

Simultaneous esterification and transesterification of andiroba oil using niobium oxide-sulfate as catalyst

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Abstract— The rising market in biofuels has been encouraging researchers to develop new routes for biodiesel production in order to increase the yields of the process. Heterogeneous acid catalysts represent an alternative to avoid the traditional alkaline pathway for producing alkyl esters from oils with a high content of free fatty acids. In this study, sulfated - niobium oxide catalyst was developed by impregnating Nb_2O_5 with H_2SO_4 (0.5 mol/L) and used to carry out simultaneous esterification and transesterification of andiroba (*Carapa guianensis*) oil with high free fatty acid content (acid value: 33.1 mg KOH/g). Reactions were performed with anhydrous ethanol under different conditions of temperature and molar ratio of oil to ethanol, using the $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$ catalyst at 5% (w/w reaction mixture). The oil conversion was determined by the ^1H -NMR spectroscopy method and the maximum conversion of andiroba oil into ethyl esters was 90.9%, which was achieved in a pressurized reactor.

Keywords— Acid oil, esterification/transesterification, ethyl esters, free fatty acids, niobium oxide-sulfate.

I. INTRODUCTION

A large expansion of the world's biodiesel industries along with the increasingly demand for raw-materials has been stimulating biofuel companies to seek new alternatives in order to increase the profitability of the biodiesel production process, either through the use of non-edible vegetable oil as raw material or in the development of new and efficient catalysts.

The most commonly used technologies for ester production are based on a chemical transformation of vegetable oils with alcohol by using homogeneous catalysts (basic or acid) to promote the cleavage of triglyceride molecules and generate a mixture of esters with fatty acids [1]. The search for sources of triglycerides and more efficient and low-cost continuous production processes are key factors for a sustainable biodiesel industry [2]. Oilseed sources, including oils from unusual kinds of fruit such as andiroba (*Carapa guianensis*), macaw palm (*Acrocomia aculeate*) and jatropha (*Jathropa curcas*), many of them with high acidity levels, represent an excellent source of raw material for the production of biodiesel [3].

The high concentration of free fatty acids (FFA) in vegetable oils that are used as raw material in transesterification processes can negatively affect the ester production, since FFAs can react with the base homogeneous catalyst (traditionally being NaOH or KOH) to form metallic esters (soap). This secondary reaction decreases the selectivity for esters, interferes with glycerol removal, contributes to the formation of emulsion during washing, promotes low ester productivity, and increases the overall cost of the downstream processes [4 – 5]. Nonetheless, to solve this problem, several studies have proposed a treatment step prior to the alkaline transesterification based on FFAs esterification with alcohol in the presence of an acid catalyst, typically being sulfuric acid. The major disadvantage of this catalyst is its corrosive force and the difficulty in being separated from the product at the end of the reaction. In addition, a considerable amount of alkaline is required to neutralize the acidic catalyst [1 – 2].

In the latest years, the study of heterogeneous acid catalysts to be used in transesterification processes applications as replacement for homogeneous acid catalysts is becoming relevant. Some of the most important examples of these materials are solid super acids, i.e. materials, which present greater acidity than the sulfuric acid [5 – 9]. The solid super acids are obtained by acids that increase the intrinsic acidity of a solid acid, through adding another acid or supporting a liquid in a solid super acid, which normally presents Lewis active site [5,10].

Among the major heterogeneous catalysts are zeolites combined with inorganic salts ($\text{AlCl}_3\text{-CuCl}_2$; $\text{AlCl}_3\text{-CuSO}_4$), oxides of niobium, titanium, zirconia, silica, iron, bismuth and aluminum impregnated with inorganic acids (HCl , H_2SO_4 and H_3PO_4), and liquid acids in non-reactive supports [6,8,10,11].

Sulfates correspond to oxide catalysts of greater industrial interest due to their reactivity and recoverability to be used in consecutive reactions. However, the processes conducted with these heterogeneous catalysts for esterification usually require

great amounts of alcohol to oil molar ratio, high temperatures and long reaction times to attain satisfactory yields when compared to homogeneous systems [6,10].

Most researches in this area are focused on the production of esters by a two-step process, including a previous hydrolysis of the vegetable oil's triglycerides followed by an esterification of the free fatty acids generated with methanol or ethanol through a unique heterogeneous catalyst [4,12]. In this sense, heterogeneous acid catalysts emerge as promising alternative to homogeneous catalyst systems, since they provide a considerable increase in the yields of production processes, allow the use of high-acidity oils, generally non-edible, and promote environmentally sustainable processes [2,9,10].

Hence, this work is aimed at the development of a niobium oxide-sulfate catalyst ($\text{SO}_4/\text{Nb}_2\text{O}_5$), its characterization and application in a simultaneous esterification and transesterification for ethyl ester production using vegetable oil with high free fatty acid content and ethanol as raw materials.

