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Preparation and Study of Bimetallic Compounds Efficiency in the Synthesis of Biodiesel Fuel

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Abstract In this work, biodiesel was obtained by the transesterification of babassu oil into methanol, employing as catalysts heterogeneous CuO/Al_2O_3, CoO/Al_2O_3, and MnO/Al_2O_3. The catalysts were prepared by the method of co-precipitation, which is a mixture prepared using a solution of nitrate of Al^{3+} and nitrate of Cu^{2+}, Co^{2+} and Mn^{2+}. The catalysts were calcined into two temperatures: 400 °C and 650 °C. The best catalytic activity was obtained with the catalysts calcined at 400 °C because at 650 °C, there was a reduction in the amount of nitrates and carbonates in the structures of catalysts. The conditions for the transesterification reaction's oil babassu using the heterogeneous catalysts were evaluated and the best parameters were: 6:1 (molar ratio oil and methanol time of 24 h. The optimum condition was applied to all biodiesel obtained using the catalysts $CuO(0.25)/Al_2O_3$ (CuO400), $CoO(0.4)/Al_2O_3$ (CoO400), and $MnO(0.4)/Al_2O_3$ (MnO400) with yields of 66.70, 98.23, and 68.10, and for biodiesels transesterified twice obtained with the catalysts $CuO(0.25)/Al_2O_3$ (CuO650), $CoO(0.4)/Al_2O_3$ (CoO650), and $MnO(0.5)/Al_2O_3$ (MnO650) with yields of 83.67, 97.86, and 94.13%,. The use of heterogeneous catalysts was very satisfactory with respect to conversion of methyl esters (biodiesel).

Keywords Catalysis · Biodiesel · Babassu

1 Introduction

Energy is fundamental to a country's development, and the energy sources most readily available are petroleum, charcoal, and natural gas. However, these sources are in danger of becoming exhausted in the near future [1]. Moreover, it is important to remember that the limited quantity of oil as a source of energy is not the only problem. When fossil fuels are burned, they release harmful environmental gases. It is also necessary to reduce the environmental gases released from the burning of these energy sources. So is important to look for an alternative energy that can replace, if even partly, fossil fuels, and which can meet the challenge of the growing demand for energy in a sustainable way, therefore reducing the impact on the environment.

Biomass has attracted a large amount of attention in recent decades because it is a renewable energy source and its use has not damaged the environment [2]. Among the sources of biomass readily available, vegetable oils have been widely investigated as candidates for renewable energy programs; they provide decentralized energy generation and support to family farms, thereby creating better conditions of life in poor areas, enhancing regional capabilities and offering alternatives to solve economic, social and environmental problems with difficult solutions [3].

Biodiesel is being treated as a great source of renewable energy because it is derived from vegetable oils or animal fats, it is biodegradable, environmentally benign, and can be used in diesel engines and heating systems with little or no modifications [4, 5].

According to studies by the National Biodiesel Board, Brazil has the potential to become the largest producer of biodiesel in the world, because of its large diversity of oleaginous cultures that are cultivated and which have a

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high potential of producing biodiesel from castor, babassu, sunflower, African oil palm and soybean oils and these oleaginous have a great amount of oils [6, 7]. Brazilian law has decreed that in 2008, the mineral diesel that will be sold in the country must contain 3% biodiesel [8]. Therefore, 1.000,000 m^3 of biodiesel will be necessary to attend this demand. Cultivated areas of some oleaginous crops raised in Brazil must be expanded along with the exploitation of the native plants principally the palm tree, which is an excellent source of oil [9, 10]. The biodiversity of palm trees in Brazil is very extensive and there is a palm tree that could be a source of oil.

The Babassu is a Brazilian palm that can grow up to up to 20 m, where the main commercial products extracted from Babassu are, oil (extracted from nut) and cake (which follows the procedure). This oil accounts to 7% of the total weight from fruit. In numbers, the Babaçu employs approximately 4 million people (vintage 2004), covering 16.5 million hectares, producing approximately 7 million tonnes a year, with an estimated potential of 15 million tonnes per year. The area of occurrence is concentrated in the Northeast (largest producing region), North, Central and West of Brazil, also happening in Mexico and Bolivia. It can found eight species of genus *Orgbnya* and four species of *Attalea*, that to adapt to different types of soil. The northeast of Brazil has an area planted with babassu, about 12 million ha, where the majority is concentrated in the states of Maranhão and Piaui, and monthly are extracted around 140,000 tonnes of these babassu coconut [11]. However, the potential of babassu still unexplored and is possible to utilize for economic production of coal, fuel oil, gas, eatable oil and pressed wood. With regards to the production of oil fuel, babassu oil has excellent characteristics for production of biodiesel, because its composition is predominantly lauric (Table 1) [12]. This fact facilitate the transesterification reaction, as the lauric esters are composed of short and saturated chains that interact more efficiently and effectively with the alcohol and catalyst in order to get a product (biodiesel) with excellent physical and chemical characteristics. Thus, the oil babassu presents itself with an excellent alternative for the production of biodiesel.

