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Article

Heterogeneous Catalysis Afford Biodiesel of Babassu, Castor oil and Blends

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Este trabalho descreve a preparação de biodiesel proveniente de óleo de babaçu, mamona e misturas destes em várias proporções, utilizando compostos alcalinos de estrôncio ($SrO + SrCO_3 + Sr(OH)_2$) como catalisadores heterogêneos. A mistura de óleos dessas oleaginosas foi utilizada na produção de biodiesel com parâmetros de qualidade que atendam a legislação vigente. O catalisador foi caracterizado por difratometria de raios X (XRD), fisissorção de gas (método BET), microscopia eletrônica de varredura (SEM), espectroscopia de raios X por dispersão em energia (EDX) e espectroscopia no infravermelho com transformada de Fourier (FTIR). Os parâmetros reacionais foram acompanhados através da viscosidade dos biodieseis obtidos. As reações de transesterificação usando os compostos de estrôncio apresentaram taxas de conversões de 97,2% (óleo de babaçu), 96,4% (óleo de mamona) e 95,3% (mistura de óleo de babaçu com óleo manona na proporção de 4:1).

This work describes the preparation of babassu, castor oil biodiesel and mixtures in various proportions of these oils, using alkaline compounds of strontium ($SrCO_3 + SrO + Sr\ (OH)_2$) as heterogeneous catalysts. The mixture of oils of these oleaginous sources was used in the production of biodiesel with quality parameters that meet current legislation. The catalyst was characterized by X-ray diffractometry (XDR), physisorption of gas (BET method), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and Fourier transform infrared spectroscopy (FTIR). The viscometric technique was used to monitor the optimization. The transesterification reactions performed using strontium compounds reached conversion rates of 97.2% babassu biodiesel (BB), 96.4% castor oil biodiesel (COB) and 95.3% Babassu/Castor Oil Biodiesel 4:1 (BBCO41).

Keywords: strontium oxide, biodiesel, heterogeneous catalysis

Introduction

Renewable and non-polluting energy has generated research on the use of biomass and has demonstrated success in some areas. Vegetable oils and animal fats have been used to produce an alternative fuel compared to petroleum diesel, commonly called biodiesel.[1] Biodiesel is synthesized by the transesterification of vegetable oils or animal fats with an alcohol in the presence of a catalyst.[2-5] The transesterification of these oils and fats is carried out using homogeneous or heterogeneous catalysts.[6] The homogeneous catalysis has good conversion rates, and the kinetic is very fast in relation to the heterogeneous one.[6] However, it presents enormous difficulties related to the separation of products, which leads to an increase in the production cost. The heterogeneous catalysis is ecologically and economically more viable than the homogeneous transesterification reaction, because it presents an easy separation of the end products, and the catalyst can be reused any time.[7,8]

The origin of the oil primarily reflects in the constitution and kind of fatty acid chains present in triglycerides. Thus, vegetable oils present varied composition of chain fatty acids (Table 1).[9] Therefore, the properties of the biodiesels are derived from the fatty acid chains present in oils or fats.

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Table 1. Composition of babassu and castor oil fatty acids

Fatty acid	Composition / %	
	Babassu oil[9]	Castor oil[7]
Caprilic	5.0	–
Capric	6.0	–
Lauric	44.0	–
Miristic	17.0	–
Palmitic	8.0	0.7
Stearic	4.5	0.9
Oleic	14.0	2.8
Linoleic	2.0	4.4
Ricinoleic	–	90.2
Licosanoic	–	0.3
Dihidroxiestearic	–	0.5

The main source of raw material in Brazil for biodiesel production is soybean oil. However, this oil is also consumed as food products. Therefore, it is necessary to diversify the supply option of raw material for this purpose.[10] Fortunately, Brazil has a great diversity of plants that can be used to manufacture biodiesel. One of these is babassu coconut oil. Northeast Brazil has an area of about 12 million planted hectares, with most being concentrated in the Maranhão and Piauí States.[9] Monthly, around 140,000 tons of almonds are drawn from this culture, and it is possible to use the entire coconut. With regard to the production of fuel oil, babassu oil has excellent characteristics for biodiesel production because it is composed predominantly of lauric ester.[9] This facilitates the transesterification reaction because the lauric ester is composed of short chains that interact more effectively with the alcohol and the catalyst in order to obtain a product with excellent physicochemical characteristics, even though the catalyst is different from NaOH. However, this composition can compromise some parameters of biodiesel, such as cold filter plugging point (CFPP). Castor oil is another feedstock that can be made into biodiesel, but it has unique characteristics when compared to other vegetable oils.[7] Ricinoleic acid (12-hydroxy-9-octadecenoic) is the most abundant in the constitution of castor oil (Table 1). The presence of the hydroxyl group reflects in its colligative properties, particularly viscosity.[7] The biodiesel produced from castor oil has good physicochemical characteristics, which are required by the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP Resolution 14/12)[11] with the exception of the viscosity parameter.[12]

In order to fix the parameters that compromise babassu and castor oils, such as viscosity and CFPP, the proper biodiesel synthesis of these oils, and mixtures in various proportions, is quite important.