II. MATERIAL AND METHODS

2.1 Chemicals

Hydrated niobium oxide HY340 (amorphous) with high surface area ($\text{BET} \sim 180 \text{ m}^2/\text{g}$) containing 80% Nb_2O_5 was donated by Companhia Brasileira de Metalurgia e Mineração-CBMM (Araxá, Minas Gerais State, Brazil) and used as support for catalyst preparation. The support was calcined at 500°C for 5 h to eliminate volatile compounds and for structural stabilization. Sulfuric acid 98% VETEC[®] Sigma-Aldrich (São Paulo, São Paulo State, Brazil) was conveniently diluted and used as a doping agent. Anhydrous ethanol 98% VETEC[®] Sigma-Aldrich (São Paulo, São Paulo State, Brazil) was used as an acylant agent in the transesterification reactions.

2.2 Biodiesel feedstock

Andiroba (*Carapa guianensis*) oil with high free fatty acid content was acquired from Basf (Jacareí, São Paulo State, Brazil) and used as raw material for the ethyl ester synthesis. The oil fatty acid composition was determined by gas chromatography (GC) according to the AOCS [13] Ce 1-62 method. The physico-chemical characterization was conducted according to the following standard methods: acid value (AOCS Cd 3d-63), viscosity (ASTM D 445), density (ASTM D 4052) and moisture content (AOCS Ca 2b-38) and results are given in Table 1.

2.3 Catalyst preparation

The niobium oxide-sulfate $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$ catalyst was prepared from a mixture of 5 g of niobium oxide, 5 mL of sulfuric acid (0.5 mol L^{-1}) and 15 mL of deionized water in a glass reactor at 90°C under reflux and constant agitation (500 rpm) for 3 h. The solid was washed twice with deionized water, filtered and dried at 100°C for 12 h. The catalyst was calcined at 500°C for 5 h and characterized regarding its crystallinity, thermal properties, porous volume and acidity index.

TABLE 1
PROPERTIES OF ANDIROBA OIL USED AS RAW MATERIAL

Property	Value
Fatty acid (%)	
Lauric acid (C12:0)	0.1
Myristic acid (C14:0)	0.1
Palmitic (C16:0)	29.0
Stearic acid (C18:0)	10.0
Oleic acid (C18:1)	47.0
Linoleic acid (C18:2)	10.7
Others	2.6
Saturated total	39.2
Unsaturated total	60.3
Molar mass (g/mol)	830
Acid value (mg KOH/g)	33.11
Kinematic viscosity at 40°C (mm^2/s)	35.7
Density at 20°C (kg/cm^3)	931.0
Moisture content (%)	1.00

2.4 Heterogeneous catalysis for ethyl ester production

The catalytic strength of the niobium-sulfate $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$ was analyzed in the transesterification reactions of andiroba oil with anhydrous ethanol. The catalyst was previously dried at 120 °C for 2 h before utilization. Reactions were conducted in a stainless steel ampoule reactor ($\varnothing=30$ mm, $h=100$ mm) with 150 mL of working-volume, being operated under variable conditions of temperature (160 – 260 °C), with a molar ratio of ethanol to oil (55 – 120) and 5% of catalyst. The internal pressure in the reactor corresponds to the vapor pressure of the component with the highest volatility in the reaction mixture. The reaction system was heated and maintained under constant magnetic agitation for 8h using a stirring hot plate.

Once optimal reaction conditions were set, the transesterifications were conducted in a pressurized stainless steel reactor (ALPHATEC, Uberlandia, Brazil) with 300 mL of working volume and equipped with an electrical heating jacket covering the reaction vessel with an automatic temperature controller. The experiments were run at least in duplicate for no more than 3 h.

2.5 Purification of ethyl esters

At the end of the transesterification process, the catalyst was separated from the mixture containing products and reagents by centrifugation at 1570x g for 15 min. The supernatant containing ethyl esters was transferred to a separating funnel and washed with the same volume of hot water for 12 h, allowing the phase of decantation and separation of glycerol and ethyl ester (higher phase). This procedure was carried out three times to assure total glycerol removal. The catalyst was re-suspended in *tert*-butanol, centrifuged and dried at 105 °C for 24 h. The liquid phase containing ethyl esters was submitted to evaporation in a vacuum rotary evaporator to remove the remaining ethanol. Finally, the ethyl esters were dried with anhydrous sodium sulfate to remove water traces.

2.6 Analytical methods

2.6.1 X-ray diffraction (XRD)

The crystallinity was determined by X-ray diffraction (XRD) in a Pan Analytical diffractometer (Xpert PRO model) using Cu K ($= 1.5418 \text{ \AA}$) as incident radiation, operating at 40 kV and 30 mA. The XRD spectra were analyzed based on the JCPDS card data.