Table 1 Chemical composition of babassu oil

Fat acids	Percentual (%)
Caprilic acid (C8:0)	5.0
Capric acid (C10:0)	6.0
Lauric acid (C12:0)	44.0
Myristic acid (C14:0)	17.0
Palmitic acid (C16:0)	8.0
Stearic acid (C18:0)	4.0
Oleic acid (C18:1)	14.0
Linoleic acid (C18:2)	2.0

Biodiesel is being treated as a great source of renewable energy because it is derived from vegetable oils or animal fats, it is biodegradable, environmentally benign, and can be used in diesel engines and heating systems with little or no modifications [4, 5].

Biodiesel is defined as mono-alkyl esters of fatty acids usually produced by transesterification of triglyceride with mono-alkyl alcohols, such as methanol. Also known as methanolysis, this reaction can be catalyzed by either acidic or basic catalysts. Acidic catalysts, such as sulfuric acid, sulfonic acid, or hydrochloric acid catalyze triglyceride transesterification. However, the reaction time is very long (about 96 h) even at reflux of methanol, a high molar ratio of methanol to oil is needed (30–150:1 mol%) and it produces a large amount of wastewater [13, 14]. Potassium or sodium hydroxides are usually used as basic catalysts for this reaction. As the catalyst activity of a base is higher than that of an acid and acidic catalysts are more corrosive, the basic catalysts is preferred to acid-catalyzed routes and is thus more frequently used commercially. However, in the alkaline-metal-hydroxide-catalyzed transesterification, even if a water-free vegetable oil and methanol are used, a certain amount of water is produced from the reaction of hydroxide with methanol. The presence of water leads to the hydrolysis of the esters, and as a result, soap is formed. The formation of soap reduces the biodiesel yield and causes significant difficulty in the separation of esters and glycerol [15]. To avoid and resolve the problems of product separation, the use of heterogeneous catalysts has been proposed [16]. This type of catalyst allows the production of methyl esters to be simplified, thus reaching over 95% conversion, additionally long alcohol chains could be used [17]. The use of heterogeneous catalysts, especially the basic catalysts, has been developed to catalyze the transesterification of vegetable oils with methanol [17]. As a result, a great variety of catalysts such as alkaline-earth metals oxides and hydroxides [18], alkaline metals hydroxides or salts supported on alumina [19], zeolitas [20], and hydrotalcites [21] have been checked at very different reaction conditions and with a variable degree of success. Among these basic catalysts, there are those that are supported on alumina because alumina has adequate structural features that allow the occupation of their vacancies by alkali metals that increase the basicity of catalysts [22].

In an attempt to solve the problems caused by using hydroxide in transesterification reaction of triglycerides and also show the potential of new oleaginous to obtain biodiesel, this paper describes the preparation of mixed oxides such as: CuO/Al_2O_3, CoO/Al_2O, and MnO/Al_2O_3 and their uses as heterogenous catalysts in transesterification reaction of babassu oil and methanol.

2 Experimental

2.1 Materials and Instruments

Babassu oil was purchased in a Teresina city market. All the other reagents supplied were of analytical grade and used without further purification. Metal content was quantified by flame atomic absorption using a spectrometer Varian Spectra AA 200 FS model with a GTA-100 with fire and bottom broker deuterium lamp. Other instrumental parameters were selected in agreement with the recommendations of the Analytical Methods Flame Atomic Absorption Spectrometry (Varian) [23]. In this analysis, the samples were previously digested with HCl. The infrared spectra were obtained in tablets of CsI using a Perkin Elmer spectrometer Spectrum GX FT-IR System. BET surface pore diameters and BJH cumulative pore volume were obtained using N_2 adsorption in a Micromerities ASAP 2010 V4.00 H. Prior to N_2 adsorption, the sample was outgassed for 12 h.

