

Purificação do glicerol industrial: Produção de ésteres etílicos a partir de ácidos graxos residuais usando catalisador nióbia**Purification of industrial glycerol: Production of ethyl esters from residual fatty acids using niobia catalyst**

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Resumo

A reutilização de resíduos gerados no processo de purificação de glicerol é de grande importância devido ao comprometimento das indústrias com a sustentabilidade, redução de custos e uso de tecnologias mais limpas. O objetivo do presente trabalho é utilizar ácidos graxos residuais, obtidos na purificação bruta de glicerol, para produzir ésteres etílicos usando óxido de nióbio como catalisador e etanol como agente esterificante. Os ésteres gerados nessa reação foram misturados ao biodiesel da reação industrial de transesterificação, que utiliza metanol como agente esterificante e metilato de sódio como catalisador homogêneo. Com misturas contendo 5% desses ésteres etílicos, todos os parâmetros medidos estavam dentro das respectivas faixas da especificação brasileira de biodiesel. Os resultados obtidos mostraram que a reutilização dos resíduos de ácidos graxos presentes no glicerol industrial gera um combustível mais verde, compatível com os padrões atuais.

Palavras-chave: Uso do ácido graxo residual; Esterificação; Biodiesel; Óxido de Nióbio.

Abstract

The reuse of residues generated in the glycerol purification process is of great importance due to the commitment of the industries with sustainability, cost reduction and use of cleaner technologies. The objective of the present work is to use residual fatty acids, obtained in crude glycerol purification, to produce ethyl esters using niobium oxide as catalyst and ethanol as esterifying agent. The esters generated in this reaction were mixed with biodiesel from the industrial reaction of transesterification, which uses methanol as an esterifying agent, and sodium methylate as the homogeneous catalyst. With mixtures containing 5% of these ethyl esters, all measured parameters were within the respective Brazilian biodiesel specification ranges. The results obtained showed that the reuse of the fatty acid residues present in industrial glycerol generate a greener fuel, compatible with current standards.

Keywords: Use of fatty acid residue; Esterification; Biodiesel; Niobium oxide.

Introduction

The fatty acids generated during the crude glycerol purification is a factor of loss of environmental and also financial efficiency in the biodiesel production industry. One alternative is to use these acids as feedstock for the production of esters [7, 22], and this is allowed in Brazilian law 11,097, created in 2005 [2]. Such use does not compete with the interests of the food industry, and presents advantages both from an environmental and economic - financial point of view [11].

Although ethanol has a great importance in the process of producing cleaner biodiesel, the product (fatty acids ethyl esters) has received less attention compared to the process using methanol [9, 20]. The purity of glycerol produced in conventional biodiesel processes lies between 75 and 85%, and can reach up to 95% if the transesterification reaction is optimized [14].

According to [6], the compounds present in crude glycerol from a conventional biodiesel production process in Brazil can be: fatty acids, resinous compounds, nitrogen compounds (since the feedstock is usually a mixture of vegetable oils and animal fat), hydrocarbons, aldehydes and ketones, in addition to unreacted alcohol.

The use of residues generated in the glycerol purification step as a feedstock for ester production is justified by the amount of fatty acids present in its composition. The use of these residues generates the possibility of producing biodiesel at a lower cost when compared to many other inputs used [23]. The use of industrial fatty residues as raw materials for the production of biodiesel via catalytic esterification, despite the need for further studies when applied on a large scale, can contribute to increase the environmental efficiency of the overall process and to minimize operating costs, limiting the number of separation and purification steps. However, the process is more suitable with the use of heterogeneous catalysts, which can accept feedstock with high acidity index [6].

In the present work, fatty acids derived from the crude glycerol purification produced in the homogeneous transesterification of soybean oil mixed with animal fat were used as feedstock. Niobium oxide, an important product in the Brazilian mining industry, was chosen as an esterification catalyst, and the esterifying agent used was ethanol, replacing methanol, a chemical reagent of fossil origin. The esters produced in the esterification reaction were mixed with the industrial biodiesel.

With the beginning of its exploration in the 1950s, niobium became abundant and gained importance in the development of new materials. For example, FeNb alloys were developed for the automobile industry, and after niobium compounds started to be considered in catalysis [12, 13].

