studies have been developed reporting the use of heterogeneous acid catalysts for the hydrolysis reaction. The advantages of these catalysts are the ease of removal after the process and the possibility of reuse, in addition to reducing the reaction time. Some examples are SAC-13 and tungstenized zirconia[23], double metal cyanide catalysts, polymeric resins, zeolites, oxides and sulfated zirconia[22]. The use of catalysts tends to considerably accelerate the hydrolysis reaction, in addition to allowing the process to be carried out under moderate conditions of temperature and pressure. The catalyst promotes higher solubilization of water in oil, in addition to more significant contact between reagents. A smaller amount of fission occurs due to the action of water dissolved in the oil phase[21]. The characteristics of catalysts play an important role during the reaction, in general. The use of homogeneous catalysts presents, as the main disadvantages, the

difficulty of separating the reaction medium and the impossibility of reuse, in most cases. Also, these catalysts can often be toxic and corrosive. One way of improvement would be through the use of heterogeneous catalysts. These materials have the advantage of significantly reducing the product purification stage, in addition to the possibility of reuse[22]. Recently studies have been developed reporting the use of heterogeneous acid catalysts for the hydrolysis reaction. The advantages of these catalysts are the ease of removal after the process and the possibility of reuse, in addition to reducing the reaction time. Some examples are SAC-13 and tungstenized zirconia[23], double metal cyanide catalysts, polymeric resins, zeolites, oxides and sulfated zirconia[22].

The batch process, using autoclaves, is the oldest commercial method used for the hydrolysis reaction. In this process, pressures ranging between 10-30 bar and temperatures between 180-230°C are used[18]. Generally, a catalyst is used, such as ZnO or CaO[24]. Stirring is done by injecting superheated steam to promote surface contact between the fat/oil and the water. Over 95% conversion can be achieved, around 6-10 h. However, the process has some disadvantages, such as the possible formation of soap, due to the metallic species present in the catalyst, in addition to the high consumption of steam[15,18]. In the oleochemical industry are generally used, with temperatures between 100- 280°C and pressures around 70 bar. Typically, the yield of chemical hydrolysis is over 97%. Subsequently, the final mixture must be distilled to remove the by-products formed during the reaction[21]. The product of the hydrolysis reaction consists of two layers: one less dense (oily) that can be composed of free fatty acids (AGL), mono (MG), di (DG) and triglycerides (TG), non-polar phase; and a denser layer, consisting of water and glycerol, polar phase. These phases can be separated with a separating funnel, or by centrifugation[22]. Glycerol can be separated from water by vacuum distillation. Free fatty acids, on the other hand, are usually subjected to physical purification processes, such as simple or fractional distillation, solidification and pressing, fractional crystallization (direct or in solvents). After the purification process, they can have direct application in the industry or be subjected to various chemical transformation processes[25].

In this work, USY zeolite and phosphated niobia (H_3PO_4/Nb_2O_5) were used as catalysts for the hydrolysis reaction of macauba oil. Most of the results found in the literature indicate that the acid strength of zeolites is comparable to 90% sulfuric acid solutions. Koltunov and Sobolev (2008), even concluded that the acid strength of the studied H-USY zeolites was equal to that provided by sulfuric acid for the cleavage of cumene hydroperoxide, for the formation of phenol and acetone. Phosphated niobia (H_3PO_4/Nb_2O_5), in addition to presenting high catalytic activity, selectivity and stability similar to niobic acid, has a greater acid strength ($H_0 \leq -8.2$), equivalent to 90% of that found in sulfuric acid (H_2SO_4), and its acidic and catalytic surface properties have been widely reported in the literature[26-35, 51].

RESULTS AND DISCUSSION

The catalysts chemical compositions were determined by the X-ray Fluorescence (FRX), the results was presented in Table 2 for H-USY zeolite and niobia phospateted (H_3PO_4/Nb_2O_5). The niobic acid analysis was performed to compare the effect of your impregnation with phosphoric acid (H_3PO_4) on material.

Table 2. Solids chemical composition by FRX, H-USY zeolite was calcined at 450°C for 5h, H_3PO_4/Nb_2O_5 was calcined at 300°C for 3h and $Nb_2O_5.nH_2O$ was dried at 100°C and uncalcined

Composition (%)	H-USY	$Nb_2O_5.nH_2O$	H_3PO_4/Nb_2O_5
SiO_2	97.10	-	-
Al_2O_3	1.68	-	-
Nb_2O_5	-	98.00	65.50
P_2O_5	-	-	23.30
Impurities	1.22	2.00	11.20
SAR*	98	-	-

*SAR: silica alumina ratio.

As showed in the Table 2 the solids chemical composition was approximated to nominal value and the slight divergences may be related to impurities present during the industrial process and/or due to losses during preparation in the case of phosphatetedniobia. Impurities as Fe_2O_3 and CaO were found in the solids. The technique utilized to prepare phosphatetednióbia was effective and can significantly influence the solids acid properties for used as catalyst. The Figure 1 showed the X-ray diffractograms of H-USY zeolite and phosphatetedniobia solids. In phosphateted niobium (H_3PO_4/Nb_2O_5) diffractogram only two intense bands in the range of $2\theta=15-40°$ and $2\theta=40-60°$ are observed, which indicates the amorphous nature of its pores according to the literature[36]. An expected result, since phosphated niobia prepared at the right molar ratio can conserve its amorphous phase and prevent crystallization of Nb_2O_5, even at high temperatures[37]. Non-crystalline phases $H_4P_2O_7$ and Nb_2O_5 were detected in these samples. For the H-USY zeolite show peaks regarding the faujasite type structure, presenting in the diffractometric pattern intense reflections at $2\theta = 6.2°$ (14.16 Å), 15.6° (5.69 Å), 23.5° (3.79 Å), 26.8° (3.32 Å) and 31.1° (2.87 Å), showing similarity to those found for NaY zeolite (ICCD).

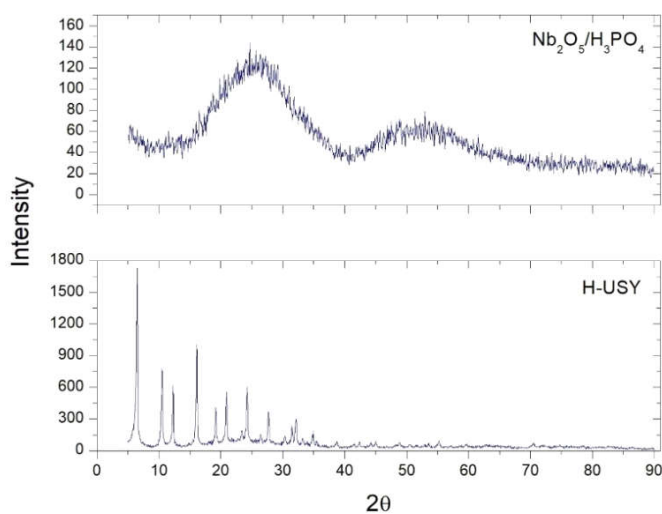**Figure 1. Solids structural analysis by DRX, H-USY zeolite was calcined at 450°C for 5h and H_3PO_4/Nb_2O_5 was calcined at 300°C for 3h**

Table 3 presented the relevant information obtained with the aid of this technique, such as: the superficial área, determined from the data obtained by B.E.T. method with adsorption values. The average pore diameter and the pore volume of the solids analyzed determined by the BJH method with dessorption values.