Chemical characterizations were accomplished according to the Instituto Adolfo Lutz Norms [24], United States Pharmacopeial (USP) [25] and AOCS-Cd-1c-85 method [26]. Viscosity was measured using a viscosimetric cinematic tube Cannon Fensk 350 in thermal bath Koehler KV3000 in agreement with NBR-10441. Density was measured in an automatic densimeter Anton Par DMA 4500 following at ASTM D-4052. Ray-X and Horiba SLFA 1800 H determined sulfur in accordance to ASTM D-4994. Pensky Martens HFP 380, closed cup, measured Flash Point in accordance to ASTM D-93. Atomic absorption analysis was performed using a spectrometer, [Spectra-AA 220 FS models, Varian,] with a GTA-100 with fire and bottom broker deuterium lamp. Also used were hollow cathode lamps and fire of air-acethylene in the following wavelengths: 324.7 nm (Cu), 279.5 nm (Mn), and 240.7 nm (Co). Other instrumental parameters were selected in agreement with the recommendations of the Analytical Methods Flame Atomic Absorption Spectrometry [23]. Thermogravimetric analysis (TGA) data were obtained with a TA Instruments Model TGA-2050 thermobalance. At ambient pressure, a 50 mL $\min^{-1}$ nitrogen purge flow was used. The heating rate was 10 °C $\min^{-1}$ and an aluminum pan of 20 mL was used with a ± 0.5 mm diameter hole. The initial temperature was 30 °C and the final one was 450 °C for the biodiesels and 550 °C for the *in natura* oils. DSC curves were obtained using TA Instruments, DSC 2920, with heat flow at room pressure, a 50 mL $\min^{-1}$ N_2 purge flow. The quantities of esters were analyzed by gas chromatography on a Varian CP-3380 chromatograph with FID detector equipped with a polar polyethylenoglycol column BP 20, 12 m, 0,32 i.d. and film thickness of 0.25 mm. Oven temperature ranged from 150 to 260 °C using a heating rate of 10 °C $\min^{-1}$. Spectra ^{1}H-NMR was obtained under ambient conditions on a Bruker advances DRX-500 spectrometer using $CDCl_3$ as solvent and TMS as reference.

2.2 Catalyst Preparation

The catalysts were prepared by co-precipitation method in accordance to the procedure described by Alejo et al. [27]. A mixture of 40% v.v of the $Cu(NO_3)_2$ (1.25 mL L^{-1}) or $Co(NO_3)_2$ (1.25 mL L^{-1}) or $Mn(NO_3)_2$ (1.25 mL L^{-1}) and 60% v.v of the $Al(NO_3)_3$ (1.25 mL L^{-1}) solutions was vigorously stirred and then a 0.25 mL L^{-1} Na_2CO_3 solution was added. During precipitation, the solution was kept at 333 K and pH ca. 8.5. The precipitate was then aged for 2.5 h and washed with water, separated by centrifugation, and then dried at 110 °C for 12 h and calcined in air at 400 °C and 650 °C for 24 h. 3 catalysts calcined at 400 °C were obtained along with 3 catalysts calcined at 650 °C. They were labeled CuO400, CoO400, MnO400, CuO650, CoO650, and MnO650.

2.3 Transesterification Reaction

Transesterification reaction was optimized and variables, time, and molar ratio methanol/oil were studied. The variable temperature (room temperature) and quantity of catalysts (2.5%) were kept constant. The data are presented in Table 2.

According to the test results of optimization, the best condition is the ratio 6:1 methane/oil in 24 h. Thus, this condition was used for all catalysts tested. The babassu oil was transesterified in the presence of methanol alcohol using 2.5% of solids (catalyst). The reaction was kept in a 100 mL glass reactor under magnetic stirring for the desire time. After the course of reaction, the catalyst was separated by filtration and the reaction mixture was then loaded into a rotary evaporator to remove excess alcohol. The biodiesel was recovered in a separating funnel followed by washing many times with distilled water and dried with Na_2SO_4. The biodiesels obtained with these catalysts were labeled BCu400, BCo400, and BMn400.

Biodiesels prepared with the catalysts calcined at 650 °C were transesterified twice because one transesterification did not convert the oil with a good yield.

Table 2 Optimization of transesterification reaction

Experiment	Molar ratio methanol/oil	Time (h)
1	12:1	24
2	6:1	24
3	12:1	12
4	6:1	12

These biodiesels were labeled BCu650, BCo650, and BMn650.

3 Results and Discussion

3.1 Characterization of Catalysts

3.1.1 Chemical Analysis (Flame Atomic Absorption)

By FAA analysis, it was verified that the amounts of Cu, Co, Mn, and Al present in BCo400 and BMn400 were in the following proportion: 0.4:1.0 (MO/Al_2O_3). However, for the catalyst BCu400, 0.25:1.00 was found (see Table 3). The chemical analysis was performed on the catalysts calcined at 650 °C and the values found were not significantly different from those found for catalysts calcined at 400 °C.