Liu *et al.*[2] have studied heterogeneous catalysts such as alkali metal oxides for the transesterification of soybean oil and obtained good results. The best results were found when SrO was used as a catalyst. SrO was obtained by thermal decomposition of $SrCO_3$ in the uncontrolled atmosphere.[13] SrO showed high catalytic activity due to its high basicity.[13]

There are many methods for characterization of biodiesel, including gas chromatography (GC),[14] high-pressure liquid chromatography (HPLC),[15] nuclear magnetic resonance (NMR) spectroscopy,[16,17] and Fourier transform near-infrared (FTNIR) and infrared (FTIR) spectroscopies.[18] Among these, NMR and GC are standard techniques that many researchers employ.[19] However, the equipment required for these techniques as well as the cost of analysis are expensive and sometimes take a long time to be realized. When an industry needs to monitor production, needs accurately and quickly, and requires techniques that are inexpensive and easily accessible. One such technique is the viscometry that can be used to monitor this reaction in an industry.

This work describes the preparation of babassu, castor oil biodiesel and mixtures in various proportions between these oils using a heterogeneous catalyst, which is a mixture of carbonate, oxide and strontium hydroxide. The optimization of these biodiesels was made using the viscometric technique because this technique is likely to become viable and convenient for use in industry.

Experimental

Materials and methods

Methyl alcohol (Synth), sodium sulfate (Vetec) and strontium carbonate (Vetec) of analytical grade were used without further purification. The vegetable oils (babassu and castor oils) were obtained from commercial sources (Novo Nilo, Piauí State, Brazil) and used as received. Chemical characterizations were accomplished according to the Instituto Adolfo Lutz norm (Brazil),[20] The United States Pharmacopeia[21] and AOCS Official Method Cd 1c-85 (American Oil Chemists' Society).[22]

Viscosity was measured using a viscometric kinematic tube Cannon Fenske 350 immersed in a Koehler KV3000 thermal bath in agreement with ABNT NBR-10441 norm (Brazilian Association of Technical Standards).

Density was measured in an automatic densimeter Anton Paar DMA 4500 following the ASTM D-4052 norm (American Society for Testing and Materials norm).

Sulfur content was determined by X-ray fluorescence in a Horiba SLFA 1800 H in accordance to ASTM D-4294 norm.

Flash point was measured in a Pensky Martens HFP 380, closed cup apparatus, in accordance to ASTM D-93 norm.

Analysis of fatty acid esters (ester content) was performed by gas chromatography in accordance to ABNT NBR-15764 norm using a Shimadzu QP 2010 gas chromatograph with flame ionization detector (FID), equipped with a carbowax capilary column, stationary phase of polyethylene glycol, 30 m, 0.32 i.d. and 0.25 µm film thickness. The oven temperature ranged from –60 to 400 ºC, using a heating rate of 10 ºC min^{-1}. Triglyceride, diglyceride, monoglyceride and total and free glycerol to COB and BBCO41 biodiesels were measured by gas chromatograph in accordance with ABNT NBR-15344, ABNT NBR-15342 and ABNT NBR-15341 using the same equipment described to measure ester content.

The infrared spectra were obtained in tablets of KBr using a spectrometer Bomer MB series B 100 and an attenuated total reflectance (ATR) cell with ZnSe crystal and angle of 45°.

The X-ray diffractograms (XDR) were carried out in an Rigaku Rotaflex X-ray diffractometer, using monochromatic Cu K_α radiation (λ at 1.54056 Å) and graphite monochromator. The tests were made with a voltage of 40 kV and filament current of 150 mA, the 2θ angle was varied from 5 to 75°. The XRD patterns of the samples were analyzed and compared with JCPDS-ICDD cards (Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data) available on the product software. Quantitative multi-elemental analyses were performed by energy dispersive X-ray spectroscopy (EDX800, Shimadzu, Tokyo, Japan).

Analysis by scanning electron microscopy (SEM) was performed in a ZEISS DSM 940 A electron microscope, using SE (secondary electrons) with acceleration voltage of 20 kV, a current of 0.79 µA and working distance of about 11 mm.

^{1}H NMR spectra were obtained under ambient conditions in a Bruker DPX-250 spectrometer, using $CDCl_3$ as solvent and TMS (tetramethylsilane) as reference. To calculate the rate of conversion (%) of oil to esters, equation 1 was employed.[23]

$$\text{Conversion} = \frac{2\,A_{CH_3}}{3\,A_{CH_2}}100 \qquad (1)$$

where, A_{CH_3}: integration area of signal at 3.64 *d* related to methoxylic and carboxylic acid hydrogen; A_{CH_2}: integration area of the signal at 2.3 *d* related to a-methylene hydrogen of carbonyl molecules of methyl esters and triacylglycerol.