2.6.2 Thermo-gravimetric analysis

The thermo-gravimetric analysis was conducted in a DSC-TGA NETZSCH STA 449F3 equipment using 20 mg of sample under dynamic nitrogen atmosphere at a heating rate of 10 °C in a temperature range of 30 °C to 900 °C (DSC range 0 to 50000 μV).

2.6.3 Scanning Electron Microscopy

The crystal morphology of the catalyst was analyzed by high-resolution scanning electron microscopy (SEM), LEO Model 1450 VP (ZEISS, Germany), operating with an accelerating voltage of 20 kV.

2.6.4 Specific Surface Area

The specific surface area was determined by Brunauer, Emmett and Teller (BET) method in a Quanta chrome equipment (new 1000 model). A sample of 0.2 g was added into a glass cell and heated at 200 °C for two hours under vacuum to remove the impurities adsorbed on the catalyst surface. After the sample's heat treatment, the N_2 relative pressure varied and its volume was monitored to obtain the adsorption and desorption isotherm of gas. For determining the pore size distribution, the method proposed by Barrett, Joyner and Halenda [14] was used.

2.6.5 Ethyl ester quantification

The vegetable oil conversion into fatty acid ethyl esters (FAEEs) was analyzed by nuclear magnetic resonance spectrometry ($^1\text{H NMR}$) in a Mercury 300 MHz Varian spectrometer. FAEEs were dissolved in deuterated chloroform (CDCl_3) using 0.3% tetramethylsilane (TMS) as internal standard. The yield of oil conversion into esters was determined according to the method validated by Paiva et al. [15]. This method allows the identification of ester molecules produced during the transesterification, whose peaks are in the region of 4.05 to 4.35 ppm of the spectrum. According to Equation 1, the signal of the ethoxyl hydrogen atoms of the ethyl esters is a split quartet.

$$\% \text{ EE} = [(A_{C4} \times 8)/(A_{dd+ee})] \times 100 \quad (1)$$

Where:

A_{C4} = area of the component fourth peak (quartet)

A_{dd+ee} = area of all signals between 4.35 and 4.05

% EE = yield of fatty ethyl esters

In this equation, the A_{C4} was obtained from integrating the peak at 4.08 ppm. The area corresponds to 1/8 of the entire ethoxy-carbon hydrogen area ($-OCH_2$), whose signal appears in the region ranging from 4.05 to 4.20 ppm. The region near 4.08 ppm is the only region where crossover does not occur, and this integrated signal can be assigned to ethyl esters.

2.6.6 Glycerides analysis

The remaining amount of glycerides (monoacylglycerol and diacylglycerol) in the purified samples was determined in an Agilent 1200 Series liquid chromatograph (Agilent Technologies, USA) equipped with an Evaporative Light Scattering Detector and a Gemini C-18 (5 μ m, 150 x 4.6 mm, 110 Å) column at 40 °C. The mobile phase contained a mixture of acetonitrile (80%) and methanol (20%) at a flow rate of 1 mL min⁻¹ for 6 min, 1.5 mL min⁻¹ until 30 min and 3.0 mL min⁻¹ until 35 min. All samples were dissolved in ethyl acetate-hexane (1:1, v/v), filtered through 0.22 μ m membrane filters (Millipore) and injected in a volume of 10 μ L. All solvents were of HPLC grade, and the assays were conducted at least in duplicate [16].

2.6.7 Density and viscosity

Density values of oil and ethyl esters were determined by a DMA 35N EX digital densimeter (Anton Paar) at 20 °C with 2 mL of sample. The oil and ethyl esters absolute viscosity were determined with a LVDVII Brookfield viscosimeter (Brookfield Viscometers Ltd, England) equipped with a CP 42 cone at 40 °C using 0.5 mL of sample. Shear stress measurements were taken based on shear rate, and the dynamic viscosity was determined as a slope constant. The measurements were replicated three times.

III. RESULTS AND DISCUSSION

3.1 Catalyst properties

The catalyst SO_4^{2-}/Nb_2O_5 was prepared by wet impregnation and characterized in terms of crystallinity, morphology, acidity, specific surface area and volume of pores. Figure 1 displays the X-ray patterns of both niobium oxide-sulfate and niobium oxide. The diffractogram of niobium oxide without any thermal treatment (Figure 1a) showed a characteristic profile of a non-crystalline material without peaks, corresponding to an amorphous solid. This lack of peaks is also associated with structural water and impurities [17].