3.1.2 Infrared Analysis

The infrared spectra of catalysts thermally activated at 400 °C showed similar profiles. The broad band was observed in the spectral region of 3,800–3,400 cm^{-1} corresponding to the OH^- stretching mode νOH^-. The extension of these bands may mean that the surface of the alumina is covered by other species because pure alumina presents three typical bands at 3,764, 3,721, and 3,677 cm^{-1} corresponding to the OH^- stretching mode [28]. These modes are very sensitive to the presence of other ions incorporated in the lattice [29]. This broad band is attributed to strongly perturbed OH^- bands indicating substantial hydroxylation on the surface. Moreover, a band at 642 cm^{-1} attributed to the M–O stretching mode was observed. Bands in the spectral region (1,450–1,360 cm^{-1} and 810–720 cm^{-1}) were observed corresponding to the CO and NO stretching mode, respectively. These bands were not expected to appear in the infrared spectrum, since the solids were calcined at 400 °C. However, because of this occurrence we then resolved to increase the temperature of calcinations to 650 °C. In the infrared spectrum obtained for catalysts calcined at 650 °C, there was no significant difference from those obtained at 400 °C, i.e., the thermic treatment did not decrease the carbonates and nitrates present in the catalysts.

Table 3 Analysis chemical of catalysts calcined at 400 °C and 650 °C

Catalysts	Composition	Cu	Co	Mn	Al
CuO400[a]	Calculated	2.091			70.917
	Found	2.438			71.340
CuO650[b]	Calculated	3.130			71.502
	Found	3.071			71.532
CoO400[a]	Calculated		4.926	0.862	71.760
	Found		4.614	0.598	72.308
CoO650[b]	Calculated		4.302		49.761
	Found		4.541		53.532
MnO400[a]	Calculated			0.862	82.310
	Found			0.598	82.780
MnO650[b]	Calculated			2.951	85.380
	Found			2.011	81.223

[a] CuO400, CoO400 and MnO400 correspond, respectively to ($CuO(0.25)/Al_2O_3$, $CoO(0.4)/Al_2O_3$ and $MnO(0.5)/Al_2O_3$ calcined af 400 °C

[b] CuO650, CoO650 and MnO650 correspond, respectively to $CuO(0.25)/Al_2O_3$, $CoO(0.4)/Al_2O_3$ and $MnO(0.5)/Al_2O_3$ calcined af 650 °C)

3.1.3 Specific Surface Area (BET)

Textural properties are essential to understand the activity of a particular species. Results of surface area and porosity of the catalyst calcined at 400 °C and 650 °C were quite different as can be seen in Table 4. The catalysts calcined at 400 °C presented micro pores (<20 A), and those calcined at 650 °C presented mesoporos [30]. When there is an increase of specific surface area, generally the catalytic activity also increases. Therefore, the specific surface area is directly proportional to the amount of active sites present on the surface. According to these results, it is expected that catalysts calcined at 400 °C show greater activity that those calcined at 650 °C.

3.1.4 Thermogravimetric Analysis

Thermogravimetric analysis of catalysts calcined at 400 °C showed similar profiles and presented three main events. The first, which had mass loss from room temperature to

Table 4 Textural properties of catalysts

Catalyst	BET (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
CuO400[a]	22.5573	0.0568	100.8864
CuO650[b]	9.2025	0.0223	97.3356
CoO400[a]	47.3919	0.2049	172.9853
CoO650[b]	35.9482	0.0807	89.8179
MnO400[a]	43.5474	0.1682	152.4775
MnO650[b]	21.3729	0.0500	93.6082

[a] CuO400, CoO400 and MnO400 correspond, respectively to ($CuO(0.25)/Al_2O_3$, $CoO(0.4)/Al_2O_3$ and $MnO(0.5)/Al_2O_3$ calcined at 400 °C

[b] CuO650, CoO650 and MnO650 correspond, respectively to $CuO(0.25)/Al_2O_3$, $CoO(0.4)/Al_2O_3$ and $MnO(0.5)/Al_2O_3$ calcined at 650 °C

115 °C was attributed to the physically absorbed water. In the second one, a heavy weight loss of about 55% was observed and was visible around 220 °C to 600 °C, which was attributed to nitrate decomposition [31]. The third event had a weight loss of about 25%, which could be seen around 600 °C to 880 °C, and was attributed to carbonate decomposition. TG curves of catalysts calcined at 650 °C showed the same events observed in TG curves at 400 °C. These results suggest that the complete elimination of the carbonate ions would be possible if the temperature of calcination was up to 800 °C (Fig. 1).