Table 3. Characteristics textural values, H-USY zeolite was calcined at 450°C for 5h, H_3PO_4/Nb_2O_5 was calcined at 300°C for 3h

Characteristics	H-USY	Nb_2O_5/H_3PO_4
Area BET [m²/g]	768	204
Area EXTERNAL [m²/g]	273	199
Volume MICROPOROS [cm³/g]	0.22	0.003
Volume BJH/DES [cm³/g]	0.12	0.28
Pore Size BET [nm]	2.20	5.10
Pore Size BJH/DES [nm]	4.40	4.80

Note that the zeolite H-USY had a high pore diameter (maximum peak at 5 nm). In H_3PO_4/Nb_2O_5, this region is more concentrated in pores between 2.5 and 5 nm. The value of the specific area was calculated by the BET equation, whose model is the most accepted to interpret the adsorption and desorption isotherms, from the formation of a monolayer of the adsorbed gas on the outer surface and the pores of the particles. For the determination of pore size distribution, the method proposed by Barret, Joyner and Halenda (BJH) was used, whose calculations are based on the Kelvin equation and are valid for different pore formats[38]. All these calculations were performed by the equipment software itself. Figure 2 shows the pore size distribution of solids.
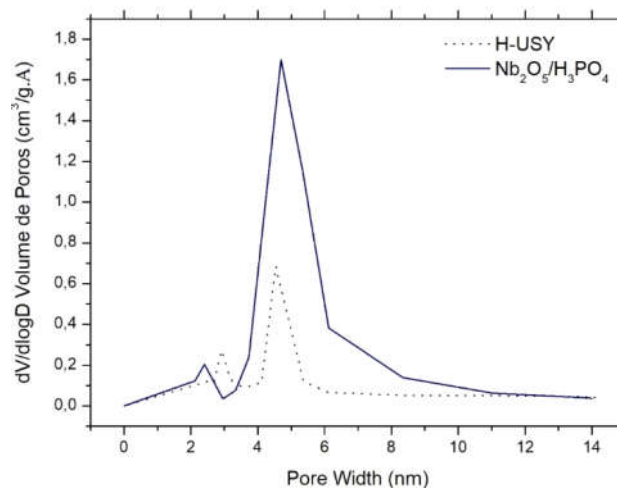

Figure 2. Pore size distribution, H-USY zeolite was calcined at 450°C for 5h, H_3PO_4/Nb_2O_5 was calcined at 300°C for 3h

In textural analysis there are two important properties for solids to be used in heterogeneous catalysis because, while specific area influences the amount ofavailable active sites of a solid catalyst, the geometry and pore volume control transport phenomena and can determine the selectivity in catalytic reactions. Ammonia is often used as a probe molecule in acidity analyses because it has small molecular size, is stable, and possesses strong basic strength. The NH_3 thermoprogrammed desorption results of the H-USY and H_3PO_4/Nb_2O_5 are shown in Table 4.

Table 4. Characteristics textural values, H-USY zeolite was calcined at 450°C for 5h, H_3PO_4/Nb_2O_5 was calcined at 300°C for 3h

Solids	Acid Sites (μmol NH_3/g_{cat})			
	weak	Strong	Total	Strong:weak
H-USY	43.68	107.32	151.00	2.46
H_3PO_4/Nb_2O_5	868.42	371.58	1240.00	0.43

The H_3PO_4/Nb_2O_5 had the superior acid sites quantity (1240 μmol NH_3/g_{cat}), a smaller ratio of the Strong:weak sites (0.43 μmol NH_3/g_{cat}) and a smaller acid strength than the H-USY zeolite, since this characteristic can contribute to a higher catalytic activity of the H_3PO_4/Nb_2O_5 for hydrolysis reaction.

Macauba Oil Characterization: The physicochemical properties of macauba oil are presented in Table 5. The iodine index of macauba oil agrees with its chemical composition data, due to the majority presence of monounsaturated and polyunsaturated carbon chains. The saponification index found was high, showing that the oil has a high saponificable content, similar to other vegetable oils, such as soybean oil (177.8 mg KOH g^{-1}) and andiroba (193.84 mg KOH g^{-1}). It was also observed that, due to the peroxide index result, the oil apparently was partially degraded, since the reference[39] value cannot be higher than 10 meq kg^{-1}. The kinematic viscosity presented a value allowed by the reference[39]. According to, the viscosity increases with the length of the triglyceride fatty acid carbon chains and decreases when the unsaturation increases[39].

Table 5. Physicochemical characterization of macauba oil

Parameters	Macauba Oil	Method
Acidity index	79.6 mg KOH g^{-1}	AOCS Cd 3d-63
Free fatty acids	35.4%	AOCS Ca 5a-40
Saponification Index	198.1 mg KOH g^{-1}	ASTM D-94
Iodine Index	86.10 g I_2 .100g^{-1}	EN ISO 14111
Peroxide index	10 meq Kg^{-1} oil	ISO 3960
Viscosity at 40ºC	31.73 mm² s^{-1}	ASTM D-445
Oxidation Stability	1.72h	EN 14112
Density at 25°C	911.6 Kg m^{-3}	ASTM D-1298
Water	3130ppm	ASTM D-6304
Ashes	0.22%	ABNT NBR 9842
Fusion point	25°C	AOCS Cc 1 –25

Experimental Design and Statiscal Analysis: The Table 6 showed the 2^{3-0} design experiments array of central rotatable composite design and the response to fatty acid yield using H-USY and H_3PO_4/Nb_2O_5 as catalysts in the tryglycerides hydrolysis reactions. Were calculated values all effects values. their interactions and standard error for macauba oil fatty acids as a function of fatty acid conversion (%) are presented in Table 6. Yields were estimated using the oleic acid acid index (control) of 198.04 mg KOH g^{-1} (experimentally obtained value) and the macauba oil acidity index of 79.6 mg KOH g^{-1} (according to the characterization chemical structure).

Table 6. Design experiments array of central rotatable composite design (CCRD) and the response to fatty acid yield using H-USY and H_3PO_4/Nb_2O_5 as catalyst in the triglyceride hydrolysis reactions

Reactions	T (°C)	w_{cat} (%)	MR (W:O)	FA Yield (%) H-USY	FA Yield (%) H_3PO_4/Nb_2O_5
1	182	5	6	31.38	26.51
2	182	5	12	24.36	33.62
3	182	19	6	32.72	26.98
4	182	19	12	28.10	26.49
5	270	5	6	45.14	36.60
6	270	5	12	64.30	53.98
7	270	19	6	70.26	63.72
8	270	19	12	80.12	79.30
9	152	12	9	37.16	14.49
10	300	12	9	83.62	85.04
11	226	0	9	55.20	53.95
12	226	24	9	71.82	49.27
13	226	12	4	31.39	34.81
14	226	12	14	55.45	49.51
15	226	12	9	51.53	50.89
16	226	12	9	50.46	49.76
17	226	12	9	49.33	51.53
18	226	12	9	51.37	52.71
19	226	12	9	50.60	26.51

Since the intention of the experimental design was to detect the relative importance of the effects and to verify the possibility of eliminating factors that were not statistically relevant. The effects and interactions of the variables that did not have a 95% significance in fatty acid conversion were ignored. Only maintaining significant and marginally significant effects.