Catalyst synthesis

The catalyst was prepared following the method described by Liu *et al.*,[2] using calcination of $SrCO_3$ at 1100 ºC for 5 h in a muffle furnace without controlled atmosphere, after calcination of the powder, it was kept in a desiccator.

Basic strength of catalyst

The basic strength of the catalysts (H_) was determined by using the Hammett indicator method.[24] Approximately 100 mg of the catalyst were shaken with the appropriate amount of Hammett indicator diluted with methanol and left to equilibrate for 2 h until no further color changes were observed. The color of the catalyst was then recorded. The following Hammett indicators were used: neutral red (H_ = 6.8), bromothymol blue (H_ = 7.2), phenolphthalein (H_ = 9.3), 2,4-dinitroaniline (H_ = 15.0) and 4-nitroaniline (H_ = 18.4). The base strength of the catalysts was defined as being stronger than the Hammett indicator if it showed a color change but weaker if it showed no color change.

Biodiesel synthesis

The experimental plan involved six catalyst concentrations, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 (%, m m^{-1}, oil); three sets of reaction times, 1.0, 2.0 and 3.0 h; and the temperature was kept at 65 ºC and the molar ratio of methanol:oil was 6:1. The oil (babassu or castor oil, 200 g) was heated at 100 ºC to eliminate water or other impurities in a beaker and then it was cooled at 65 ºC (first beaker). The catalyst quantity was dissolved in 40 g mL^{-1} of methanol, and the mixture was stirred for 30 min, at 65 ºC, to ensure that part of the catalyst dissolved in alcohol because it is insoluble in this solvent (second beaker). After this, the first beaker was dropped to the second one and the mixture was kept to 65 ºC for the duration of the reaction (1, 2 or 3 h). The mixture was centrifuged and filtered off, and the residual alcohol was evaporated under vacuum; then the remaining mixture was transferred to a decanting funnel. The esters were washed with water, and afterwards, they were filtered through anhydrous sodium sulfate. The biodiesels obtained were called BB (babassu biodiesel) and COB (castor oil biodiesel).

The syntheses of biodiesel blends (babassu:castor oil) were carried out using the same apparatus described above. The following ratios of babassu to castor oils were applied: 1:1, 2:1, 3:1 and 4:1. The reactions were performed at 65 ºC during 1 h using 1.0 % of catalyst.

These biodiesels were called by BBCO11, BBCO21, BBCO31, BBCO41.

Reusability of catalyst

The reusability aspect of the catalyst after several successive runs was also tested using only babassu oil. The experimental runs were conducted at a methanol to oil molar ratio of 6:1 catalyst to oil mass ratio of 1%, a reaction time of 60 min. After the reaction, the catalyst was separated from the reaction mixture by filtration, washed with petroleum ether and methanol to remove glycerin and undesired material attached on the surface of the catalyst and then dried at 120 ºC for 24 h. Before reuse for the next run, the recovered catalyst was calcined at 1100 ºC for 6 h. The conversion into ester was measured by GC following the same methodology described earlier in this work.

Solubility and heterogeneity tests of catalyst

Solubility

A study of the catalyst solubility by monitoring its conductivity was performed in this study. 0.25 g of catalyst was added at 50 g of methanol and the mixture was stirred for 30 min, then the mixture was filtered and the conductivity was measured using a CD-830 conductivimeter, platinum electrode at 25 ºC.

Heterogeneity

50 g of oil, 10 g of methanol and 0.5 g of catalyst were stirred and heated at 65 ºC for 15 min. The catalyst was filtered from the reaction mixture, and the filtrate was allowed to react up for 30 min. After 30 min, the reaction mixture was analyzed by gas chromatograpgy. The catalyst was washed with hexane, dried at 100 ºC, calcined at 1100 ºC for 6 h, and then analyzed by XRD and FTIR.

Results and Discussion

Catalyst results

Figure 1 shows the diffractograms of $SrCO_3$, SrO + $SrCO_3$ + $Sr(OH)_2$, and $SrO.xH_2O$. Figure 1a shows that the diffraction peaks are characteristic of $SrCO_3$, in accordance with the crystallographic cards (JCPDS 00-05-0418).[25] The diffratogram also shows that the strontium carbonate has a highly crystalline structure.