3.2 Characterization of Biodiesels

3.2.1 *Viscosymetric Analysis*

Viscosity is one of the main aspects that differentiate biodiesel from oil in *natura,* and their values must be within those allowed in accordance with ANP for fuel-cycle diesel engines (6.0 cSt). Therefore, the viscosities of biodiesels obtained with the catalyst calcined at 650 °C (Table 5) were measured for this purpose.

In the first transesterification, it was observed that all biodiesels showed values above the maximum allowed for fuel-cycle diesel engines (6 cSt). These viscosity values above the allowed limit indicate that only part of the oil was transesterified. So, a second transesterification was performed based on the weight of the product obtained from the first transesterification.

3.2.2 *Physical–Chemical Analysis*

Physical–chemical characteristics of BCu400, BCo400, BMn400, BCu650, BCo650, and BMn650 obtained in this work are listed in Table 6. The biodiesel viscosities found were within the parameters established by Resolution No. 07 de 19 de março de 2008 [8] of the Agência Nacional de Petróleo, Gás Natural e Biocombustíveis (ANP). The density of biodiesels presented were in agreement with the value accepted by ANP, except for biodiesel BCu400 and

Table 6 Boiling point of babassu oil and biodiesels

Biodiesel	Step	Boiling point (°C)	Loss weight (%)
Babassu Oil	1	318.68	97.57
BCu400[a]	1	205.76	94.80
	2	321.17	4.20
BCo400[a]	1	216.79	97.88
BMn400[a]	1	215.44	92.27
	2	325.25	4.80
BCu650[b]	1	215.98	98.87
BCo650[b]	1	217.89	96.15
BMn650[b]	1	219.12	96.25

[a] Biodiesel obtained using the catalyst (CuO(0.25)/Al_2O_3, CoO(0.4)/Al_2O_3 and MnO(0.5)/Al_2O_3) calcined at 400 °C

[b] Biodiesel obtained using the catalyst (CuO(0.25)/Al_2O_3, CoO(0.4)/Al_2O_3 and MnO(0.5)/Al_2O_3) calcined at 550 °C

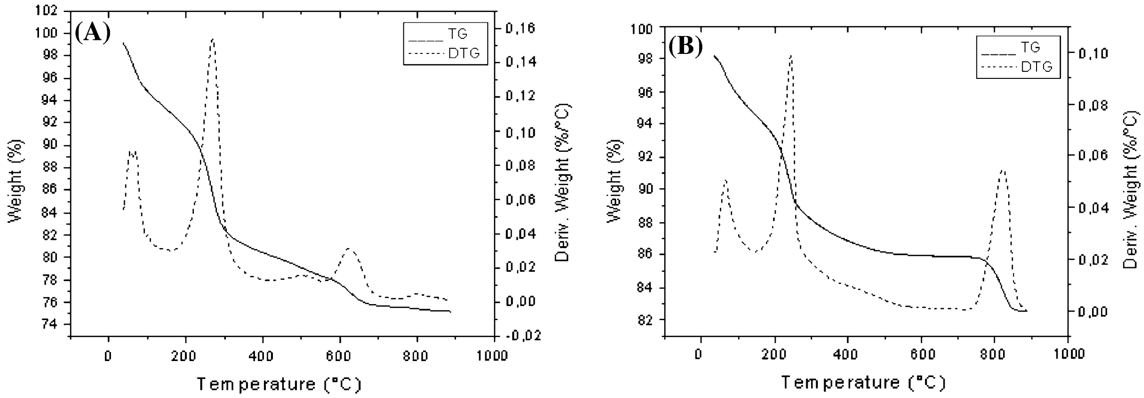


Fig. 1 TG curves of catalysts CoO400 (CoO(0.4)/Al_2O_3 calcined af 400 °C) and CoO650 (CoO(0.4)/Al_2O_3 calcined at 400 °C)

Table 5 Viscosities of biodiesels of catalysts calcined at 650 °C

Viscosity at 40 °C (mm^2/s)	CuO650	Co650	MnO650	Resolution ANP no 07/08 [29]
1[a] Transesterification	7.93	6.36	7.87	3.3–6.0
2[a] Transesterification	5.32	3.22	5.18	

[a] CuO650, CoO650 and MnO650 correspond, respectively to CuO(0.25)/Al_2O_3, CoO(0.4)/Al_2O_3 and MnO(0.5)/Al_2O_3 calcined at 650 °C

BCu650, but the greatest viscosity found were these biodiesels.