Table 7. Effects valuefor central rotatable composite design (CCRD) and the response to fatty acid yield using H-USY and H_3PO_4/Nb_2O_5as catalysts in the triglyceride hydrolysis reactions
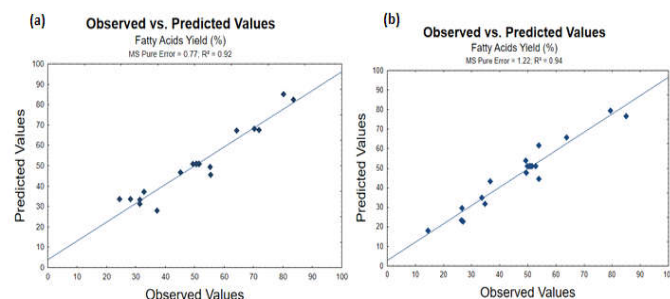
H-USY				
Factor	Effects	Std.Err. Pure Err	t(4)	p-value
Mean/Interc.	51.0080	0.3916	130.2713	2.08E-08
Temperature (°C) L	32.4227	0.4744	68.3454	2.75E-07
Temperature (°C) Q	3.0281	0.4745	6.3816	3.09E-03
w_{cat} (%) L	10.8329	0.4744	22.8351	2.18E-05
w_{cat} (%) Q	5.2343	0.4745	11.0310	3.84E-04
MR (W:O) L	8.4710	0.4744	17.8565	5.78E-05
MR (W:O) Q	-8.9715	0.4745	-18.9068	4.61E-05
1 by 2	8.9650	0.6198	14.4637	1.33E-04
1 by 3	10.1650	0.6198	16.3997	8.09E-05
2 by 3	-1.7250	0.6198	-2.7830	4.97E-02
H_3PO_4/Nb_2O_5				
Factor	Effects	Std.Err. Pure Err	t(4)	p-value
Mean/Interc.	51.2625	0.4927	104.0421	5.12E-08
Temperature (°C) L	34.9496	0.5970	58.5465	5.10E-07
Temperature (°C) Q	-2.7540	0.5971	-4.6123	9.94E-03
w_{cat} (%) L	5.5517	0.5970	9.3000	7.44E-04
w_{cat} (%) Q	-1.4494	0.5971	-2.4274	7.22E-02
MR (W:O) L	9.4169	0.5970	15.7748	9.44E-05
MR (W:O) Q	-8.1315	0.5971	-13.6184	1.68E-04
1 by 2	14.7750	0.7800	18.9433	4.57E-05
1 by 3	6.5850	0.7800	8.4428	1.08E-03
2 by 3	-2.3500	0.7800	-3.0130	3.94E-02

Thus, the factors ignored in the model are incorporated in the lack of fit model. The effects values obtained from experimental design for the yield (%) of fatty acids, of linear and quadratic effects indicates how large the effect must be to have statistical significance. Variables with positive values indicate that increasing their levels provides a higher conversion (%), and negative values inversely. Was showed in the Table 5, for the H-USY and H_3PO_4/Nb_2O_5 catalysts the variable that most interferes with the fatty acids yield was the temperature. Note that the variables and interactions were statistically significant, as they presented p-value <5,00E-02. This is because only significant factors were considered, *i.e.,* those that had na influence on the response variable. The Variance Analysis (ANOVA) for assessing the fit quality of the model for both catalysts are presented in Table 8. For the model applied the determination coefficients (R^2) was 0.92 for H-USY and 0.94 for H_3PO_4/Nb_2O_5 catalysts. By the Fisher Test it was observed that the regression model analyzes were significant, since the F calculated values are higher than the F tabulated ($F_{cal}>F_{tab}$) and there is no need for a new adjustment in the model.

Table 8. Variance Analysis (ANOVA) results for assessing the fit quality of the model in the triglyceride hydrolysis reactions using H-USY and H3PO4/Nb2O5 as catalysts

H-USY ($R^2 = 0.92$)					
ANOVA	QS	DF	QM	Fcal	Ftab
Regression	5076.13	9	564.01	12.06	3.18
Residues	420.80	9	46.75		
Lack of Fit	417.73	5	83.54		
Pure Error	3.07	4	0.77		
Total	5496.93	18			
H_3PO_4/Nb_2O_5 ($R^2 =0.94$)					
ANOVA	QS	DF	QM	Fcal	Ftab
Regression	5346.87	9	594.10	15.11	3.18
Residues	353.76	9	39.31		
Lack of Fit	348.89	5	69.78		
Pure Error	4.87	4	1.22		
Total	5700.63	18			

To assess the adequacy of the adjustment performed, it was also verified whether the hypotheses of normality of the residuals are satisfied, as shown in Figure 3. Analyzing the graphs of the Figure 3 it can be concluded that the residuals of the adjusted model follow normal distribution, since it is observed that the points approach the line. The adjusted multiple linear regression equations obtained from the regression coefficient valuescalculated for the yields was obtained in the macauba oil hydrolysis reactions for both catalysts in the specific experimental region only are presented in equations 1 and 2. The variations in fatty acid yield (%) can be explained by the adjusted model, It can also be said that the regression models are significant and can be used for approximate purposes as long as it is limited to the experimental range.
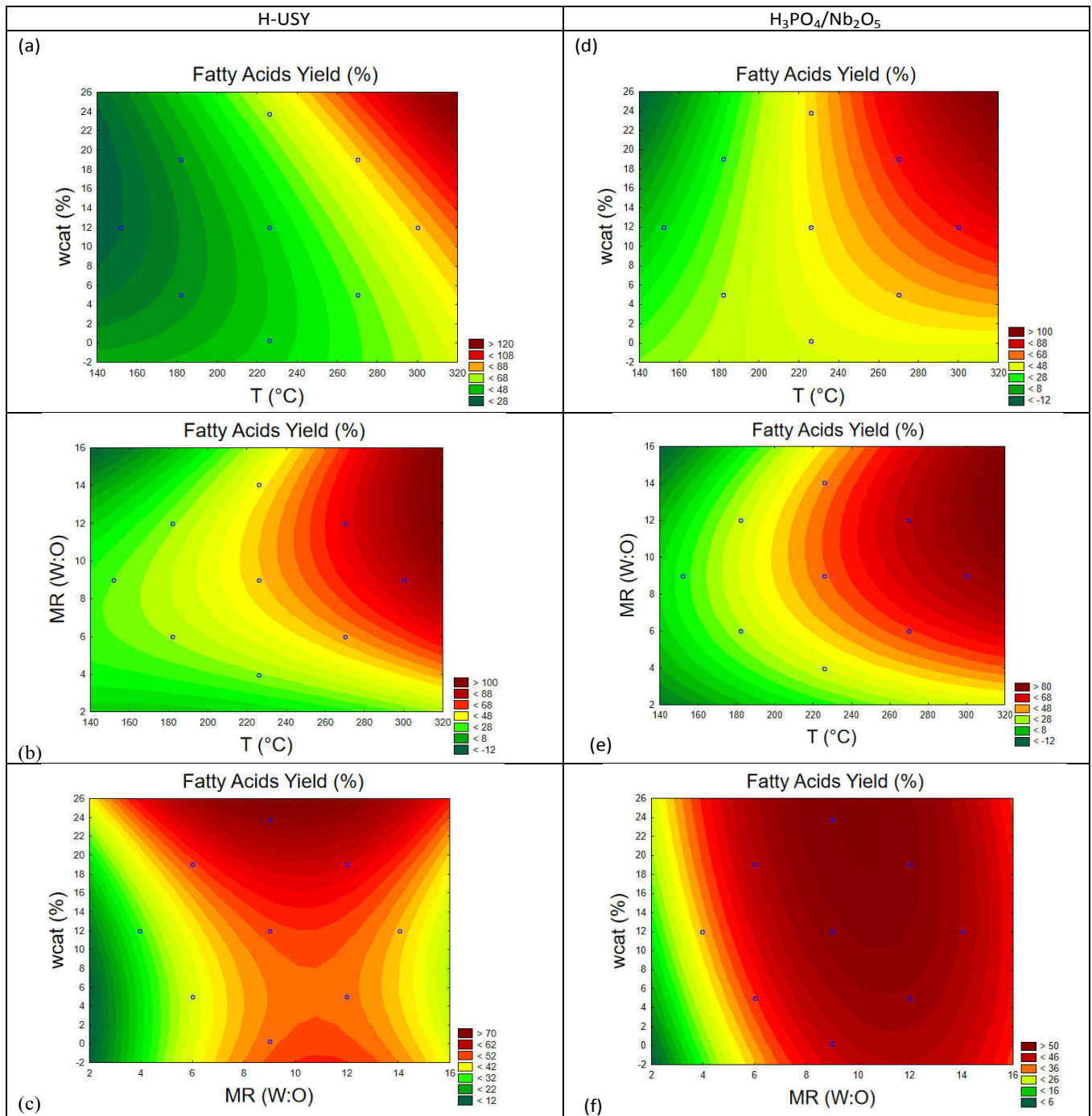