The use of niobium oxide as a catalyst in the present study can be explained for two main reasons: Brazil has the world's largest reserves of niobium ore [18], and niobium compounds have already shown positive results in areas of catalytic oxidation and isomerization due to redox properties of niobium oxides, and on the other hand, to the acidic properties of some niobium compounds such as niobic acid.

Materials and Methods

Raw materials

The residual fatty acids used were obtained from the treatment of the crude glycerol generated in a commercial biodiesel production process, by acid hydrolysis using 33% hydrochloric acid. The acid was homogenized with the crude glycerol until the pH reached the range of 2.5 to 3.5, at a temperature of 60°C.

The ethanol used in the esterification process has a purity of 99.5% (Dynamics, PA).

The niobium oxide in its acidic state was provided by CBMM – Companhia Brasileira de Mineração e Metalurgia, and is referenced as HY-340. The niobium catalyst used in the present work was obtained by moderate heat treatment of HY-340 in air (200°C, 2 h), and is referenced in this work as Nb2O5-200.

The biodiesel used in the blend with the ethyl esters was supplied by Oleoplan Nordeste. This biodiesel was produced from a mixture of 60% degummed soybean oil (0.67 wt% of free fatty acids), and 40%

animal fat (2.0 wt% of free fatty acids), 1:6 molar ratio triglycerides/methanol, 0.8% of catalyst sodium methylate by volume, 60 minutes of reaction at the temperature of 65°C.

The blend of industrial biodiesel with the ethyl esters produced in the present work was carried out in an amber glass bottle, homogenized by agitation before being submitted to the various quality tests.

Characterization of the raw materials

Measurement of acidity index

The measurement of the acidity index before and after the esterification reaction was performed by volumetric analysis according to the Ca-5a-40 standard of the American Oil Chemistry's Society [1]. 5 g of the sample was introduced into an Erlenmeyer flask containing 50 mL of previously neutralized ethyl alcohol and 1 mL of phenolphthalein. Titration was then carried out with a previously standardized 0.25N NaOH solution until the turning point of the indicator used was reached for at least 30 seconds.

The percentage acidity index (IA) was calculated in relation to the equivalent mass of oleic acid, according to Equation 1.

$$IA = [Vg \times 7.05] / Ma \quad (1)$$

Where: Vg (mL) = volume of sodium hydroxide 0.25 mol / L spent in titration, 7.05 is a constant (g/mL) obtained by multiplying the concentration of sodium hydroxide (0.00025 mol/mL), the molar mass of the oleic acid (282 g/mol) and the value of 100 (to obtain the result in percent), and "Ma" is the mass of the sample (g) used in the titration. These acidity indexes were used to estimate the degree of conversion of the esterification reaction under study, through Equation 2:

$$\% \text{ Conversion} = ((IA^0 - IA) / IA^0) \cdot 100 \quad (2)$$

Where: IA^0 = acid number before reaction; IA = acid number at the end of the reaction.

Characterization of Fatty Acids and Ethyl Esters in a Mixture

The profile of the reactive fatty acids was determined by gas chromatography using the methodology EN14103.

The ethyl esters from the esterification of the residual fatty acids were mixed with commercial methylated biodiesel. A mixture of this biodiesel containing 5% by volume of the ethyl esters was submitted to certification analyses, according to the specifications of the National Agency for Petroleum, Natural Gas and Biofuels - ANP, including the following methodologies and procedures: Visual, ASTM D 4052, ASTM D 445, ASTM D 664, ASTM D 6684, ASTM D 6584, EN 12662, EN 14103, EN 14110, EN 14111 and NBR 1555.

Characterization of the catalyst

Thermogravimetric analysis (TG)

Thermal analysis of HY-340 was performed using a DTG-60H (Shimadzu) thermo-balance with a sensitivity of 0.1 µg, under a 50 mL.min⁻¹ flow of ultra-pure synthetic air. The heating rate was 10°C.min⁻¹ and the heating interval was between 20 and 1000°C, employing a sample mass of approximately 9.0 mg in a platinum sample holder.

X-ray diffraction (XRD)

The structural analysis of HY-340 and Nb₂O₅-200 were performed on a Shimadzu XRD-6100 diffractometer using CuK α radiation, a scanning rate of 1 degree/min. The voltage and current used were 40 kV and 30 mA, respectively.

Thermo programmed ammonia desorption (TPD-NH₃)

Thermo programmed ammonia desorption (TPD-NH₃) was performed using the Micromeritics Chemisorb 2720 equipment.