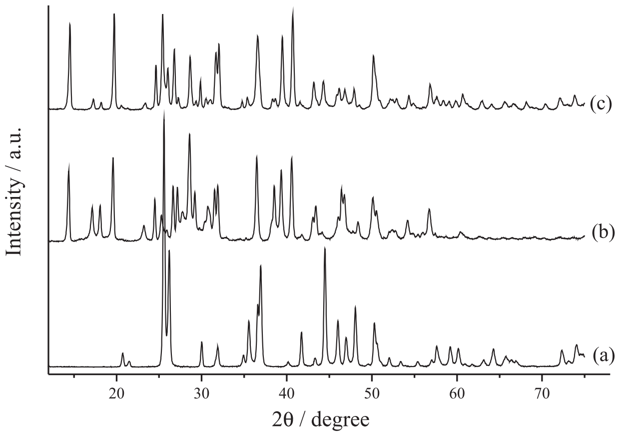

Figure 1. Diffratograms of (a) $SrCO_3$, (b) [$SrCO_3$ + SrO + $Sr(OH)_2$] and (c) $SrO.xH_2O$.

After a heat treatment of $SrCO_3$ at 1100 ºC for 5 h (in an uncontrolled atmosphere) to form SrO, it was expected to observe a diffractogram of a single phase corresponding to the pure oxide. But as illustrated in Figure 1b, instead it was identified diffraction peaks that are characteristic of a mixture of phases between SrO (JCPDS 00-006-0520),[26] SrO•xH_2O (JCPDS 00-019-1276)[27] and $SrCO_3$. After calcination, the catalyst was kept in a desiccator under vacuum; even so, with these results, the catalyst may have been exposed to moisture in the air and then graduated from the other compounds like SrO•xH_2O because SrO is very hygroscopic.[28] $SrCO_3$ in the product may be due to the reactivity of SrO and CO_2 present in the air, indicating the strong basic property of SrO.[9] The peaks observed in the XRD pattern in Figure 1c for the SrO hydrated mixture were less intense when compared with the peaks in Figure 1b probably due to the masking by water molecules.

The quantitative multi-elemental analyses performed by energy dispersive x-ray spectroscopy (EDX) showed the following results: 84.7% (SrO), 12.5% [$Sr(OH)_2$] and 2.1% ($SrCO_3$). These results show that the product obtained after calcinations is the SrO, although XRD technique presented a combination phases of the product.

The FTIR spectra of the catalysts and the precursor $SrCO_3$ show an intense broad band in the region 3600-3000 cm^{-1} attributed to OH stretch corresponding to hydration of the samples, before and after the heat treatment. In the product, there was also a decrease in the intensity of the bands located at 1473, 856 and 700 cm^{-1} related to stretching and deformation of CO_3^{2-} ion bonds, indicating the thermal decomposition of carbonate to form the oxide. The band at 592 cm^{-1} was attributed to the stretch of Sr–O bond.[10] The FTIR spectrum of the catalyst shows the presence of bands corresponding to the carbonate within the structure of the oxide or formed by adsorption of CO_2 from the air.

Figure 2 shows the morphology of $SrCO_3$ and of the catalyst $SrCO_3$ + SrO + SrO•xH_2O obtained by SEM.

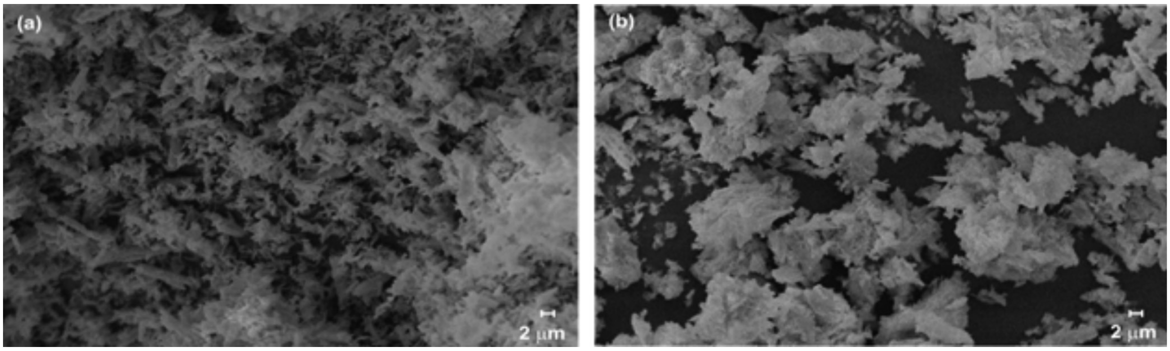

Figure 2. SEM of (a) $SrCO_3$ and (b) $SrCO_3$ + SrO + $Sr(OH)_2$]

These micrographs reveal that $SrCO_3$ presents rod-shaped particles with different sizes forming irregular clusters (Figure 2a). This clustering leads to a decrease in the surface area of the catalyst (a particle is covered by the other, causing this effect), which would not be interesting because the catalytic activity depends on the surface area available to the substrate.[29] The synthesized catalyst (Figure 2b) is composed of chipboard, presenting dense particles with a heterogeneous distribution of particle sizes. The increase of the temperature causes the coalescence of the particles increasing the particle size.[13] Since catalysis is a surface phenomenon, the knowledge of the specific surface area and pore distribution of a catalyst is very important in the interpretation of the catalytic activity.[30] One of the most useful methods to study the specific area of catalysts is the BET (Brunauer-Emmet-Teller) method. The results relating to the catalyst obtained in this study and its precursor $SrCO_3$ by BET method are presented in Table 2.