Figure 3. Predict and observed values of fatty acids yields when was used (a) H-USY and (b) H_3PO_4/Nb_2O_5catalysts

H-USY:

$$FA = 66.32-0.51(T)-3.42(C)+2.17(MR)+0.0008(T^2)+0.05(C^2)-0.50(MR^2)+0.01(T\cdot C)+0.04(T.MR)-0.04(C\cdot MR)$$
Eq. (1)

Figure 4. Predict and observed values of fatty acids yields when was used (a) H-USY and (b) H_3PO_4/Nb_2O_5 catalysts

H_3PO_4/Nb_2O_5:

FA = -22.69-0.21(T)-4.16(C)+7.73(MR)-0.0007(T^2)+ 0.01(C^2)-0.45(MR^2)+0.02(T·C)+0.02(T.MR)-0.06(C·MR)
Eq. (2)

The Figure 4 show the contour curves for fatty acid yields (%) using H-USY and H_3PO_4/Nb_2O_5 as catalyst.

Contour curves show fatty acid yields (%) for the variables studied. When the catalyst interacts with temperature, Figure 4a, at 300°C and 24% H-USY catalyst, 70% fatty acid yield is obtained. Figure 4b, refers to the interaction between temperature and water: oil molar ratio, when these variables were crossed, 88% yield was obtained for temperatures above 300°C and 9:1 (water:oil) molar ratio. Interactions of the amount of catalyst with the molar ratio (24% H-USY and 9:1 water:oil molar ratio) showed 70% fatty acid yield, Figure 4c. Contour curves show fatty acid yields (%). When the catalyst interacts with temperature, Figure 4d, at 300°C and 12% H_3PO_4/Nb_2O_5

catalyst, 68% fatty acid yield is obtained. Figure 4e, refers to the interaction between temperature and water:oil molar ratio, when these variables were crossed, 80% yield was obtained for temperatures above 300°C and 9: 1 water: oil molar ratio. Interactions of the amount of catalyst with the molar ratio (24% H_3PO_4/Nb_2O_5 and 9:1 water:oil molar ratio yielded 50% fatty acid yield, Figure 4f. According to the results the highest fatty acid yields (%) are obtained for both catalysts when the higher levels of the temperature and catalyst content variables and the central point of the water:oil molar ratio variable are used. In fact, when higher temperatures and higher catalyst concentrations are used the yields are higher. However, increasing the levels of these factors to obtain an optimal result was not possible because conditions above those imposed in this study for temperature and catalyst concentration could not be used in an industrial process. hydrolysis for economic and energy reasons. Thus, it was considered that the highest conversion (%) of fatty acids in the hydrolysis of macauba oil is obtained when using the following conditional ranges: water:oil 9:1 molar ratio, 24% catalyst

temperature and 300°C. With the conditions of the macauba oil hydrolysis process determined, the reaction kinetic study was performed.
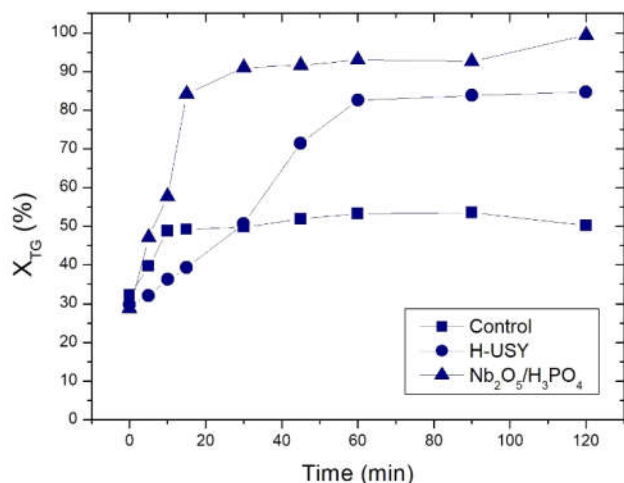

Figure 5. Kinetic curve hydrolysis reaction when used H-USY and H₃PO₄/Nb2O5catalysts.

Kinetic Study: The Figure 5 showed the macauba oil (triglycerides - X_{TG}) conversion (%) versus time (min), it is clear that both catalysts were active, with higher conversions than the reaction conducted in the absence of catalyst (control). In addition, the results also show that H_3PO_4/Nb_2O_5 was the catalyst that showed the highest activity to convert macauba oil triglycerides to fatty acids (around 99%) with 2h of reaction, when compared to H-USY and the control reaction. The reaction activity waswell correlated with the total acidity results of the catalyst, considering thatthe phosphate niobium (H_3PO_4/Nb_2O_5), showed much higher acidity than H-USY zeolite and the surface catalytic activity of phosphated niobium (H_3PO_4/Nb_2O_5), as it is considered an important water-tolerance Lewis acid sites in solid[36-32]. According to studies reported by several authors on the NbO_6 distorted octahedral structure of niobic acid, Nb=O bonds are highly polarizable, so that a portion of the OH groups on the surface acts as Brönsted acid. While the octahedral structure NbO_4 functions as Lewis acid sites[40,41,51] and rapidly forms NbO_4-H_2O complexes in the presence of water. Such active and inactive complexes attribute differences to the surrounding environment of NbO_4 tetrahedra, but do not influence the effectiveness of Lewis acid site density or catalytic activity[42]. According to Prasetyoko (2008) there are H_3O^+ ions and H_2O–OH species, and there is a continuous increase in the concentration of H_3O^+ ions with the number of water molecules. For example, at full hydration 50% of acid sites become ionized, so only one in two acid sites is strong[43].

Table 9. Yield of the vacuum distilled fatty acid purification

Hydrolysis*		Vacuum distillation		
Catalyst	Reaction time (min)	Initial fatty acid mass (g)	Final fatty acid mass after purification (g)	η (%)
H-USY	120	262.15 ± 16.89	216.7 ± 14.99	82.65 ± 0.35
H_3PO_4/Nb_2O_5	120	256.9 ± 8.91	239.55 ± 8.55	93.35 ± 0.07

*Reaction conditions: Catalyst concentration: 24%; Molar ratio water: oil 1:9; Temperature: 300°C.