Approximately 100 mg of sample was pre-treated at 300°C for 1 h under helium flow (30 mL.min⁻¹). After cooling to 30°C, NH₃ (10% in helium, v/v mixture) adsorption was performed using a flow of this mixture (30 mL.min⁻¹) at 30°C for 1 h. The poorly adsorbed ammonia was removed at 150°C for 1 h at the helium flow rate (30 mL.min⁻¹) for 1 h. At 30°C, thermo programmed desorption was performed by heating the sample from 30 to 800°C at a rate of 10°C.min⁻¹ under helium flow (30 mL.min⁻¹). The amount of desorbed ammonia was monitored by a thermal conductivity detector.

Textural Characterization

The textural characterization of Nb₂O₅-200 was performed using a Quantachrome Instruments model Nova 2200. Before the measurement, the sample underwent a vacuum pre-treatment (100°C for 15 min and 200°C for 15 min). After cooling, the nitrogen adsorption was realized at the temperature of 77 K. The surface area of the sample was calculated using the BET method.

Catalytic Tests

The esterification reaction between fatty acids and ethanol was done in a 200 mL glass reactor equipped with a reflux system, thermometer well and magnetic stirring system. The reactor containing 100 mL of the fatty acids under stirring was heated to the reaction temperature (Table 1). Then ethanol with Nb₂O₅-200 catalyst in suspension was added in the desired amount. This addition determined the zero reaction time. At the end of the reaction, the reaction medium was transferred to a separatory funnel; the upper phase was separated from the reaction medium and subsequently from the residual solid phase in suspension by filtration. This product, referred here as ethyl esters, was finally mixed to the commercial biodiesel at the indicated percentage, 5%, thus allowing the characterization of the mixture.

Table 1 presents the parameters studied, temperature of the reaction medium, ethanol / fatty acid ratio, relative amount of catalyst in relation to fatty acids expressed in g / 100 mL of fatty acids, and reaction time, with the respective values adopted.

Table 1: Experimental planning of the esterification tests

Test	Temperature (°C)	Volume Ratio ethanol/fatty acids	Amount of Catalyst (g/100mL)	Reaction time (hours)
1	150	0.15	10	6,0
2	150	0.15	15	8,0
3	150	0.15	20	6,0
4	150	0.20	10	8,0
5	150	0.20	15	6,0
6	150	0.20	20	8,0
7	200	0.15	10	6,0
8	200	0.15	15	8,0
9	200	0.15	20	6,0
10	200	0.20	10	8,0

11	200	0.20	15	6,0
12	200	0.20	20	8,0

Results and Discussion

Characterization of the catalyst

Figure 1 shows the TG-DTG and DTA curves of the precursor HY-340. A mass loss of approximately 18% on the TG curve is observed between room temperature and about 200-220°C. Above 220°C, no further significant mass loss was noted, suggesting that in the presence of air, the precursor HY-340 was transformed into niobium oxide. The DTG and DTA curves at temperatures lower than 200-220°C show that the mass loss occurs in two events, both endothermic. The initial low temperature event was attributed to moisture loss, and the second ascribed to dehydroxylation of HY-340 compound to generate a "dehydrated" niobium oxide. The DTA curve also shows an exothermic event, with no detectable mass variation at the temperature of 570°C. This event was related to the crystallization of the niobium oxide generated at low temperature, according to literature data [21, 22].