The results show that the thermal decomposition of $SrCO_3$ to the catalyst obtained ($SrCO_3$ + SrO + SrO•xH_2O) caused an increase in surface area due to coalescence of particles as shown in Figure 2b. Although the surface area is an important factor for a particular type of catalytic reaction, it does not mean that catalysts with low surface area may not provide high conversion rates.

An important factor that has to be considered is the base strength of the catalyst. Sung Jin Yoo *et al.*[31] measured the base strength of various metal oxides (ZrO_2 $H\_ < 6.8$, TiO_2 $6.8 < H\_ < 7.2$, ZnO $7.2 < H\_ < 9.3$, CaO $9.3 < H\_ < 15.0$, SrO $15.0 < H\_ < 18.4$). In this study, the base strength of the catalyst obtained was measured by the Hammett indicator method, and the result was $13.7 < H\_ < 18.4$.

Optimization of reaction parameters

Catalysts that have a lower reaction time and can be used in small amounts in the reaction medium bring benefits such as reducing costs of product separation steps and minimizing the possible contamination of the desired product. These benefits make the utilization of catalysts adequate to use for biodiesel production on a large scale.[8] Transesterification reaction is a process that removes glycerin from the triglycerides, so this process provides lower viscosity of the desired product.[3] Therefore, the viscometer analysis was used to monitor the activity of the catalyst in this study. Figure 3 shows the results of viscosity found for BB and COB.

The results of viscosity for babassu biodiesel showed that when the reaction was running above 2 h and 1% of catalyst, it was within the limits established by ANP 14/12 Resolution.[11] Therefore, these results suggested that the best reaction conditions were 1.0% catalyst, 65 ºC and 1h of reaction time.

The results of viscosity for castor oil biodiesel (Figure 3b) showed that the transesterification reaction occurred in all cases, but the values are outside the limits established by ANP 14/12 Resolution.[11] In this case, castor oil has 90% of ricinoleic acid in its composition. The hydroxyl group at the 12th carbon and a double bond at the 9th carbon, as shown in Figure 4, are characteristics that affect directly the viscosity of castor oil and the biodiesel from this oil.[30]

Although the high viscosity of castor oil methyl esters is the biggest drawback for its use as biofuel, it has other advantages such as good lubricity when mixed with mineral diesel, good miscibility in alcoholic solutions due the hydroxyl group, high cetane number and calorific

Table 2. BET specific area, pore volume and pore size

Sample	Specific surface area / (m^2g^{-1})	Pore volume / (cm^3g^{-1})	Pore size / Å	Pore width
$SrCO_3$	2.0229	0.002304	45.5633	mesopore
[$SrCO_3$ + SrO + $Sr(OH)_2$]	2.9398	0.003176	43.2083	mesopore

content, as well as low phosphorus and carbon residues.[32,33] Taking these facts into consideration, it was performed the synthesis with a mixture of both babassu and castor oil.

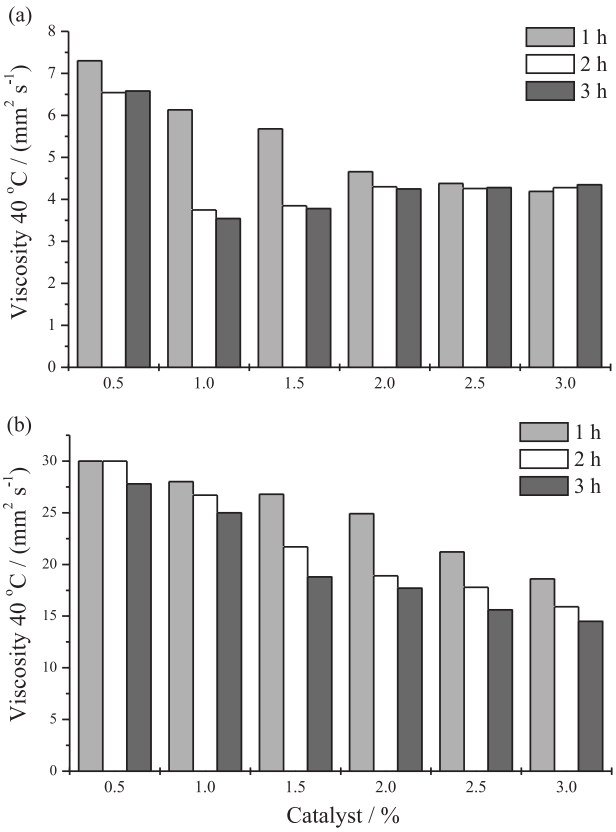

Figure 3. Viscosity of (a) BB and (b) COB.