The minimum temperature necessary for combustion in the presence of a flame (Flash Point) was above that established by the ANP. The values found in this analysis pointed to increased security in the handling and transportation of biodiesels with respect to diesel, which enters into combustion around 76 °C [4].

Acidity index and alkalinity value found for the biodiesels studied in this work are in accordance with those permitted by Resolution N°07/08 ANP and show that the process of washing and purification was efficient.

Sulphur content is not standardized by the ANP; however, it is recommended that it be analyzed along with other characteristics and reported to the agency. The values of the sulphur content of biodiesels BMn400, BCu650, and BMn650 were not determined because they were below the detection limit of the apparatus used, and for biodiesels BCu400, BCo400, BCo650, their values were low when compared with those found in diesel and may be considered negligible.

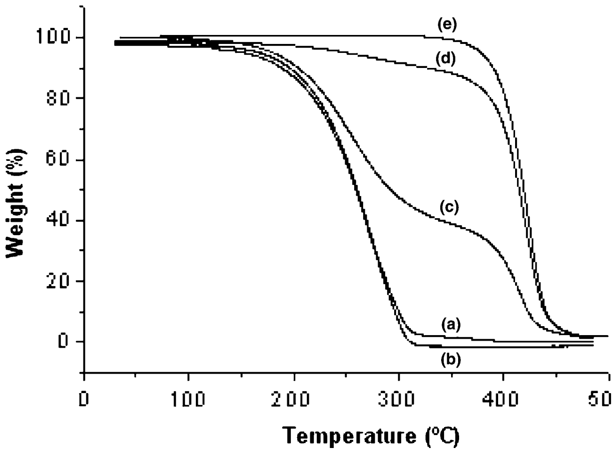


Fig. 2 TG curves: (a) 12:1/24 h, (b) 6:1/24 h, (c) 12:1/12 h, (d) 6:1/12 h, (e) BO (babassu oil)

3.2.3 *Thermogravimetric Analysis*

The thermal behavior of biodiesel was determined by thermogravimetric studies. Boiling point is an important property of biodiesels and it is a parameter that relates to the quality of the biodiesel, as determined by ANP [2]. Thermogravimetric analysis is a fast, easy, cheap, and very useful technique to measure the biodiesel boiling point [32, 33]. Besides, thermogravimetric analysis can confirm the occurrence of transesterification reaction because the boiling points of the triglycerides and esters (biodiesel) are different [34].

Figure 2 shows the TG curves of the study of optimization variables, time, molar proportion alcohol/oil using catalyst CuO400.

The study showed that in condition *d*, the conversion of transesterification reaction was quite small and can be considered void. TG curve ***c*** presented two mass losses; the first loss was attributed to the formation of methyl esters and the second one, the babassu oil that was not converted.

Curves *a* and *b* show the same behavior in which only a mass loss can be seen. Therefore, condition *b* has been chosen for the catalytic tests in this work because the proportion of methanol/oil was lower.

TG curve of babassu oil (BO) showed boiling point at 318.68 °C. This can be attributed to a single substance or mixture of substances with small differences in their molecular weights. TG curves of BCu400, BCo400, BMn400 and Bcu650, BCo650 and BMn650 (Table 7) present similar thermic behavior by having a boiling point around at 215 °C. The decrease of boiling temperature can be attributed to the formation of methyl esters because they have a lower molar mass showing the occurrence of transesterification reaction. However, the TG curves of the

Table 7 Properties of babassu oil and its methylester

Parameter	Babassu oil	Catalysis/biodiesel						ASTM D651-06	EN 14214	ANP n° 07/08
		BCu400^{a}	BCu650^{b}	BCo400^{a}	BCo650^{b}	BMn400^{a}	BMn650^{b}			
Kinematic viscosity at 40 °C (mm^2/s)	31.05	5.27	5.32	4.34	3,22	4.35	5.18	1.9–6.0	3.5–5.0	3.3–6.0
Density at 20 °C (g/cm^3)	0.9153	0.887	0.881	0.876	0,878	0.879	0.878		0.86–0.90	0.85–0.90
Flash point (°C)	300	110	110	110	110	112	110	130.0 min	>101	100 min
Acidity index (mg KOH/g)	0.2300	0.2397	0.2513	0.2210	0.1794	0.0268	0.2333	0.5 max	0.5 max	0.50 max
Free glycerin (%)	ND	0.0153	0.031	0.0037	0,0150	0.0153	0.0140			0.02 max
Sulphur content (ppm)	ND	1.8	ND	1.8	1.7	ND	ND	15 ppm	10 ppm	50 ppm