Table 10. Glycerides compositions (%) in purified and esterified fatty acid samples obtained from hydrolysis in the best non-catalytic reaction condition and using the H-USY zeolite and H_3PO_4/Nb_2O_5 catalysts after 120 min

Glycerides (%)	H-USY	H_3PO_4/Nb_2O_5	CONTROL
Triglycerides	0.039± 0.002	0.010± 0.002	0.110± 0.000
Diglycerides	0.111± 0.000	0.039± 0.001	0.123± 0.001
Monoglycerides	0.264± 0.002	0.250± 0.002	0.258± 0.001
Free Glycerol	0.006± 0.001	0.006± 0.001	0.001± 0.000
Total Glycerine	0.418± 0.001	0.305± 0.001	0.492± 0.001

Table 11. Comparison of fatty acid composition (%) between macauba oil prepared by the Hartman and Lago method (1973) and samples after 120min hydrolysis reactions: with the application of H-USY and H_3PO_4/Nb_2O_5 catalysts after 120 min

Free Fatty Acids	Composition (%)			
	Macauba Oil	H-USY	H_3PO_4/Nb_2O_5	CONTROL
C6:0	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.00 ± 0.00
C8:0	0.10 ± 0.01	0.01 ± 0.00	0.03 ± 0.01	0.14 ± 0.01
C10:0	0.44 ± 0.02	0.26 ± 0.01	0.09 ± 0.00	0.12 ± 0.00
C12:0	1.01 ± 0.01	1.43 ± 0.01	1.08 ± 0.02	1.18 ± 0.00
C14:0	0.39 ± 0.01	1.05 ± 0.01	0.29 ± 0.01	0.85 ± 0.01
C16:0	15.5 ± 0.01	30.3 ± 0.02	13.5 ± 0.02	26.5 ± 0.02
C16:1	2.40 ± 0.01	0.59 ± 0.01	1.10 ± 0.00	0.79 ± 0.01
C18:0	1.22 ± 0.02	6.34 ± 0.01	1.08 ± 0.00	7.52 ± 0.02
C18:1-cis (n9)	43.3 ± 0.03	40.0 ± 0.01	33.5 ± 0.02	50.5 ± 0.03
C18:1-cis (n11)	2.50 ± 0.02	2.16 ± 0.02	1.06 ± 0.00	0.69 ± 0.02
C18:2-cis (n6)	12.3 ± 0.02	2.06 ± 0.02	1.03 ± 0.01	0.82 ± 0.01
a-C18:3 (n3)	0.73 ± 0.01	0.19 ± 0.01	0.02 ± 0.01	0.27 ± 0.01
C20:0	0.09 ± 0.01	0.12 ± 0.00	0.11 ± 0.00	0.08 ± 0.00
C20:1 (n9)	0.06 ± 0.01	0.04 ± 0.01	0.01 ± 0.00	0.01 ± 0.00
C20:2 (n6)	0.09 ± 0.01	0.12 ± 0.02	0.01 ± 0.00	0.05 ± 0.00
C20:4 (n6)	0.00 ± 0.00	0.01 ± 0.00	0.03 ± 0.00	0.09 ± 0.01
C22:0	0.05 ± 0.01	0.26 ± 0.01	0.01 ± 0.00	0.14 ± 0.01
C22:2 (n6)	0.27 ± 0.02	0.09 ± 0.01	0.01 ± 0.01	0.17 ± 0.01
C24:0	0.06 ± 0.01	0.12 ± 0.01	0.04 ± 0.00	0.15 ± 0.00
C24:1 (n9)	0.45 ± 0.01	0.14 ± 0.02	0.18 ± 0.02	0.66 ± 0.00
Saturated Fatty Acids	18.90	39.90	36.70	16.30
Monounsaturated Fatty Acids	48.80	42.90	52.70	35.80
Polyunsaturated Fatty Acids	13.40	2.46	1.40	1.11
Others	18.90	14.80	8.20	-
Average molar mass of free fatty acids	222.3 g/mol	231.0 g/mol	248.2 g/mol	145.2 g/mol

In contrast, when zeolites are used as heterogeneous catalysts in liquid media, affinities for this liquid can have a negative or positive influence on the type of substrate that will have access to the active site within channels and cavities. In this case, zeolite functions as a "solvent within a solvent", extracting substrate molecules from the liquid phase only if there is compatibility between the physicochemical characteristics of the zeolite with the substrate[44]. Therefore, in addition to the appropriate pore size, the water affinities (hydrophilicity) of the substrate and zeolite must be coincident[45,46]. Thus, in the hydrolysis reaction, the affinities by water possibly exerted anegative influence on the active sites, which hindered the diffusion of reagents and products, justifying the lower fatty acid conversion observed.

Products Characterization: From Table 9 it can be seen that among the tests, the best purification results were obtained with the phosphate niobium catalyst (H_3PO_4/Nb_2O_5). This result is consistent with the higher fatty acid conversions obtained in hydrolysis reactions. Finally, the results obtained allow us to conclude that the method used was efficient. Purification as an esterification step allows residual contaminants as well as unreacted glycerides (mono-, di- and tri- glycerides) to be minimized as much as possible. In the results of free glycerol content, total, mono, di and triglycerides in Table 10, it is evident that the hydrolysis reaction catalyzed by phosphatedniobia (H_3PO_4/Nb_2O_5) was the one that presented the lowest remaining triglycerides content (0.010%). In addition, it was possible to prove the efficiency regarding the purification of fatty acids, since the results obtained remained at maximum levels of 0.006% free glycerin. Fatty acid yields result (%) for hydrolyzed samples after Hartman and Lago esterification method application are listed in Table 11. Twenty fatty acids were quantified the main ones being: oleic acid, which ranged from 33.5% to 53.5%, and palmitic acid, with value between 13.5% and 30.3%. In order to evaluate the effect of the hydrolysis reaction on the fatty acids constituting the crude macauba oil, a sample of the vegetable oil was also prepared according to the method proposed by Hartman and Lago (1973)[47] and quantified in relation to the internal tricosanoate standard. Comparing the fatty acid composition of macauba oil with the fatty acid composition obtained in the hydrolysis reactions (catalytic and non-catalytic), a decrease in the percentage of polyunsaturated fatty acids is observed, mainly for linoleic acid C18:2-cis (n6). When analyzing the experiments performed with the application of catalysts, the behaviour between the produced fatty acids is very similar. There is a significant increase in palmitic acid contents, with the highest yields in 120min. Note also the significant presence of low molecular weight fatty acids such as C10:0, C8:0 and C6:0. Similarly, the results confirm the high content of saturated and monounsaturated fatty acids, mainly due to the high content of oleic acid. The highest yields of oleic acid were obtained with the phosphate niobium catalyst (H_3PO_4/Nb_2O_5). These results favour the oxidative stability of the oil for biodieselproduction, but depending on the temperature crystallization of saturated methyl esters may occur during storage.

Experimental

Macauba Oil Analysis: The pulp macauba crude oil was supplied from Brazil by the RiachoD'antas Small Rural Workers Association.The purchased oil was stored in plastic packaging at 27°C until the beginning of the experiments. The macaúba oil was characterized by acidity index was (mg KOH g^{-1}) was determined following AOCS (American Oil Chemists' Society) Cd 3d-63 standard. Free fatty acids (%) was determined following the AOCS Ca 5a-40 standard. The water content was obtained by titration according to Karl Fischer method (Schott, Tritoline KF model), using the official ASTM D-6304 method. Saponification Index (mg KOH g^{-1}) was determined following the AOCS Cd 3-25 standard. Iodine index (g of I_2 $100g^{-1}$) was determined following AOCS Cd 1–25 standard. Peroxide Index (meq kg^{-1}) was determined following the ISO 3960 standard. Oxidation stability (h) used following EN14112 standard in Rancimat equipment. Kinematic Viscosity at 40°C (mm^2 s^{-1}) was determined following ASTM D-445. Relative density at 25°C (kg m^{-3}) was determined following ASTM D-1298. The melting point

(°C) was determined by the capillary method following AOCS Cc 1–25. Ash (%) determination was made following AOCS Ca 11 –55 standard.