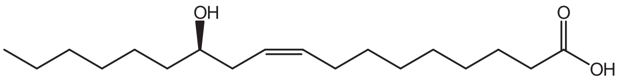

Figure 4. Chemical structure of the ricinoleic acid.

The viscosities of BBCO are shown in Figure 5, and we can see that just the BBCO41 sample is considered within the limit established by legislation (ASTM D651-09, EN 14214 and ANP 14/12).

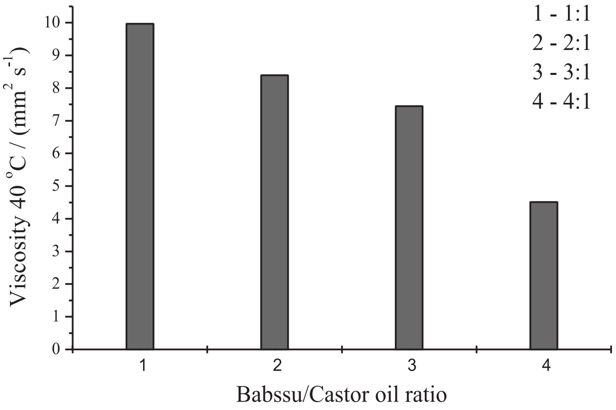

Figure 5. Viscosity of BBCO.

The synthesis of babassu biodiesel that was used above 2.0% of catalyst presented some problems, especially regarding the separation and purification stages of methyl esters so, the measure of NMR, GC and physicochemical were made with the samples that run using 1% of

Table 3. Physicochemical characterization of BB, COB and BBCO41

Parameter	Feedstock		Biodiesel			ASTM D651-09	EN 14214	ANP 14/12[11]
	Babassu	Castor oil	BB	COB	BBCO41			
Kinematic viscosity at 40 ºC / (mm² s⁻¹)	30.4	255	3.5	15.5	4.5	1.9-6.0	3.5-5.0	3.3-6.0
Density at 20 °C / (g cm⁻³)	0.9249	0.9598	0.880	0.924	0.902	na	0.86-0.90	0.85-0.90
Flash point, min. / °C	310	300	115	120	122	130	> 101	100
Acidity index / (mg KOH g⁻¹)	0.85	0.89	0.13	0.40	0.45	0.5 max.	0.5 max.	0.50 max.
Sulphur, max. / (mg kg⁻¹)	0.00	0.00	0.00	0.00	0.00	15	10	10
Ester content, min. / %, mass			97.2	96.4	95.3	na	96.5	96.5
Cold filter plugging point, max. / ºC			-4	12	8	na	na	14
Iodine index / (g I_2 *per* 100 g)			22.61	92.23	36.89	na	120	na
Free glycerin, max. / %, mass			0.00	0.043	0.00	0.02	0.02	0.02
Total glycerin, max. / %, mass			0.19	0.951	0.18	0.240	0.25	0.25
Monoacilglycerol / %, mass			0.64	0.695	0.531	na	0.8	0.8
Diacilglycerol / %, mass			0.22	0.05	0.101	na	0.2	0.2
Triacilglycerol / %, mass			0.00	0.035	0.00	na	0.2	0.02
Copper strip corrosion at 50 °C	1b	1b	1b	1b	1b	max. 3	max. 1	max. 1

na: not applicable.

catalyst and 1 h of reaction. Table 3 shows the results of physicochemical parameters to BB, COB and BBCO41, as can be seen they are in accordance to ANP 07/08 Resolution.[11]

The catalytic activity of the catalyst used in this study has been shown to be quite satisfactory since the conversion rates were BB (97.2%), COB (96.4%) and BBCO41 (95.3%), as shown in Figure 6. These conversion rates determined by NMR are using the levels of esters obtained by gas chromatography and NMR. The conversion rates obtained by the NMR technique are much closer to GC, which is the official method. The results differ by 1.9% (BB), 1.9% (COB) and 1.4% (BBCO41).

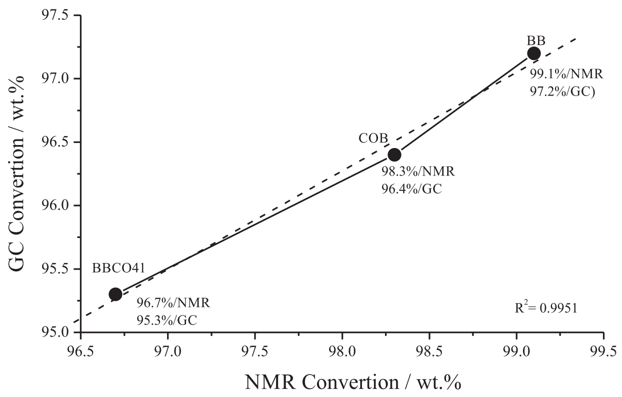

Figure 6. Conversion rates NMR *versus* GC.