ND Not detected

[a] Biodiesel obtained using the catalyst (CuO(0.25)/Al_2O_3, CoO(0.4)/Al_2O_3 and MnO(0.5)/Al_2O_3) calcined at 400 °C

[b] Biodiesel obtained using the catalyst (CuO(0.25)/Al_2O_3, CoO(0.4)/Al_2O_3 and MnO(0.5)/Al_2O_3) calcined at 650 °C

samples BCu400 and BMn400 showed a loss mass at 321.17 and 325.25 °C, respectively, which was attributed to a residual oil in *natura*. Figure 3 shows the thermogravimetric curves of BCo400 and BCo650.

Biodiesels prepared using the catalysts BCu650, BCo650, and BMn650 showed the same thermic behavior that catalysts BCu400, BCo400, and BMn400, but please note that biodiesels BCu650, BCo650, and BMn650 were obtained through two transesterifications.

DSC can be defined as a technique that measures the temperature and the flow of heat associated with the transitions of materials depending on temperature and time. These measurements provide information on qualitative and quantitative physical changes and chemical processes involving endothermic (absorption of heat), exothermic (evolution of heat), or changes in calorific capacity [35]. Analyzing the DSC curves of biodiesels obtained using the catalysts calcined at 400 °C and 650 °C, endothermic transitions were observed and were attributed to the process of volatilization and/or decomposition of methyl esters.

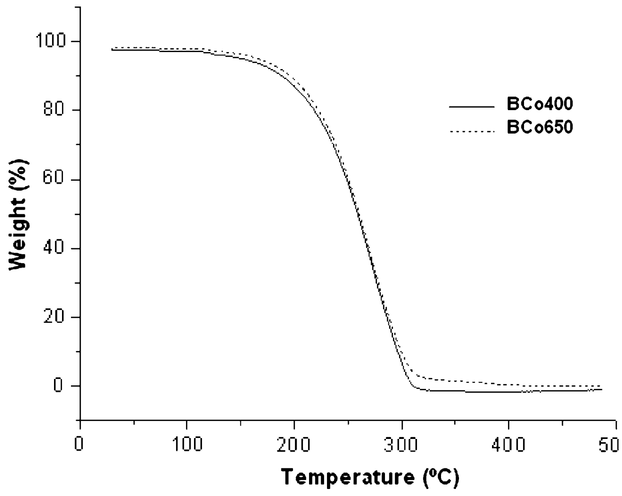


Fig. 3 TG curves of biodiesel obtained using the catalyst CoO(0.4)/Al_2O_3 calcined at 400 (BCo400) and 650 °C (BCo650)

3.2.4 *Chromatography Analysis*

Technical GC/MS analyzed biodiesels and the results can be seen in Table 8. The composition of babassu biodiesels presented methyl laureate as the major constituent. The babassu biodiesel, whose major component is methyl laureate, is composed of a blend of fatty acid esters. More than 70% of these esters are saturated.

Total ions chromatograms (TIC) obtained for the methyl esters of babassu oil shown is relatively similar for all samples; therefore, we present only the chromatogram of the sample ions total BMn400 (Fig. 4).

Chromatograms pointed to the presence of 14 peaks, of which 12 peaks correspond to methyl esters obtained and 02 correspond to the presence of mono, di, and triglycerides as identified by comparing the mass spectra obtained with the library of the equipment.

3.2.5 *NMR ^1H and ^{13}C*

There were spectra of ^{1}H and ^{13}C NMR of the OB, BCu400, BCo400, and BMn400 with the purpose of confirming the conversion of babassu oil in methyl esters.

