

Sequential Acid-Catalyzed Esterification and Base-Catalyzed Transesterification of Babassu (*Attalea speciosa* Mart. Ex Spreng.) and Pequi (*Caryocar brasiliense* Camb.) Oils of High Acid Values Over Functionalized Mesoporous Silicas

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Abstract

In this work Babassu (*Attalea speciosa* Mart. Ex Spreng.) and Pequi (*Caryocar brasiliense* camb.) vegetable oils of high acid values were transformed in the respective methyl esters, through sequential acid-catalyzed esterification and base-catalyzed transesterification over functionalized mesoporous heterogeneous catalysts. The vegetable oils were firstly esterified with methanol over SBA-15 functionalized with propylsulfonic acid (Pr-HSO₃/SBA-15) or K-10 Montmorillonite. The oil to methanol molar ratio, temperature, catalyst loading, and time were varied to assess the best conversion of the free fatty acids. The esterification with Pr-HSO₃/SBA-15 catalyst yielded 94% and 83% in the esters for the Babassu and Pequi oils, respectively, at the best reaction conditions studied. K-10 Montmorillonite showed a poorer performance in the esterification, yielding 70% of methyl esters for the Babassu oil. The Pr-HSO₃/SBA-15 acid catalyst showed negligible loss of activity for three consecutive reuses, whereas K-10 is significantly poisoned upon the first use. These results may be explained by the higher acidity of the hybrid catalyst. The esterified oils were subject to transesterification with methanol in the presence of MCM-41 mesoporous silica grafted with 1,5,7-triazabicyclo [4,4,0] dec-5-ene (TBD/MCM-41) basic catalyst. At the best conditions studied, the esterified Pequi oil achieved 89% conversion in the methyl esters. The results may be explained by the relatively low incorporation of the organic base on the silica support. The sequential esterification and transesterification of Babassu and Pequi oils over functionalized silica heterogeneous catalysts may be a sustainable alternative to the production of biodiesel in remote regions.

1. Introduction

Renewable energy sources have attracted interest to replace or reduce the use of fossil sources, such as crude oil, coal, and natural gas. One of these renewable options is biodiesel, which may be blended with the petrodiesel in different proportions, because of the similar physical properties and cetane index [1–3]. Biodiesel is composed of fatty acid methyl esters, usually produced through the transesterification of different lipid sources in the presence of acid, basic or enzymatic catalysts.

Several raw materials can be used to produce biodiesel [4–6]. In Brazil, soybean oil accounts for roughly 70% of the raw material for biodiesel production, whereas tallow corresponds to approximately 25% [7]. The remaining 5% are distributed among different oils, such as cotton, corn, and sunflower. Most of these crops are cultivated in the central and western region of the country, whereas tallow is also representative in the southern region. On the other hand, there are incentives for the development of regional arrangements, that give emphasis on the use of local biomass feedstocks, to avoid the high costs associated with biodiesel transportation for the remote regions of the country.

Among the options of raw materials for the regional production of biodiesel in Brazil, Pequi and of Babassu oils appears as promising. Pequi (*Caryocar brasiliense* camb.) is a fruit from the Brazilian Cerrado biome [8, 9], and Babassu (*Attalea speciosa* Mart. Ex Spreng.) is a South American palm tree that occurs in forests of the Northern Brazil region and Colombia. The oils are rich in saturated and

monounsaturated fatty acids, as shown in the Table 1 [10, 11] and can be important feedstocks for the production of biodiesel. However, most of the studies on biodiesel production from Pequi and Babassu oils involves homogeneous catalysts, which may not be recovered for reuse at the end of the process [12–17]. In addition, the costs of transportation of the homogeneous catalysts and the non-correct disposal of the generated wastes are other drawbacks associated with biodiesel production in remote parts of the country. Nevertheless, studies concerning the biodiesel production from Pequi and Babassu oil using heterogeneous catalysts are scarce [18–20]. This approach would be important for the implementation of plant productions in remote parts of the nation. In addition, Pequi and Babassu oils present high acid values making the task of producing biodiesel using heterogeneous basic catalysts extremely difficult.

Table 1
General fatty acid composition of Pequi and Babassu oils.

Fatty Acid	Pequi Oil (%)	Babassu Oil (%)
Caprylic	5.3–5.5	-
Capric	5.5–5.9	-
Lauric	44–47	-
Myristic	15–18	-
Palmitic	6–9	40–44
Palmitoleic	3–5	0.5–1.4
Stearic	12–16	1.9–2.6
Oleic	1–2	49–54
Linoleic	-	0.9–1.5
Linolenic	-	0.2–0.7
Arachidic	-	0.2
Gadoleic	-	0.2–0.7

The biodiesel production at industrial scale usually occurs with the use of sodium hydroxide, potassium hydroxide or sodium methoxide as homogeneous catalysts. In this process, the oil must be of high purity, with water content up to 0.25 wt% and free fatty acids up to 0.5 wt%, as undesired reactions, such as saponification and hydrolysis of the triglyceride may take place. Furthermore, the free fatty acids may poison the basic catalyst, leading to low conversions and formation of soap. On the other hand, the use of low purity vegetable oil is gaining importance worldwide to reduce the overall process costs [21].