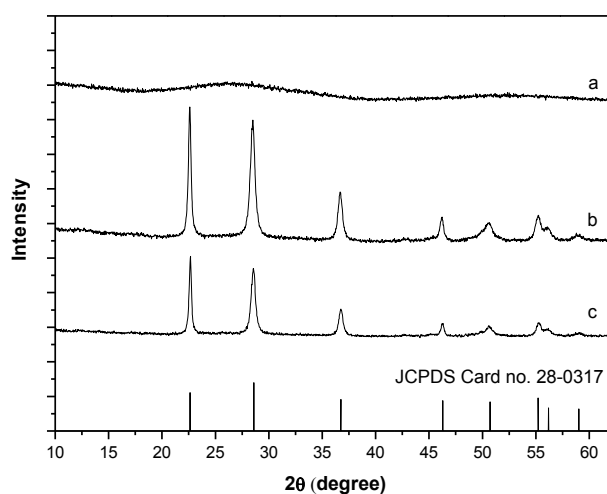


FIGURE 1: X-RAY DIFFRACTION (XRD) OF NIOBIUM OXIDE - Nb_2O_5 (A), Nb_2O_5 THERMALLY TREATED AT 500 °C (B) AND SO_4^{2-}/Nb_2O_5 CATALYST OBTAINED BY WET IMPREGNATION WITH A SULFURIC ACID SOLUTION AT 500 °C (C).

The diffractogram of the catalyst $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$ showed pronounced peaks corresponding to a crystalline phase at the region of 23, 28, 36, 46, 51 and 56 (2θ) (Figure 1c), which are similar to those observed for calcined niobium oxide at 500 °C (Figure 1b). Although, it is clear that a drop in the crystallinity occurs upon impregnation with sulfuric acid.

The characteristic diffraction peaks of niobium oxide are attributed to the hexagonal phase ($\text{H-Nb}_2\text{O}_5$), according to JCPDS Card. no.28-0327/JCPDS Card no. 28-0317. Calcined niobium oxide usually presents a polycrystalline structure (polymorphism) depending on temperature and the presence of oxygen during the thermal treatment [18]. The formation of crystals on this oxide initiates at 500 °C, promoting hexagonal, monoclinic and orthorhombic systems structures [17]. As the calcination temperature increases, the specific surface area decreases due to crystal formation and compaction. However, this arrange reduces the number of active acid sites available for catalysis and promotes higher structural stability. The crystalline structure of the catalyst was also confirmed by the images obtained in SEM (Figure 2).