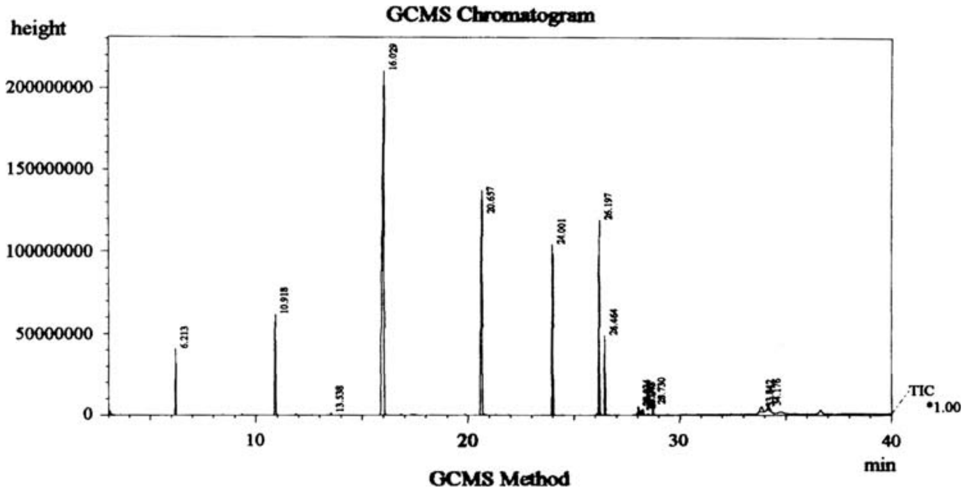
For triglycerides, protons on acyl groups resonate at 0.8–2.9 ppm, while, H-1, H-2 and H-3, which are the protons attached to glycerol carbons, appear at a downfield of 4.0–5.2 ppm. The signal due the methoxy protons of the methyl esters appears at 3.7 ppm [37]. So, the ^{1}H-NMR spectra of BCu400 and BMn400 showed signs of H-1, H-2, and H-3 residual indicated that the conversion was not complete. Moreover, a signal appeared at 3.65 was attributed to methylic hydrogen. The ^{1}H-NMR spectrum of the BCo400 presented a singlet at 3.41 ppm that was attributed to the methylic hydrogen and not presented to signals of H-1, H-2, and H-3 residual. ^{13}C NMR spectrum of BCu400 and BMn400 were observed signs of glycerol carbon in the 60–70 ppm and a signal at 51 ppm of methyl carbon. ^{13}C NMR spectrum of BCo400 presented a signal at 51 ppm and not presented to signals referent to glycerol carbon.

Table 8 Composition of fatty acids present in methanol babassu biodiesel

Common name	Described in the literature [36]	Found		
		BCuO400[a]	BCoO400[a]	BMnO400[a]
Caprylic acid (C8:0)	5.5	5.01	3.69	5.44
Capric acid (C10:0)	6.1	7.23	4.75	5.97
Lauric acid (C12:0)	34.0	44.132	35.67	40.92
Myristic acid (C14:0)	19.2	15.28	18.14	15.97
Palmitic acid (C16:0)	10.6	9.29	11.76	9
Stearic acid (C18:0)	4.3	3.42	4.75	3.17
Oleic acid (C18:1, 9)	17.1	13.07	15.26	13.55
Linoleic acid (C18:2, 9, 12)	3.1	2.57	5.99	3.04

[a] Biodiesel obtained using the catalyst (CuO(0.25)/Al_2O_3, CoO(0.4)/Al_2O_3 and MnO(0.5)/Al_2O_3) calcined at 400 °C

Fig. 4 Chromatogram of Biodiesel obtained using the catalyst MnO(0.4)/Al_2O_3 (BMn400) Calcined at 400 °C



^{1}H NMR technique can be used to determine the yield of transesterification reaction. We used the areas of signals methylene and methoxy protons to monitor the yield of transesterification according to the Eq. 1 [38].

$$C = 100 \times 2A_{ME}/3A_{CH_2} \tag{1}$$

where C is percentage conversion of triglycerides to corresponding methyl ester; A_{ME} is integration value of the protons of the methyl esters (the strong singlet); and A_{CH_2} is integration value of the methylene protons. Factors 2 and 3 from the fact that the methylene carbon possesses two protons and the alcohol (methanol derived) carbon has three attached protons.

Using equation 1, the following rates of conversion were found: 98.2%, 68.1%, and 66.7% for BCo400, BMn400, and BCu400.

4 Conclusion

The results obtained by atomic absorption spectroscopy in flame suggest that the metal oxides are present in the following proportions: MnO(0.4)/Al_2O_3, CoO(0.4)/Al_2O_3, and CuO(0.25)/Al_2O_3. The techniques of IV and TG indicated the presence of the groups CO_3^{2-} and NO_3^- suggesting that the temperatures of calcinations were not sufficient to dismantle these ions. Even so, the heterogenous catalysts described in this manuscript had good catalytic activity front of the transesterification reaction of babassu oil, and the catalysts that showed better conversions were CoO400 and CoO650. The physical–chemical properties of biodiesels obtained in this work attend the specifications required by national standards (ANP) and international (ASTM and EN), and can be used alone or mixed with diesel in cycle diesel engines without having to make any adjustment in these machines.

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