A good strategy to process low-quality feedstock, with high fatty acid content, is the sequential integration of esterification and transesterification [22]. The first reaction is responsible for converting

the free fatty acids into methyl esters and normally occurs upon acid catalysis, whereas transesterification is better carried out upon the use of basic catalysts to afford biodiesel. Among the acid catalysts used in esterification, those based on sulfonic acid are highly employed [23–25]. On the other hand, grafted amines over mesoporous silica materials can lead to high conversions in transesterification of triglycerides [26].

Lane and co-workers tested SBA-15 functionalized with Propylsulfonic acid as a heterogeneous catalyst in the production of biodiesel from soybean oil and 1-butanol. Upon microwave irradiation at 190 °C for 15 minutes, about 40% yield of biodiesel was obtained. After washing and reusing the catalyst, the biodiesel yield decreased to 34–36%, with authors suggesting the loss of material during the washing as the most probable cause for the decrease in conversion [27].

Lima and co-workers synthesized MCM-41 mesoporous silica functionalized with different amines and applied them in the transesterification of soybean oil with methanol [28, 29]. Upon grafting of 3-aminopropyl by the post-synthesis method, the yield of biodiesel was 15% after 6 h, at 160°C, using 45:1 of methanol to oil molar ratio. The results were significantly improved when 1,5,7-triazabicyclo [4,4,0] dec-5-ene (TBD) was functionalized on the MCM-41 surface, yielding 99% biodiesel under mild reaction conditions (70°C, for 3 h and methanol to molar oil ratio of 9:1). The catalytic activity greatly decreases after 5 consecutive cycles due to neutralization of the basic sites by the free fatty acids present in the oil.

In this work, we report the sequential esterification and transesterification of Pequi and Babassu oils, of high free fatty acid content, with acid and base functionalized mesoporous silica as heterogeneous catalysts, aiming at producing biodiesel (Scheme 1). The aim is to find out potential heterogeneous catalysts and reaction conditions for both reactions (esterification and transesterification) that may lead to satisfactory yields of biodiesel from Babassu and Pequi oils of high acid content, and, by consequence, could be implemented in remote regions.

2. Experimental Part

2.1. Characterization of the vegetable oils

Babassu and Pequi oils were extracted from Alto Turi, Maranhão, Brazil and were characterized in terms of acidity, saponification, water content and specific mass, according to standard procedures used elsewhere [5].

To determine the acid value, about 2.0 g of the vegetable oil were solubilized in 1:2 vol/vol ether/ethanol. The solution was heated to 40°C for 2 min and titrated with a standard 0.1 mol L⁻¹ solution of NaOH. The acidity was calculated using Eq. 1:

$$AcidValue = \frac{V_{NaOH} \times C_{NaOH} \times f_c \times 56,1}{oilmass} \quad \text{Eq. 1}$$

The saponification value was determined by weighting 2.0 g of the oil and solubilizing it in an alcoholic solution of 4 wt% KOH. The mixture was kept under reflux for 30 min and then titrated with a standard 0.5 mol L⁻¹ solution of HCl. The same procedure was applied to a blank sample and the saponification value was calculated using the Eq. 2:

$$\text{Saponification value.} = \frac{(V_{\text{blank}} - V_{\text{HCl}}) \times C_{\text{HCl}} \times f_c \times 56,1}{\text{oilmass}} \quad \text{Eq. 2}$$

The water content was obtained upon weighting 1.0 g of the oil on a plate and subjecting to heating at 100 °C for 3 h in an oven. At the end, the system was weighted again, and the water content was estimated by the mass difference using Eq. 3:

$$\%H_2O = \frac{\text{watermass}}{\text{oilmass}} \times 100 \quad \text{Eq. 3}$$

The specific mass of the oils was obtained in a pycnometer. The device was weighted empty and an aliquot of 5.0 mL of the oil was added. The system was weighted again and, by the difference between the initial and final weights, the specific mass was determined using Eq. 4.

$$\rho = \frac{\text{oilmass(g)}}{5,00\text{mL}} \quad \text{Eq. 4}$$

2.2. Preparation of the heterogeneous catalysts

Tetraethylorthosilicate (TEOS) 98% was employed as the silica source. Pluronic P123 95% and cetyltrimethylammonium bromide (CTAB) 99% were used in the synthesis of SBA-15 and MCM-41, respectively, following standard literature procedures [30, 31]. The 3-mercaptopropyl-trimethoxysilane (MPTMS) 95% was used in the functionalization of the SBA-15 silica, whereas chloropropyl triethoxysilane, and 1,5,7-triazabicyclo [4,4,0] dec-5-ene (TBD) were used for the synthesis of the amino-functionalized MCM-materials. All these chemicals were purchased from Sigma-Aldrich. Hydrogen peroxide (H₂O₂), hydrochloric acid (HCl) 37 wt% and ammonium hydroxide (NH₄OH) 30 wt% were purchased from Vetec. Methanol 99.8%, also from Vetec, was used in the esterification and transesterification studies.