Reusability of catalyst

In this work, the reusability of the catalyst was tested only for babassu oil It was used a molar ratio of methanol to oil of 6:1 and 1% of catalyst based of mass oil, a reaction time of 60 min because these conditions resulted in the best conversion. The effects of repeated use of the catalyst on biodiesel conversion are illustrated in Figure 7. As can be seen, the results indicated that SrO is active to biodiesel production for six times, and the conversion into esters was only slightly decreased. Fairly similar results were reported by Liu *et al.*[2] These results demonstrated that SrO is very attractive as a catalyst to biodiesel production despite it having a slightly higher cost when compared to the homogeneous catalysts used for biodiesel industry.

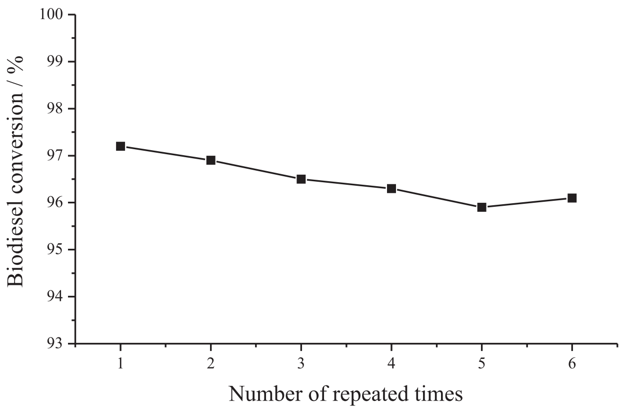

Figure 7. Reusability of catalyst on biodiesel conversion.

Solubility and heterogeneity tests

Granados *et al.*[34] have used conductivity to evaluate the leaching and homogeneous contribution of methanolysis of triglycerides using CaO. This methodology is simple, easy to work with and inexpensive compared to other techniques. Some works in the literature describe the use of the atomic absorption spectroscopy (AAS) technique for measuring the leaching of catalysts in the reactions of triglyceride methanolysis. However, the detection of metal by AAS into biodiesel may not be due to solubility of the catalyst, but instead, due to non-removal of the same during purification steps. The conductivity results are excellent indicators of catalytic activity since it reflects the ionization of methanol, i.e., its deprotonation takes place and consequently the formation of methoxide. The conductivity results obtained in this study showed that the solubility of the catalyst in methanol is negligible (0.001 g *per* 100 g methanol). This result confirms the heterogeneous character predominant of the catalyst in the transesterification reaction. For the rigorous proof of heterogeneity, a test was done, and the CG results showed no significant change in the conversion of esters, indicating that the present catalyst is heterogeneous. Reused catalyst was analyzed by XRD and FTIR and the results are equal to those related to the fresh catalyst. This fact also confirms the heterogeneity of the catalyst.

Conclusion

The synthesis of catalyst by thermal decomposition method has resulted in a mixture of products ($SrO + SrCO_3 + Sr(OH)_2$), however the product presents a high basicity. This fact favored the good catalytic activity for transesterification reactions of babassu, castor oil and a blending of these oils. The catalytic activity of the catalyst used in this study showed quite satisfactory since the conversion rates were BB (97.2%), COB (96.4%) and BBCO41 (95.3%). The viscometric technique proved quite effective, fast in relation to monitoring the reaction of transesterification.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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References