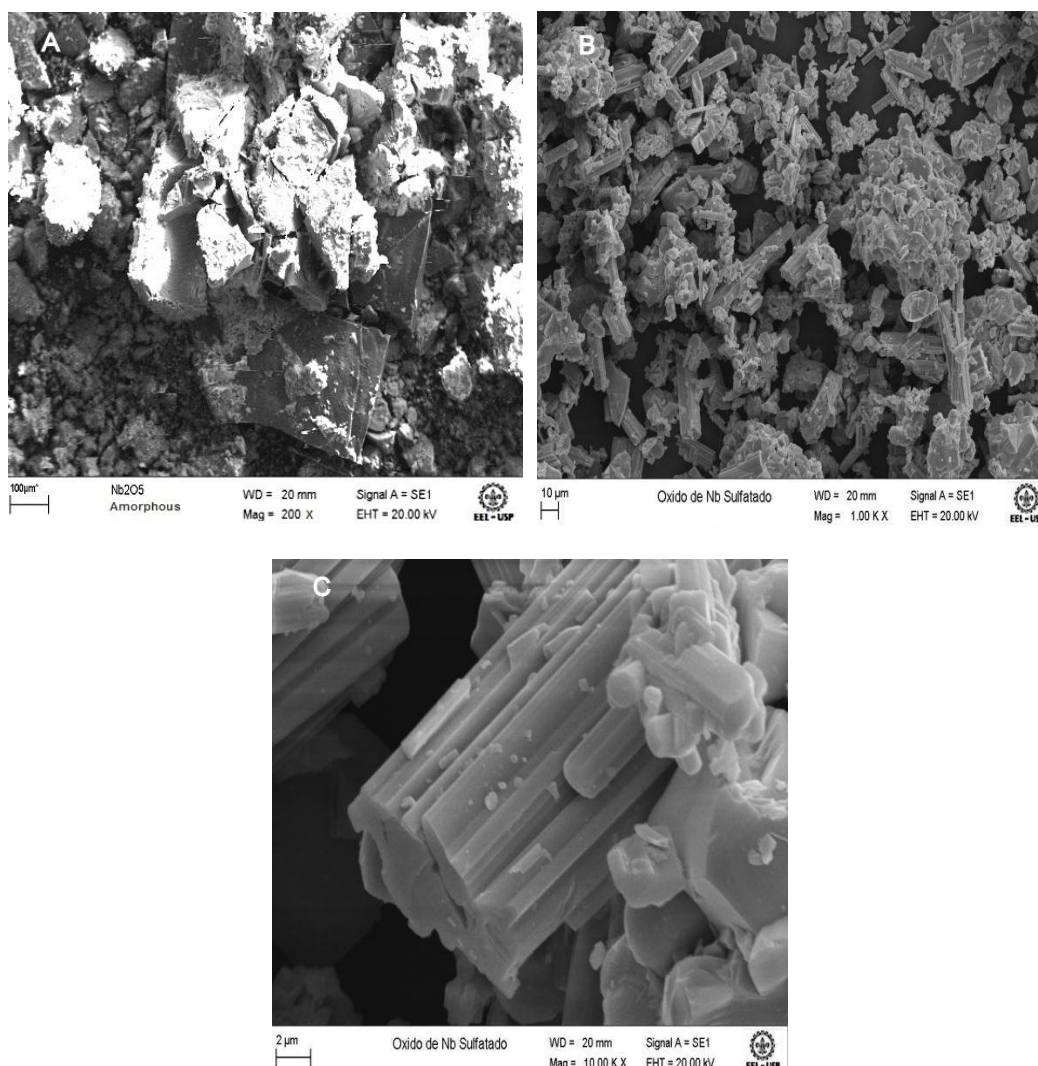


FIGURE 2: SEM IMAGES OF NIOBIUM OXIDE AMORPHOUS (A) AND OXIDE-SULFATE $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$ CATALYST (B AND C).

The DSC analysis measures the heat flow and the endo and exothermic reactions produced on account of temperature variation during chemical processes. These processes include phase transitions and chemical reactions. DSC-TGA curves for the amorphous niobium oxide and the niobium oxide-sulfate catalyst are presented in Figure 3. The peak observed for the amorphous niobium oxide (Figure 3a) and the catalyst (Figure 3b) at 100 °C is characteristic of endothermic processes of the solid's dehydration ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$). The exothermic event observed at 600 °C is associated with the crystallization of the amorphous material into crystalline niobium oxide [19].

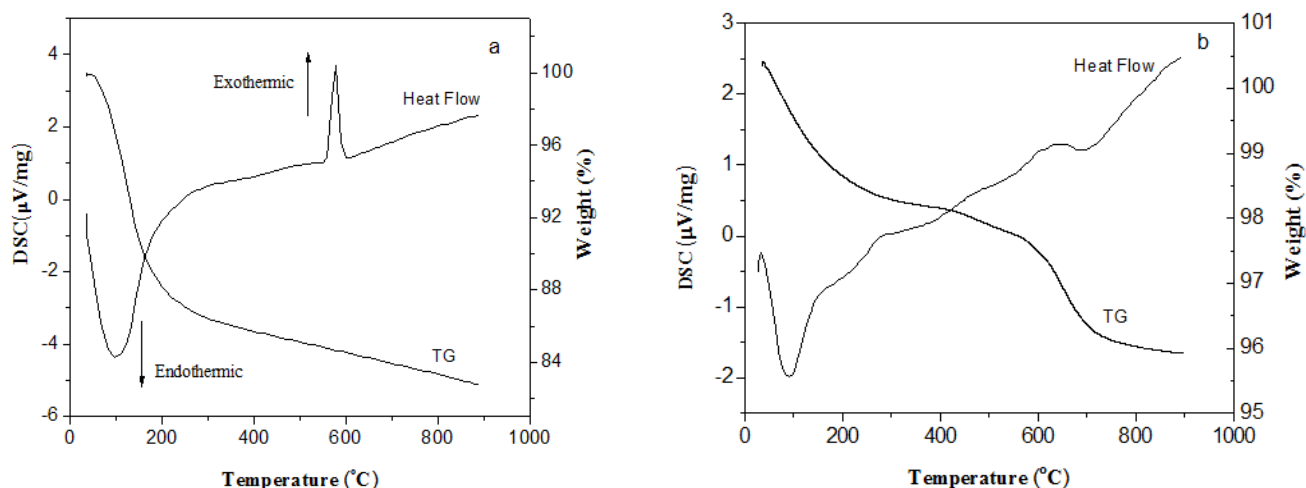


FIGURE 3: DSC-TG ANALYSIS OF (A) NIOBIUM OXIDE AND (B) NIOBIUM OXIDE-SULFATE CATALYST $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$

The thermogravimetric analysis (TGA) corresponds to the measure of weight variation due to temperature in a controlled atmosphere. Its plot confirmed the samples dehydration, thus it is assumed the formation of volatile products. The curve of the amorphous niobium oxide (Figure 3a) shows a single event between 100 and 200 °C that can be attributed to the dehydration of adsorbed and structural water with mass variation of 12%. Figure 3b shows that the niobium-sulfate catalyst underwent total variation in 4.4% of the initial mass, which is associated with loss of volatile compounds. The TG profile of the niobium-sulfate catalyst shows a loss of mass above 600 °C which is associated with the desorption of SO_2 . The loss of mass is in agreement with the thermal event observed in DSC profile at that temperature (Figure 3b). Brandão et al. [20] reported similar profile for TGA analysis of sulfated niobia.