The synthesis of the Pr-HSO₃/SBA-15 acid catalyst followed similar literature procedures [23, 25]. About 4.0 g of Pluronic P123 surfactant was added to 125 g of a HCl solution (1.9 mol L⁻¹). The mixture was vigorously stirred at 40°C. Then, 8 mL of TEOS was added and the system was stirred for 1 h at 40°C. In the next step, 0.76 mL of MPTMS was added to promote the grafting of the sulfonic group onto the mesoporous silica, followed by addition of 1.25 mL of hydrogen peroxide to oxidize the S-H groups to SO₃H. The reaction media was kept under agitation at 40°C for 20 h and then aged for 24 h at 100°C. At the end of this period, the mixture was filtered and washed with ethanol. The resulting solid was treated with absolute ethanol in a Soxhlet apparatus for 96 h to remove the surfactant, yielding a white solid that was further heated at 80°C for 12 h to eliminate the remaining ethanol molecules.

The TBD/MCM-41 basic heterogeneous catalyst was prepared by the co-condensation method as described in the literature [29]. Initially, a solution of 3.2 g of TBD dissolved in 35 mL of THF was added dropwise to a suspension of 0.88 g of NaH in 15 mL of THF, kept at 0°C under N₂ atmosphere. After addition, the system was stirred for 2 h at room temperature. Then, a solution of 5.55 mL of chloropropyl triethoxysilane in 5 mL of THF was added dropwise to the mixture at 0°C. When the addition was finished, the system was stirred for 24 h at 70°C. At the end, a white solid was obtained upon filtration and stored for use in the second part of the synthesis.

A solution containing 1.0 g of CTAB, 3.5 mL of a solution of NaOH (2.0 mol L⁻¹) and 240 g of deionized water were heated for 30 minutes. Then, 5 mL of TEOS and the solid obtained in the first step of the synthesis were added to the system, which was stirred for 2 h at 80°C. The resulting solid was filtered and treated with a methanolic solution of HCl in a Soxhlet apparatus to remove the surfactant. After this step, the solid was neutralized with Na₂CO₃ in methanol for 3 h at room temperature and dried at 100°C for 3 h.

2.3. Characterization of the catalysts

All catalysts were characterized by Fourier-transform infrared spectroscopy (FTIR). The spectra were recorded from 400 to 4000 cm⁻¹ on a Varian 660-IR FTIR spectrophotometer using KBr pellets. ¹³C and ²⁹Si solid state NMR spectra were acquired on a Bruker Avance III 400 (9.4 T), operating at Larmor frequencies 100.65 and 79.51 MHz, respectively. The analyses were performed in a ZrO₂ triple channel probe, with 3.2 rotors (Vespel caps) spinning at 10 kHz (¹³C) and 7.0 mm two channel broadband probe with 7.0 mm rotors (Kel-F caps) spinning at 5 kHz (²⁹Si). The spectra were obtained using magic angle spinning and cross polarization (CP ramp) with 2 ms contact time and 4 s repetition time for ¹³C (¹³C CPMAS), with 4 ms contact time and 4 s repetition time for ²⁹Si (²⁹Si CPMAS). Nitrogen physisorption measurements were performed on an ASAP 2020 V304 e-serial 1200 at 77 K. Thermogravimetric curves were obtained using a Shimadzu model TGA-50 equipment, using approximately 10 mg of sample, which was heated up to 800°C (10°C/min) under N₂ atmosphere (30 mL/min). The nitrogen content was assessed on a Perkin-Elmer CHN 240C analyzer at the Analytical Center of the Institute of Chemistry of the University of São Paulo, Brazil. The acidity of the heterogenous acid catalysts was estimated by Boehm titration, according to previous procedure [32].

2.4. Esterification of free fatty acids

The esterification was carried out on a Parr reactor using 3.0 g of the oil (around 11.0 mmol of oleic acid), and methanol at 600 rpm. The oil/methanol molar ratio, temperature, time, and catalyst loading were varied. The esterification was carried out with the prepared Pr-HSO₃/SBA-15 and K-10 Montmorillonite, purchased from Sigma-Aldrich for comparison purpose, as the solid acid heterogeneous catalysts [33].