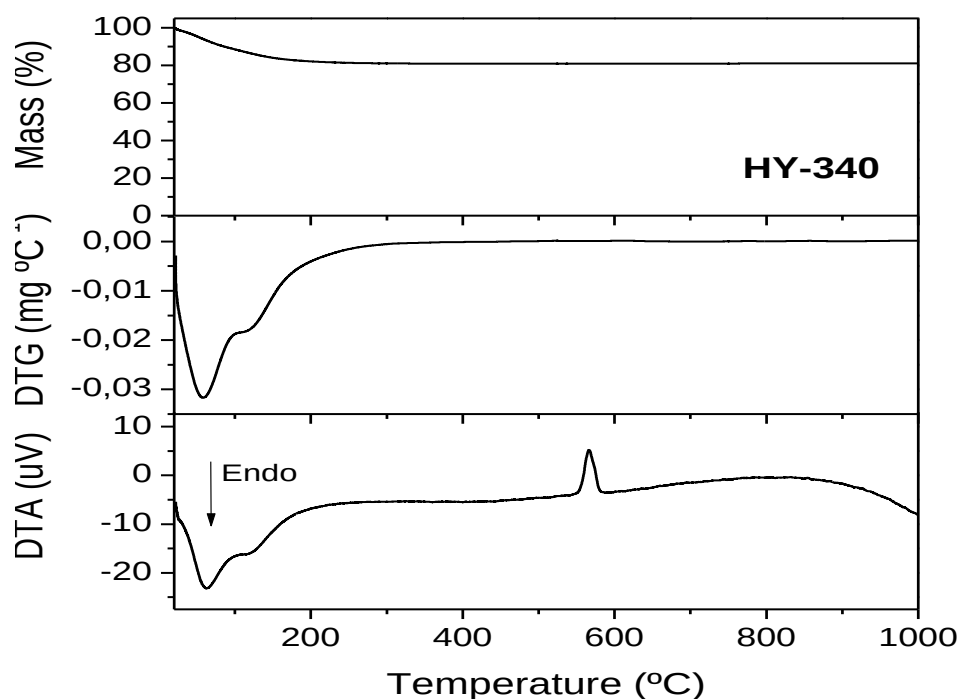


Figure 1: Profile of the thermogravimetric analysis (TG-DTG) and differential thermal analysis (DTA) of the precursor HY-340

In Figure 2, the precursor HY-340 and the catalyst Nb₂O₅-200 show an almost amorphous X-ray diffraction profile, with the presence of two halos with maxima close to $2\theta = 25.5^\circ$ and 53.4° , in agreement with literature data [19, 21]. In the case of the catalyst Nb₂O₅-200, this behavior is explained by the low pre-treatment temperature used, 200°C, since the crystallization phenomenon was observed only at 570°C in the DTA curve (Fig. 1).

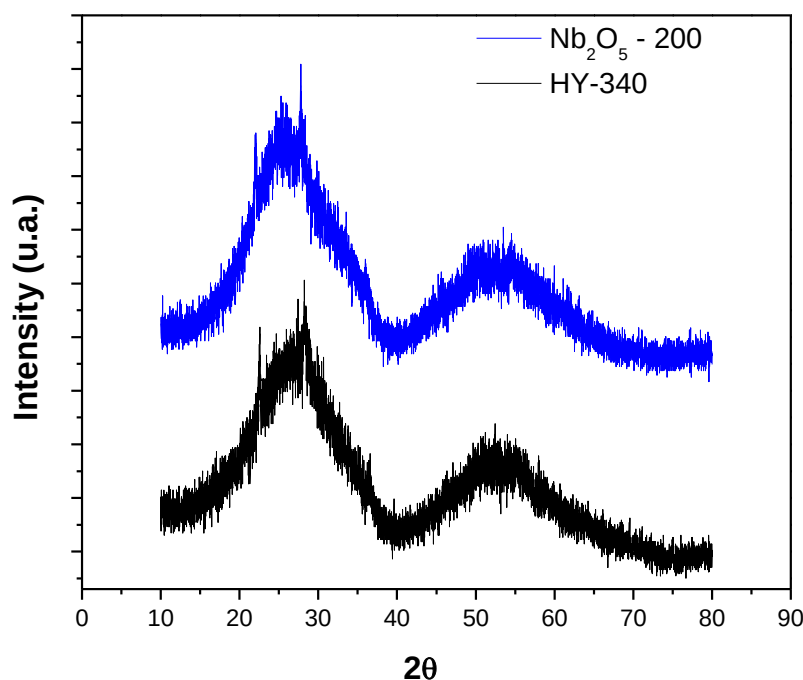


Figure 2: DRX patterns of precursor HY-340 and catalyst Nb₂O₅-200

The total specific surface area of the Nb₂O₅-200 catalyst measured by the BET method was 147 m²/g, a result close to that found in the literature [18]. This area is relatively high, and may favor the adsorption and catalysis processes. It is consistent with the low crystallinity of the material and the low pre-treatment temperature used [19].

The profile of Thermo programmed Ammonia Desorption (TPD-NH₃) of the Nb₂O₅-200 catalyst is shown in Fig. 3. Calculations indicate a total acidity of 1.1 mmol sites/g, value similar to that observed by [22]. Deconvolution of the curve unveil the presence of a small amount of physisorbed ammonia, which was not eliminated in the pre-treatment, and the presence of weak and moderate acid sites.