Table 2 displays the titratable acidity, total volume of pores and specific surface area of the support and catalyst. The niobium sulfate catalyst showed acidity of 2.764 mmol H^+ /g, which is 67 times higher than that of the niobium oxide used as support. This confirms the impregnation of sulfate groups on the crystalline structure of the niobium oxide.

TABLE 2
PROPERTIES OF NIOBIUM OXIDE AND NIOBIUM OXIDE-SULFATE CATALYST $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$.

Sample	Surface acidity (mmol H^+ /g)	Pore volume (cm^3/g)	Surface area (m^2/g)
Nb_2O_5	0.041	0.054	22.97
$\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$	2.764	0.143	63.13

According to the literature [21], niobium oxide calcined at 500 °C has no Lewis and Brønsted surface acidic sites due to the removal of water and crystallization. However, an acid treatment before the calcination of the niobia support reveals the deposition of acid species. The authors have suggested that sulfate groups interact with niobium oxide to promote the formation of a mixed Nb-S-O compound containing surface acid sites, which is not modified after calcination at 500 °C.

The total volume of pores of the catalyst was 0.14 cm^3/g , corresponding to an increase of almost three times in pore volume, indicating an acid attack on the support (Table 2). An increase was also observed for the specific area of the catalyst (63.13 m^2/g). These results suggest that the addition of sulfuric acid at low concentration increases the total surface area of the niobia support at 500 °C calcination temperature. This behavior was also reported by Jehng et al. [21], in which the niobium oxide was treated with sulfuric acid at a concentration that was lower than 10% (w/w). However, these authors indicated that a high concentration of the sulfate species (>15% w/w) can reduce the surface area due to the niobium oxide dissolution.

3.2 Ethyl ester synthesis

The catalytic strength of the niobium oxide-sulfate $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$ was evaluated in the reactions for synthesizing ethyl esters from andiroba oil under different conditions of temperature and ethanol to oil molar ratio and fixed catalyst concentration (5%). FAEE yields were calculated from the integrated area of peaks obtained by ^1H NMR, based on the variation of glycerol methylene and ester ethoxy hydrogens in the region of 4.05 - 4.35 ppm during the transesterification reaction [15] as displayed in Table 3.

TABLE 3
AREA OF INTEGRATION AND CONVERSION OF ANDIROBA OIL INTO ETHYL ESTERS DETERMINED BY ^1H NMR

Time (h)	A_{C4}	A_t	Conversion (%)
1	3.44	100	27.5
2	5.02	100	40.2
3	6.00	100	48.0
4	6.51	100	52.1
6	7.45	100	59.6
7	8.34	100	66.7

Reactions carried up in a bottom heating reactor at 120 mol ethanol/mol oil, 260 °C and 5% mass catalyst/mass reaction mixture. Where A_{C4} = area of the component fourth peak (quart), A_t = area of all signals between 4.35 and 4.05, Conversion (%) = $[(A_{C4} \times 8) / (A_t)] \times 100$

The conversions of andiroba oil into ethyl esters using the ampoule type reactor are shown in Table 4.

TABLE 4
RESULTS OF THE ESTERIFICATION AND TRANSESTERIFICATION OF ANDIROBA OIL CONTAINING HIGH FREE FATTY ACID CONTENT USING NIOBIUM OXIDE-SULFATE $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$ AS CATALYST.

Run	EtOH:Oil (mol/mol)	Temperature (°C)	Yield (%)*
1	55	160	40.1
2	95	180	47.5
3	95	200	52.1
4	95	230	54.3
5	95	260	58.3
6	120	230	60.4
7	120	260	67.0

**Area of integration and percentage conversion of andiroba oil into ethyl esters determined by ^1H NMR data.*

The andiroba oil spectrum is shown in Figure 4a. The FAEE formation was confirmed by the signal at 4.08 ppm that corresponds to 1/8 of the total area of carbon-hydrogen ethoxilic ($-\text{OCH}_2\text{CH}_3$), which appears in the region between 4.05 and 4.20 ppm (Figure 4b). The *partial disappearance* of the quarter peak near 4.16 ppm corresponds to the hydrogen atoms of the CH_2 group of glycerol. The presence of peaks in the region of the 4.26 to 4.35 ppm indicates remaining feedstock after the reaction time (Figure 4b).