Preparation and characterization of the Solids for Use as Catalysts: The phosphated niobia (H_3PO_4/Nb_2O_5) used in this work was prepared by the wet impregnation methodology and the commercial H-USY zeolite (Si/Al molar ratio = 60) was purchased from Zeolyst International. Phosphateted niobia (H_3PO_4/Nb_2O_5) was prepared from the impregnation of CBMM-supplied niobic acid (HY-340) with a 1.0M aqueous phosphoric acid solution (85%, Vetec). The H_3PO_4 impregnation in niobic acid was described by Dos Santos (1999)[48]. A suspension was prepared in which 15mL of 1.0M aqueous phosphoric acid solution was added to each gram of niobium oxide in the form $Nb_2O_5.nH_2O$. This suspension was stirred for 48h, then centrifuged and dried in an oven at 100°C for approximately 12h. Immediately afterwards it was calcined for 3h at a temperature of 300°C using a heating ramp of 10°C min^{-1}. H-USY zeolite (CBV760) in acidic form (H^+) was only calcined at a temperature of 450°C for 5h using a heating ramp of 5°C min^{-1}. To determine the chemical composition of the solids, the X-ray fluorescence technique (FRX) was used by BRUKER model S4 Explorer spectrometer with rhodium (Rh) X-ray tube was used. For the analysis, the calcined samples were pressed in tablet form. The crystallinity analysis of the compounds was performed by X-ray diffraction technique, using a Rigaku Miniflex II X-ray diffractometer, with CuK radiation (30 kV and 15 mA). The established conditions were: 0.05° angular step scan and 5°<2θ<90° intervals, using a counting time of 1s per step. Phase identification was based on data from the International Center for Diffraction Data (ICDD) Powder Diffraction. In order to obtain the textural properties of the catalysts (surface area, pore volume, etc.), N_2 physisorption measurements were performed, with the specific area being obtained by the BET method (Brunauer, Emmet and Teller). The analysiswere performed on a Tristar 3000 Micromeritics equipment. Samples after weighing in a glass cell (approximately 0.2g) were heat treated: 300°C for 3h to phosphateted niobia and 450°C for 5h for H-USY zeolite. And under $5x10^{-3}$ torr vacuum for drying and removal of adsorbed impurities on the material surface. Then the samples were weighed again and the analysis was started at a temperature of -196°C, thus obtaining the N_2 adsorption and desorption isotherms at different N_2 partial pressures. The analysis of thermoprogrammed ammonia desorption was performed to calculate the total acidic strength and to classify and to quantify the type of strength (strong/weak) of the acid sites of the zeolites. The measures TPD-NH_3 were performed on a Micrometrics 2910 equipment. The procedure took place in various steps. Firstly, the catalysts are subjected to a heat treatment in order to remove impurities physically adsorbed at the acid sites of the catalyst; for this a heating rate of 10°C/min up to 550°C for 30min was used in the presence of helium gas. After, the sample was cooled to 180°C with a stream of NH_3 (33 mL/min) for 30 min. Then, a helium flow was passed for 90 min in order to eliminate all the ammonia adsorbed physically in the catalyst. The analysis was terminated with the thermoprogrammed desorption of the ammonia which was chemically adsorbed at the acid sites of the catalyst; at this stage a heating rate of 15°C/min was used under the helium flow (30 mL/min) at temperature range between 180 and 550°C, after remaining for 30 min at 550°C. The ammonia desorbed at different temperatures was dragged by the current of helium gas that passed through a mass spectrometer (MS), thus making it possible to calculate TPD-NH_3 values of the acidity sites.

Statistic Experimental Design, TryglycerideHidrolysis and Kinetic Study: For the hydrolysis reaction of macauba oil investigation, was used a 2^{3-0} experimental design (array with 8 experiments), 6 experiments were added in the axial points and 5 experiments in the central point, totaling 19 experiments, Table 6. The effects of 3 variables were studied: reagents molar ratio (Water:Oil=4-14), amount of catalyst in relation to the initial amount of macauba oil (0.2-24%) and temperature (152-300°C), Table 2. Were used two solid types as catalysts H-USY zeolite and phosphate niobia (H_3PO_4/Nb_2O_5). All reactions were performed at autoclave batch reactor (450mL) stainless steel, with a maximum working pressure 200atm. This reactor has a

sampling tube as well as a stirring system and external heating blanket. For the hydrolysis reaction was added distilled water and macauba oil (previously heated in an oven at 50°C) in molar ratio and catalyst content relative to the macauba oil mass following the reaction conditions. The mass of macauba oil and the stirring used in each experiment were kept constant at 50g and 700rpm, respectivelly. The mixtures were placed in the temperature controlled stainless steel Parr reactor for 60min, counting the reaction time when the reaction temperature was reached (temperature stabilization lasted 80min on average). At the end of the reaction, the samples were filtered using vacuum. The filtrate was transferred to a separatory funnel and washed twice with 80mL of warm distilled water. Soon after, a strong agitation was promoted for greater phase interaction. After stirring, the mixture was allowed to stand for 60min for complete separation of fatty acids (non-polar phase) from aqueous (glycerol rich) phase. The samples were slowly heated for about 3h at a temperature of 110°C on a hot plate to evaporate any traces of water by evaporation. The acidity of the samples obtained at the end of the process was determined by acid-base titration. The acidity index was determined following AOCS Cd 3d-63 standard by titration-acid base. For titration it was necessary to standardize the 0.1N NaOH solution using potassium biftalate ($C_8H_5KO_4$). The acidity index of the produced fat samples was determined in triplicate. Regarding the water: oil molar ratio, the lowest level (4:1) was chosen because it is close to the stoichiometric ratio (1 mol triglyceride:3 mols of water) and the highest level (14:1) because it represents an excess of water, as there are no studies yet to delimit these quantities well. The minimum temperature of 152°C was employed because it was the lowest temperature at which fatty acid formation was observed and the highest temperature was limited to 300°C for no pressure increase, common in hydrolysis processes as suggested by Lima (2007)[49]. The reactions study through conversion curves (%) versus time (min) was evaluated at the best conversion condition obtained through experimental design for both catalysts. Aliquots were taken from the autoclave batch reactor at times 0, 5, 10, 15, 30, 45, 60, 90 and 120min. Afterwards they were vacuum filtered, washed, oven dried at 110°C and analyzed by acid-base titration. Still for the best non-catalytic conversion and application of the studied catalysts, a gas chromatography analysis was performed in order to predict, qualitatively and quantitatively, how much triglyceride was transformed into acid. Therefore, observe the performance of the catalysts to generate fatty acids under the evaluated reaction conditions.