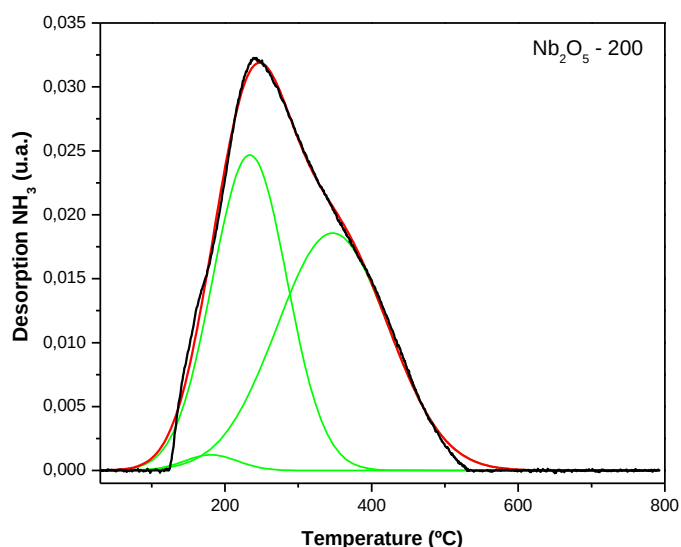


Figure 3: TPD-NH₃ profile for the catalyst Nb₂O₅ - 200

These characterization results suggest that, at 200°C, the temperature used for pre-treatment of the HY-340 precursor was suitable to generate a low crystallinity niobium oxide catalyst with high specific surface area and moderate acidity in terms of acid strength, and can therefore be considered a material with good catalytic potential [3, 4].

Characterization of Raw Material

Table 2 shows the main fatty acids identified in the product extracted from industrial crude glycerol, as well as their relative content.

Table 2: Main fatty acids extracted from glycerol

Acid	Formula	Composition (mol%)
Caproic	C6:0	6.60
Palmitic	C16:0	9.58
Stearic	C18:0	2.36
Oleic	C18:1n9c	20.76
Linoleic	C18:2n6c	52.08
Linolenic	C18:3n3	6.99

Other fatty acids, in proportions less than 1% but representing 4.6% of the total, were identified: undecanoic, lauric, myristic, myristoleic, palmitoleic, heptadecanoic, cis-heptadecanoic, arachidic, gadolinic, eicosapentaenoic, behenic, erucic, tricosanoic and lignoceric.

Catalytic Tests

The results for ethanol esterification of the fatty acids from the glycerol purification process are presented in Table 3. The overall conversion increases with the reaction time, with the temperature, with a higher amount of the catalyst and with a higher value of the ethanol/fatty acids ratio. These trends are expected, in accordance with the literature [14]. It was found that the experiment using 20 g of catalyst per 100 mL of fatty acids, 8 hours of reaction, ethanol/acids volume ratio 0.2 and temperature of 200°C showed the best conversion of the fatty acids to ethyl esters, about 70%.

Table 3: Conversion of residual fatty acids to esters

Test	Temp. (°C)	Volume Ratio ethanol:fatty acids	Amount of catalyst (g/100mL)	Time (h)	Acidity Index (Before) (After)		% Conversion
1	150	0.15	10	6	64.9	34.1	47.5
2	150	0.15	15	8	64.9	24.9	61.6
3	150	0.15	20	6	64.9	23.5	63.8
4	150	0.20	10	8	64.9	24.9	61.6
5	150	0.20	15	6	64.9	22.9	64.7
6	150	0.20	20	8	64.9	22.1	65.9
7	200	0.15	10	6	64.9	32.2	50.4
8	200	0.15	15	8	64.9	26.5	59.2
9	200	0.15	20	6	64.9	23.8	63.3
10	200	0.20	10	8	64.9	29.9	53.9

Test	Temp. (°C)	Volume Ratio ethanol:fatty acids	Amount of catalyst (g/100mL)	Time (h)	Acidity Index (Before)	Acidity Index (After)	% Conversion
11	200	0.20	15	6	64.9	27.8	57.2
12	200	0.20	20	8	64.9	19.5	70.0

Table 4 shows the analysis results of several properties of commercial biodiesel before and after mixing with the ethyl esters produced in the present work, choosing the conditions of greater conversion obtained, that means, experiment number 12 (Table 3). These esters were separated from the reaction medium by filtration of the upper phase of the reaction medium, and then added to the above-mentioned commercial biodiesel in a percentage of 5%. The certification analyses are in accordance with the specifications recommended in resolution ANP number. 45 of 08.25.2014, DOU 26.08.2014, technical regulation ANP 03/2014 for the commercialization of biodiesel in Brazil.