The highest attained yield was 67% under experimental conditions of run 7. As the temperature was raised from 180 °C to 260 °C (95 mol/mol) an increase of 10% in the yield was observed at the same ethanol to oil molar ratio. A similar performance was noted by increasing the ethanol to oil molar ratio at the same temperature (runs 5 and 7). The FAEE yield was positively affected by the ethanol concentration because the excess of this acylating agent displaces the equilibrium towards the ethyl ester, and increases the reaction kinetic.

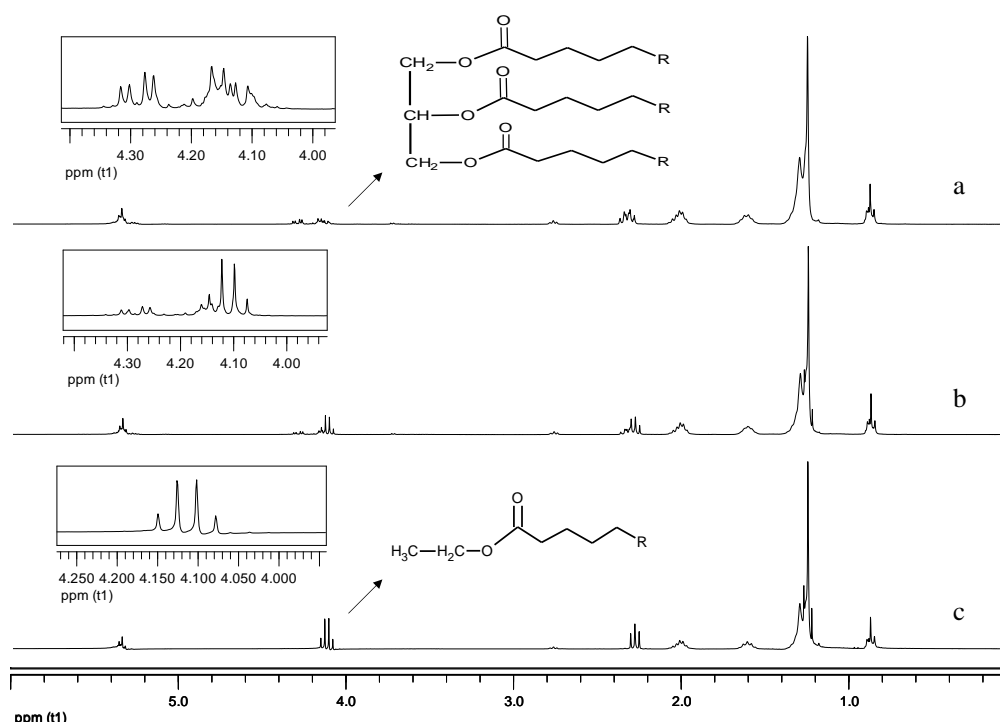


FIGURE 4: ^1H -NMR SPECTRA OF ETHYL ESTERS SYNTHESIZED USING NIOBIUM-OXIDE SULFATE CATALYST $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$. ANDIROBA OIL (A), ETHYL ESTERS PRODUCED IN AMPOULE REACTOR (B) AND ETHYL ESTERS PRODUCING IN JACKET HEATING REACTOR (C).

Figure 5 shows yields and properties (viscosity and density) of ethyl esters attained along the reaction under optimal reaction conditions (120 mol ethanol/mol oil, 260 °C). The viscosity and density curves showed similar profiles with reaction time. The viscosity of the product decreased in 79.3%, achieving 7.39 mm²/s after 7 h of reaction, with a density value of 896 kg/m³ (Figure 5). Expectedly, the product's viscosity and density decreased as the oil conversion rate increased. These results are similar to those observed by Aranda et al. [12] who had investigated niobium oxide as a heterogeneous catalyst for the esterification of free fatty acids from palm oil at 130 °C. The authors reported ester yields of 80% and 20% using methanol and ethanol as acylant agents, respectively. This difference in reaction yields is related to a greater energy demand for the esterification and transesterification with ethanol, which generally requires temperatures over 150 °C in order to achieve high oil conversion rates. Usually, the catalytic activity decreases with the alkyl chain lengths of the alcohol due to the steric effect, thus ethanol shows lower reactivity than methanol in transesterification reactions. This effect is observed in catalysis under alkaline and acid conditions, and it can be reduced by increasing the alcohol to oil molar ratio [20].