Fatty Acid Product Analysis: The fatty acids obtained in the previous were purified and dried by anhydrous sodium sulphate and filtered, in order to eliminate traces of water to promote no only the removal of unreacted glycerides, but also to remove the impurities present in macauba oil, such as: phosphatides, pigments and metal traces, common feature for all vegetable oils. The method is based on the considerable difference between the boiling points of free fatty acids and glycerides at low pressure and high temperature. All vacuum distillation tests used high temperature (200-350°C) and low pressure (5–8mmHg). At the beginning of each test the fatty acids were weighed and heated in an oven at 70°C until complete homogenization was ensured. In the end the purification yield was determined. In order to identify the fatty acids produced during the hydrolysis reaction, the samples obtained at the reaction time of 60 min and the highest conversion selected from the reaction kinetics were analyzed by gas chromatography. The developed method of analysis consisted of preparing the methyl esters from the fatty acids following the same methodology used for macauba oil, where the fatty acids are converted to more volatile compounds. However, only the second step of the Hartman and Lago methodology (1973)[47] was applied. Comparing the retention time of the sample constituents with the mixture consisting of 37 fatty acid methyl ester standards (Sigma C4:0-C24:0); by addition of internal methyl tricosanoate standard (C23:0) and verification of increase in peak areas. The quantification of fatty acids in the hydrolysed oil was then performed in relation to the internal standard methyl tricosanoate (C23:0). The internal standard solution was prepared at a concentration of 1.0mg/mL in isooctane and added before weighing the oil in the esterification

vessel. The amount added was established by maintaining a ratio of approximately 500:1 between the oil mass and internal standard mass. After addition of the internal standard solution, the solvent was evaporated under nitrogen flow Milinsk (2007)[50]. However, in order to predict qualitatively and quantitatively how much triglyceride was transformed into fatty acid samples were further analyzed according to the content of mono, di, triglycerides and free glycerol by the ASTM D6584 method and the influence of the catalyst on the evaluated reaction conditions can be observed.

Conclusions

The macauba pulp oil presented an adequate lipid profile for biodiesel production. The major fatty acids found were oleic acid and palmitic acid. These medium-chain fatty acids (C16:0 and C18:1) are considered ideal for the production of high-quality biodiesel. The Catalyst activity was closely related to acid/base strength as well as texture properties such as specific area, pores (size and volume), and concentration of active sites. The phosphated niobium catalyst is one of the most potential catalysts for oil hydrolysis processes because of its high catalytic activity in the presence of water. The statistical study proved to be effective for the evaluation of the parameters that exert the greatest influence on the macauba oil methyl biodiesel production process; The conduction of experimental designs allowed the determination of the effect of the main process parameters on the hydrolysis fatty acid conversion and the ester conversion content of esterification. The highest conversions for both catalysts were obtained in the 300°C reaction range, 9:1 water:oil molar ratio and 24% catalyst. The fatty acids can now be converted into biodiesel by the esterification reaction of fatty acids, this part will be published in the future by our research group.

REFERENCES

Mirisola Filho, L. A Cultivo e Processamento do coco macaúba para produção de biodiesel, Viçosa: Centro de Produçõestécnicas, 2009, 336.

Fabiano Pereira do Amaral, FernadoBroetto, Cesar Benedito Batistella, Sonia Maria Alves Jorge. Extração e caracterizaçãoqualitativa do óleo da polpa e amêndoas de frutos de macaúba [Acrocomia aculeata (Jacq) Lodd. ex Mart] Coletadanaregião de Botucatu-SP. Energiana agricultura, 2011, v.26(1), 2-20p. DOI: https://doi.org/ 10.17224/EnergAgric.2011v26n1p12-20

Ferrari, R. A., Azevedo Filho, J. A..Macauba as promising substrate for crude oil and biodiesel production. Journal of Agricultural Science and Technology. 2012, v.2(10B), 1119-1126p.

Montoya, S. G., Motoike, S. Y., Kuki, K. N., & Couto, A. D., Fruit development, growth, and stored reserves in macauba palm (Acrocomia aculeata), an alternative bioenergy crop. Planta, 2016, v.244(4), 927-938p.

Kaltner, F. J., Furlan Júnior, J., da SILVA, E. B., Veiga, A. S., &Vaz, J. D. C. Viabilidadetécnica e econômica de produção de ésteres de óleo de palma, para utilizaçãocomosubstituto de óleo diesel, na Amazônia. Embrapa Amazônia Oriental-Documentos (INFOTECA-E), 2004.

CETEC - Fundação Centro Tecnológico de Minas Gerais. ProgramaEnergia, Produção de combustíveislíquidos a partir de óleosvegetais, 1983, Belo Horizonte.

Mota, C. S., Corrêa, T. R., Grossi, J. A. S., Castricini, A., & Ribeiro, A. D. S., Exploraçãosustentável da macaúba para produção de biodiesel: colheita, pós-colheita e qualidade dos frutos. Informe Agropecuário, 2011, v.32(265), 41-50p.

Isabella Christina Costa da Silva. Uso de processoscombinados para aumento do rendimento da extração e da qualidade do óleo de macaúba. 2009. Dissertação (MestradoemTecnologia de

ProcessosQuímicos e Bioquímicos) – Escola de Química, Universidade Federal do Rio de Janeiro, 2009.

EntabanEcoenergéticas do Brasil Ltda. Macaúba. <http://www.entabanbrasil.com.br/>. (accessed April 2020).

Andrade, M. H. C., Vieira, Aguiar. H. F., Chaves, J. F. N., Neves, R. M. P. S., Miranda, T. L. S., Salum, A.; Óleo do fruto da palmeiramacaúba - parte I: umaaplicaçãopotencial para indústrias de alimentos. fármacos e cosméticos. I Semináriosobretecnologianaindústriaquímica. II Encontrobrasileirosobretecnologianaindústriaquímica. 7º Seminário de produtores de olefinas e aromáticos e 3º Seminário ABIQUIM de tecnologia, 2006, São Paulo.

Paradigma, A. Macaúba: Aspectos da Cultura. 2010. <http://www.paradigma.ind.br/index.php?option=com_content&view=article&id=35&Itemid=80> (accessed Maio 2020).

Faria, L. A. Hidrólise do óleo da amêndoa da macaúba com lipase extracelular de Colletotrichum gloesporioidesproduzida por fermentaçãoem substratolíquido. Dissertação (MestradoemCiência de Alimentos) - Faculdade de Farmácia. Universidade Federal de Minas Gerais. Belo Horizonte, 2010.

Da Costa, Priscila Albuquerque. Integração dos processos de extraçãolíquido-líquido e pervaporação para desacidificação do óleo de macaúba (Acrocomia aculeata), Dissertação (MestradoemTecnologia de ProcessosQuímicos e Bioquímicos) – Escola de Química, Universidade Federal do Rio de Janeiro. Rio de Janeiro, 2012.

Ramalho, H. F.; Suarez, P, A, Z. A Química dos Óleos e Gorduras e seusProcessos de Extração e Refino. Revista Virtual Quimica, 2013, v.5(1), 2-15p.

Patil, T, A.; Butala, D, N.; Raghunathan, T, S.; Shankar, H, S. Thermal Hydrolysis of Vegetable Oils and Fats - Reaction-Kinetics. Industrial & Engineering Chemistry, 1998, v.27, 727–735p.

Dieckelmann, G.; Heinz, H. J. E. The Basics of Industrial Oleochemistry. [S.l.]: Pubisher P. Pomp, 1988, 123p.

Wang, A. W. C.; Thapaliya, N.; Campos, A.; Stikeleather, L. F.; Roberts, W. L. Hydrocarbon fuels from vegetable oils via hydrolysis and thermo-catalytic decarboxylation. Fuel, 2012, v.95, 622–629p.