Table 4: Physical and physicochemical analyses of commercial biodiesel pure and mixed with 5% of fatty acid ethyl esters.

Properties analysed	Method	Unity	ANP specification	Commercial biodiesel	Mixture with 5vol.% of fatty acids esters.
Appearance / temperature read in °C	-	-	LII	LII / 20°C	LII / 24.2°C
Specific mass at 20 °C	ASTM D 4052	Kg/m ³	850 - 900	878.4	876.4
Kinematic viscosity at 40 °C	ASTM D 445	mm ² / s	3.0 – 6.0	4.24	4.26
Water content	ASTM D 6304	mg/kg	200 (máx)	93	124
Total contamination	EN 12662	mg/kg	24 (máx)	20.8	20.1
Flash point	ASTM D 93	°C	100 (min)	172	146
Ester content	EN 14103	% Massa	96.5%	98.4	98.8
Total sulfur	ASTM D 5453	mg/kg	10 (máx)	1.7	1.9
Sodium + potassium	NBR 15553	mg/kg	5 (máx)	3.3	3.1
Calcium + magnesium	NBR 15553	mg/kg	5 (máx)	1.4	1.7
Phosphor	NBR 15553	mg/kg	10 (máx)	2	1.6
Corrosion to copper, 3h at 50°C	ASTM D 130	-	1 (máx)	1	1
Clogging point	ASTM D 6371	°C	19 (máx)	+5	-6
Acid value	ASTM D 6371	mg de KOH/g	0.50 (máx)	0.43	0.44

Properties analysed	Method	Unity	ANP specification	Commercial biodiesel	Mixture with 5vol.% of fatty acids esters.
Free glycerol	ASTM D 6584	% massa	0.02 (máx)	0.01	0.01
Total glycerol	ASTM D 6584	% massa	0.25 (máx)	0.17	0.17
Monoglycerol	ASTM D 6584	% massa	0.70 (máx)	0.53	0.54
Diglycerol	ASTM D 6584	% massa	0.20 (máx)	0.11	0.14
Triglycerol	ASTM D 6584	% massa	0.20 (máx)	0.00	0.03
Methanol or etanol	EN 14110	% massa	0.20 (máx)	0.01	0.06
Iodine index	EN 14111	g de I/100g	-	63	60

LII = Impurities Free

The addition of the esters produced, in the proportion of 5% by volume, maintained all the specifications required for the commercialization of biodiesel in Brazil. A reduction in the iodine index from 63 to 60 gI / 100g is observed, pointing to a slightly better oxidation stability, which is consistent with the addition of the esters to the commercial biodiesel, since the latter results from the transesterification of a feedstock containing 60% of soybean (containing unsaturated carbon chains) and 40% of animal fat, while the esters result from the esterification reaction of glycerol contaminating free fatty acids, which are mostly from animal fat (2.0 wt.% of free fatty acids), as the soybean oil has a lower content of free acids (0.67 wt.%). Since fatty acids from animal fat essentially consist of saturated carbon chains, the resulting esters thereof will also be, which implies a greater oxidation stability. Another very important result is the significant reduction of the clogging point which can be ascribed to the lower freezing point of ethyl esters as compared to methyl esters. This property is relevant allowing a larger use of this biodiesel during the winter.

Conclusions

This work shows a promising alternative for the use of industrial waste generated in the process of glycerol purification in the biodiesel producing industries, transforming a problem into an opportunity for improvement, increasing biodiesel productivity, minimizing environmental impacts and operational costs, besides the replacement of chemical agents with high toxicity and fossil origin such as methanol by ethanol.

The work also presents an important aspect related to the environmental performance of the process: the use of a solid catalyst, the Nb₂O₅, originated from abundant raw material in Brazil, which prevents the formation of soaps, and avoids the washing and neutralization steps in the biodiesel production, greatly limiting the generation of effluents.

In summary, the tests carried out showed a real possibility of use of the residues generated from crude glycerol purification and the insertion of cleaner production steps in the biodiesel industry.

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