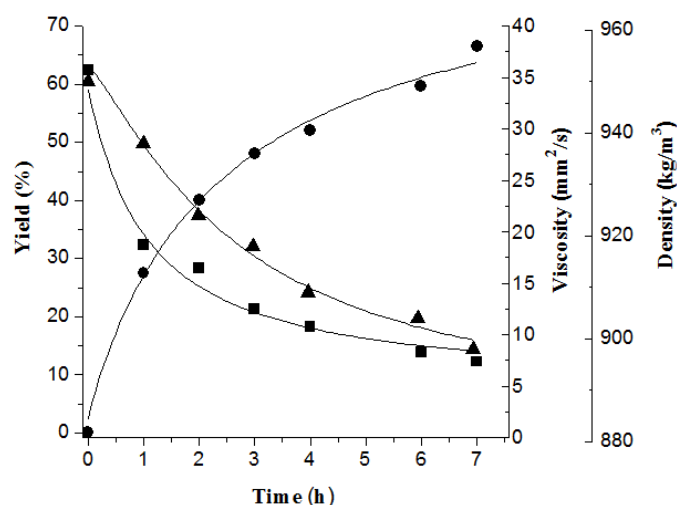


FIGURE 5: YIELD (●), KINEMATIC VISCOSITY (■) AND DENSITY (▲) OF ETHYL ESTERS PRODUCED BY ESTERIFICATION AND TRANSESTERIFICATION OF ANDIROBA OIL WITH NIOBIUM OXIDE - SULFATE CATALYST $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$.

In the methanolysis of soybean oil using niobium oxide-sulfate as catalyst, Pietre et al. [11] reported that 40% of methyl esters were formed at 70 °C in 5 h reaction. In a previous work, Rocha et al. [4] reported the use of niobium oxide for the pre-hydrolysis of soybean oil prior to the esterification with the same catalyst, achieving yields that were close to 87%. Esterification reactions with different fatty acids (lauric, palmitic, estearic, oleic and linoleic acids) using methanol and oxide niobium were reported by Aranda et al.[12] and the highest yields (70%) were reported for the esterifications conducted at 150 °C, using oil to methanol molar ratio of 1:2 (mol.mol⁻¹) and 20% catalyst. Brandão et al. [20] reported the conversion of free fatty acids derived from a previous hydrolysis of soybean oil into ester by methanolysis, achieving a yield of 57% at 160 °C after 2 h of reaction. Most of the previously cited studies describe the utilization of methanol as acylant agent. In the present study, ethyl esters were obtained without a previous hydrolysis of andiroba oil, achieving 67% of yield in a one-step process.

Furthermore, the results of the simultaneous esterification and transesterification of andiroba oil into ethyl esters under pressurized and controlled reactor conditions are presented in Figure 4c and Table 5. The spectrum of ethyl esters obtained by the ¹H-NMR after 3 h of reaction showed a high oil conversion rate (90.9%). This was confirmed by the absence of peaks (multiples) in the region of 4.26 to 4.35 ppm (Figure 4c), that corresponds to the protons of the 1st and 3rd carbon of glycerol in the triglyceride molecules.

TABLE 5
PROPERTIES OF THE PURIFIED ETHYL ESTERS SYNTHESIZED IN THE PRESSURIZED STAINLESS
STEEL REACTOR

Parameter	Value
Ester contents (% wt)	90.9
Kinematic viscosity (mm ² /s)	5.9
Density (kg/m ³)	879
Monoacylglycerol (%)	1.0
Diacylglycerol (%)	8.1
Triglycerides (%)	0
Acidity (mg KOH/g)	6.5

This value is at least 24 % higher than those attained in the ampoule type reactor. Apparently, the jacket heating of the controlled reactor promoted better heat distribution, and it also reduced heat loss through the wall. The high FAEE yield was confirmed by the absence of triglycerides, and low amounts of diacylglycerol (8.1%) and monoacylglycerol (1.0%). Although both kinematic viscosity (5.9 mm² s⁻¹) and density values (879 kg m⁻³) were within the standards required by ASTM D6751, the residual glycerides levels (MG+ DG) were higher (9.1 %) than the limit specified by the same legislation (max. 0.8%). Therefore, further work should be performed aiming at optimizing the processes parameters, as well as the reuse of the catalyst in several catalytic cycles.

IV. CONCLUSION

The development of a heterogeneous catalyst-based acid niobium oxide-sulfate SO₄²⁻/Nb₂O₅ allowed the conversion of high-acidity oil (andiroba) into ethyl esters, achieving a maximum yield of 90.9% and viscosity level below 6.0 mm²/s. Such results were obtained at reactions conditions of 120:1 molar ratio of ethanol to andiroba oil at 260°C. The niobium oxide-sulfate hereby developed is a promising catalyst for the simultaneous esterification and transesterification into ethyl esters without a previous hydrolysis of andiroba oil, well as other oils with high free fatty acid content.

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