Lascaray, L. Industrial fat splitting. Journal American Oil Chemists' Society, 1952, v.29, 362-366p.

Moretto, E., Fett, R. Tecnologia de óleos de gordurasvegetaisnaindústria de alimentos. São Paulo, Varela, 1998, v. 150.

King, J, W., Holliday, R, L., List, G, R. Hydrolysis of Soybean Oil in a Subcritical Water Flow Reactor. Green Chemistry, 1999, v.1(6), 261–264p.

Rittner, H. Tecnologia das matériasgraxas: derivadosoleoquímicos. São Paulo: LivrariaTriânguloEditora, 2002, v.3.

Satyarthi, J, K.; Srinivas, D.; Ratnasamy, P. Hydrolysis of vegetable oils and fats to fatty acids over solid acid catalysts. Applied Catalysis A: General, 2010, v. 391, n. 1-2, 427-435p.

Ngaosuwan, K.; Lotero, E.; Suwannakarn, K.; Goodwin J, R.; Praserthdam, P., Hydrolysis of Triglycerides Using Solid Acid Catalysts. Industrial & Engineering Chemistry, 2009, v. 48, 4757p.

Shreve, R. N., Brink, Journal American Chemical Process Industries – Ed. McGraw-Hill: New York, 1997.

Gervajio, C, G. Fatty Acids and Derivatives from Coconut Oil. Bailey's Industrial Oil and Fat Products, 2005, New York, 1-56p.

A. Florentino, P. Cartraud, P. Magnoux, M. Guisnet, Applied Catalysis A: General, 1992, 89(2), 143-153.

S. Okazaki, N. Wada, Catalysis today, 1993, 16(3-4), 349-359.

S. Okazaki, A. Kurosaki, Catalysis Today, 1990, 8(1), 113-122.

G. C. Diaz, Y. R. Cruz, G. G. Leite, D. A. G. Aranda, A. A. Arceo, N. C. Furtado, C. A. Taft, Current Organic Chemistry, 2013, 17(12), 1350-1357.

A.C.B. dos Santos, P. Grange, A.C. Faro Jr., Applied Catalysis A: General, 1999, 178, 29-38.

T. Iizuka, K. Ogasawara, K. Tanabe, Bull. Chem. Sot. Jpn., 1983, 56(10), 2927-2931.

I. Nowak, M. Ziolek, Chemical Reviews, 1999, 99(12), 3603-3624.

M. Ziolek, Catalysis Today, 2003, 78(1-4), 47-64.

Reguera, F. M., Araujo, L. R. R. D., Picardo, M. C., Bello, F. D. O., Scofield, C. F., Pastura, N. M. R., & Gonzalez, W. D. A. (2004). The use of niobium based catalysts for liquid fuel production. Materials Research, 7(2), 343-348.

DE PIETRE et al. $H_3PO_4^-$ and $H_2SO_4^-$ treated niobic acid as heterogeneous catalyst for methyl ester production. Reac. Kinet. Mech. Cat. v. 99, no. 2, p. 269–280, 2010. Disponívelem: http://link.springer.com/article/10.1007%2 Fs11144-009-0143-9#. Acessoem: 10 oct. 2012.

BASSAN, I.A.L.; FARO Jr., A.C; LACHTER, E.R. Esterificação de ácidosgraxos com álcooisnapresença de catalisadores de nióbio. 5º CongressoBrasileiro de Pesquisa e DesenvolvimentoemPetróleo e Gás. Fortaleza. 2009.

] ZHEN-CHEN, T. et al. Phosphoric Acid Modified Nb2O5: A Selective and Reusable Catalyst for Dehydration of Sorbitol to Isosorbide. Bull. Korean Chem. Soc. v. 31, no. 12, p.3679-3683, 2010.

SILVA, M.J.; AUGUSTI, R.; ROBLES-DUTENHEFNER, P.; SILVA, K.A. Esterificação de ácidosgraxosemf aselíquidacatalisadapelo heteropoliácido H3PW12O40 emsistemashomogêneos. In: XX SICAT - SimpósioIberoAmericano de Catálise. 2006. Gramado. Anais do XX SICAT - SimpósioIbero-Americano de Catálise. 2006.

MORETTO, E.; FETT, R. Tecnologia de óleos e gordurasvegetaisnaindústria de alimentos. São Paulo: Livraria Varela. 1998.

DENG, H. T.; KERNS, K. P.; CASTLEMAN Jr., A. W. Formation. structures. and reactivities of niobium oxide cluster ions. Journal Physical Chemistry. v. 100, no. 32, p. 13386-13392, 1996.

USHIKUBO, T.; KOIKE, Y.; WADA, K.; XIE, L.; WANG, D.; GUO, X. Study of the structure of niobium oxide by X-ray absorption fine structure and surface science techniques. Catalysis Today. v. 28, no. 1-2, p. 59-69, 1996.

NAKAJIMA, K.; BABA, Y.; NOMA, R.; KITANO, M.; KONDO, J.N.; HAYASHI, S.; HARA, MICHIKAZU. Nb2O5.nH2O as a Heterogeneous Catalyst with Water-Tolerant Lewis Acid Sites. J. Am. Chem. Soc. v.133, no. 12, p. 4224–4227, 2011.

PRASETYOKO, D.; RAMLI, Z.; ENDUD, S.; NUR, HADI. Characterization and catalytic performance of niobic acid dispersed over titanium silicalite. Advances in Materials Science and Engineering. v. 2008, p.1-12, 2008.

ARENDS, I.W.C.E.; SHELDON, R.A.; WALLAU, M.; SCHUCHARDT, U. Oxidative transformations of organic compounds mediated by redox molecular sieves. Angew. Chem. Int. Ed.. v.36, p.1144-1163, 1997.

BEIN, T. Supramolecular architecture: Synthetic Control in Thin Films and Solids. A.C.S. Sym. Ser. 499, p. 274-293, 1992.

LUNA, F. J.; SCHUCHARDT, U. Modificação de Zeólita para usoemcatalise. Química Nova. v. 24. p. 885-892. 2001. Disponivelem: <http://www.scielo.br>. Acessoem: 10 mai. 2020.

HARTMAN, L.; LAGO, R.C.A. Rapid preparation of fatty acid methyl from lipids. Lab. Pract.. v. 22, p. 474-476, 1973.

DOS SANTOS, A.C.B.; GRANGE, P.; FARO Jr., A.C. Effect of support sulphidation on the hydrocracking activity of nióbia-supported nickel and molybdenum catalysts. Applied Catalysis A: General. v. 178, p. 29-38, 1999.

LIMA, Layla Leão. Produção de biodiesel a partir da hidroesterificação dos óleos de mamona e soja. xxii. 236. il. Dissertação (MestradoemTecnologia de ProcessosQuímicos e Bioquímicos)- Escola de Química. Universidade Federal do Rio de Janeiro. Rio de Janeiro. 2007.

MILINSK, Maria Cristina. Análisecomparativa entre oitométodos de esterificaçãonadeterminaçãoquantitativa de ácidosgraxosemóleo vegetal. xii. 92 f.: il. Tese (doutorado)-Programa de Pós-GraduaçãoemQuímica. Universidade Estadual de Maringá. Maringá. 2007.

Rocha, A. S., Costa, G. C., de Araujo, L. R. R., Misael, W. A., Oliveira, R. R., & Rocha, A. B. (2019). Insights into the Phosphate Species on Niobia Treated with H3PO 4. Catalysis Letters, 1-9.

****