1. Ma, F.; Hanna, M. A.; *Bioresour. Technol.* **1999**, 70, 1.
2. Liu, X. J.; He, H. Y.; Wang, Y. J.; Zhu, S. L.; *Catal. Commun.* **2007**, 8, 1107.
3. Fréty, R.; da Rocha, M. G. C.; Brandão, S. T.; Pontes, L. A. M.; Padilha, J. F.; Borges, L. E. P.; Gonzalez, W. A.; *J. Braz. Chem. Soc.* **2011**, *22*, 1206.
4. Araújo, B. Q.; Nunes, R. C. R.; Moura, C. V. R.; Moura, E. M.; Citó, A. M. G. L.; Santos Júnior, J. R.; *Energy Fuels* **2010**, *24*, 4476.
5. Shah, S. N.; Sharma, B. K.; Moser, B. R.; *Energy Fuels* **2010**, *24*, 3189.
6. Serio, M. D.; Tesser, R.; Pengmei, L.; Santacesaria, E.; *Energy Fuels* **2008**, *22*, 207.
7. Conceição, M. M.; Candeia, R. A.; Silva, F. C.; Bezerra, A. F.; Fernandes, V. J.; Souza, A. G.; *Renewable Sustainable Energy Rev.* **2007**, *11*, 964.
8. Liu, X. J.; Piao, X. L.; Wang, Y. J.; Zhu, S. L.; He, H. Y.; *Fuel* **2008**, *87*, 1076.
9. Lima, J. R. O.; Silva, R. B.; Silva, C. C. M.; Santos, L. S. S.; Santos Junior, J. R.; Moura, C. V. R.; Moura, E. M.; *Quím. Nova* **2007**, *30*, 600.
10. Moura, C. V. R., Castro, A. G., Moura, E. M., Santos Jr., J. R., Moita Neto, J. M.; *Energy Fuels* **2010**, *24*, 6527.
11. Brazilian National Agency on Oil, Natural Gas and Biofuels, Resolution ANP No. 14 May 11, 11.5.2012-DOU 18.5.2012.
12. Pena, R.; Romero, R.; Martinez, S. L.; Ramos, M. J.; Martinez, A.; Natividad, R.; *Ind. Eng. Chem. Res.* **2009**, *48*, 1186.
13. Coluccia, S.; Deane, A. M.; Tench, A. J.; J. Chem. Soc., Faraday Trans. *1* **1978**, *74*, 2913.
14. Abreu, F. R.; Lima, D. G.; Hamu, E. H.; Wolf, C.; Suarez, P. A. Z.; *J. Mol. Catal. A: Chem.* **2004**, *209*, 29.
15. Plank, C.; Lorbeer, E.; *J. Chromatogr., A* **1995**, *697*, 461.
16. Holcapek,M.; Jandera, P.; Fischer, J.; Prokes, B.; *J. Chromatogr., A* **1999**, *858*, 13.
17. Neto, P. R. C.; Caro, M. S. B.; Mazzuco, L. M.; Nascimento, M. G.; *J. Am. Oil Chem. Soc.* **2004**, *81*, 1111.
18. Dube, M. A.; Zheng, S.; McLean, D. D.; Kates, M.; *J. Am. Oil Chem. Soc*. **2004**, *81*, 599.
19. Knothe, G.; *J. Am. Oil Chem. Soc.* **2000**, *77*, 489.
20. Instituto Adolfo Lutz (IAL); *Normas Analíticas do Instituto Adolfo Lutz: Métodos Químicos-*Físicos *para Análise de Alimentos*, 4th ed; Ministério da Saúde: Brasília, Brasil, 2005.
21. The United States Pharmacopeia, USP 24, NF 19, The United States Pharmacopeial USP Convention, Rockville, USA, 2000.
22. American Oil Chemists' Society, AOCS Official Method Cd 1c-85, 1990.
23. Meher, L. C.; Vidya Sagar, D.; Naik, S. N.; *Renewable Sustainable Energy Rev.* **2006**, *10*, 248.
24. Tanabe, K.,Misono,M., Ono, Y., Hattori, H.; *Stud. Surf. Sci. Catal.* **1989**, *51*, 5.
25. JCPDS International Centre for Diffraction Data (JCPDS-ICDD 1988), PDF number 71-2393, 74-1491 and 84-1778; Swanson, H. S.; Fuyat, R. K.; *Natl. Bur. Stand. (U.S.), Circ.* **1954**, *539*, 56.
26. JCPDS International Centre for Diffraction Data (JCPDS-ICDD 1990), PDF number 006-0520; Awanson *et al*.; *Natl. Bur. Stand. (U.S.), Circ.* **1955**, *68*, 539.
27. JCPDS International Centre for Diffraction Data (JCPDS-ICDD - 1988): PDF number 019-1276; Mercer, R. A.; Miller, R. P.; *J. Inorg. Nucl. Chem.* **1966**, *28*, 61.
28. Yan, S.; Lu, H.; Liang, B.; *Energy Fuels* **2008**, *22*, 646.
29. Figueiredo, J. L.; Ribeiro, F. R.; *Catálise Heterogênea*; Fundação Calouste Gulbenkian, Lisboa, Portugal, 2007, p. 237.
30. Shahid, E. M.; Jamal, Y.; *Renewable Sustainable Energy Rev.* **2008**, *12*, 2484.
31. Yoo, S. J.; Lee, H. S; Veriansyab, B.; Kimb, J.; Kimb, J. D.; Lee, Y. W.; *Bioresour. Technol.* **2010**, *101*, 8686.
32. Albuquerque, M. C. G.; Machado, Y. L.; Torres, A. E. B.; Azevedo, D. C. S.; Cavalcante Jr., C. L.; Firmiano, L. R.; Parente Jr., E. J. S.; *Renewable Energy* **2009**, *34*, 857.
33. Scholza, V.; Da Silva, J. N.; *Biomass Bioenergy* **2008**, *32*, 95.
34. Granados, M. L.; Alonso, D. M.; Alba-Rubio, A. C.; Mariscal, R.; Ojede, M.; Brettes, P.; *Energy Fuels* **2009**, *23*, 2259.

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