At the end of the reaction, the system was centrifuged at 2500 rpm for 15 minutes and the liquid phase was heated to 100°C for 30 minutes to evaporate the residual methanol and the water produced during

the esterification. The remaining oil was weighted, solubilized in 1:2 vol/vol ether/ethanol, heated at 40°C for 2 minutes and titrated with standard NaOH solution. The esterification yield was calculated according to the Eq. 5:

$$Esterificationyield = \frac{\%FFA_{initial}-\%FFA_{final}}{\%FFA_{initial}} \times 100 \text{ Eq. 5}$$

2.5. Transesterification of the esterified oils

The Babassu and Pequi oils that showed the highest conversion in the previous esterification procedure were subjected to transesterification with methanol using the prepared TBD/MCM-41 as catalyst. The temperature, time and catalyst loading were varied to check the impact on the biodiesel yield. At the end of the reaction, the mixture was centrifuged at 2500 rpm for 15 minutes, heated to remove residual methanol and analyzed by HPLC to assess the biodiesel yield, as reported elsewhere [28, 29].

2.6. Reusability test

The Pr-HSO₃/SBA-15 and K-10 acid catalysts were reused in consecutive reactions. The reactions were carried out at the best conditions obtained for the esterification of Pequi and Babassu oils. At the end of the reaction, the mixture was centrifuged, the catalyst was separated, washed with ethanol and n-hexane and dried at 80°C for 2 h for further reuse. The yield of methyl esters was obtained by the same procedure previously described.

3. Results And Discussion

3.1. Properties of the vegetable oils

Table 2 shows the main properties of Pequi and Babassu oils. Both present high acid values, which can be explained by the extraction method. The acid values and the water content are far above the limit indicated for basic transesterification, which are 0.5 and 0.3 wt%, respectively.

Table 2
Main properties of Pequi and Babassu oils.

Property	Babassu	Pequi
AV (mg KOH•g ⁻¹ oil)	2.36	2.88
% FFA	1.16	1.44
SV (mg KOH•g ⁻¹ oil)	207–218	182–225
Density (kg•m ⁻³)	914	904
Water content (%)	0.84	0.43

AV-acid value; FFA-free fatty acid; SV- saponification value.

3.2. Characterization of the catalysts

Figure 1 shows the FTIR spectra of the parent SBA-15, Pr-HSO₃/SBA-15 and K10 Montmorillonite catalysts used in the esterification of the vegetable oils. One can see bands at 2974 and 2941 cm⁻¹, associated to the C-H stretching of the propyl group. The bands at 1351 and 1378 cm⁻¹ refer to the asymmetric stretching of the S = O bond, which confirm the effective functionalization of the SBA-15 mesoporous material with the propylsulfonic acid moiety. The bands at 1088, 954, 801 and 463 cm⁻¹ are related to the stretching and deformation modes of Si-O-Si and Si-O bonds of the silica support. In the spectrum of K-10 Montmorillonite, there appears two bands at 3622 cm⁻¹ and 3434 cm⁻¹ attributed to the O-H stretching. They may be associated to water molecules present between the internal layers of the clay. The SBA-15 materials also presented a broad band at the same region, which may be related to physically adsorbed water. The band at 1631 cm⁻¹ refers to O-H deformation and confirms the presence of water on the materials. The bands at 1040 cm⁻¹, 525 cm⁻¹ and 467 cm⁻¹ are related to the stretching and deformation modes of Si-O bond, respectively in the K-10 catalyst.

Figure 2 shows the FTIR spectra of the parent MCM-41 and TBD/MCM-41. The bands at 2925 and 2851 cm⁻¹ can be attributed to the C-H stretching and confirm the grafting of the organic amine on the silica support. The band at 1621 cm⁻¹ is attributed to the OH deformation from physically adsorbed water. The band at 1062 cm⁻¹ can be attributed to the superposition of C-N and Si-O-Si stretching modes. The bands at 801, 569 and 457 cm⁻¹ correspond to the stretching and deformation modes of Si-O bond, respectively. The band at 699 cm⁻¹ corresponds to the deformation of N-H bond. The results demonstrated the functionalization of the MCM-41 mesoporous silica with the TBD organic moiety.

One can observe three main regions of mass loss in the TGA profile of Pr-HSO₃/SBA-15 (figure S1). The first mass loss refers to desorption of water from the mesoporous support, from room temperature to approximately 120°C. The second region goes from 120°C to approximately 350°C and can be related to the thermal degradation of the organic moiety linked to the SBA-15 mesoporous support. The third mass loss event goes from around 350°C to 450°C and may be associated with dehydroxylation of the silica support, with formation of water [29].

Figure S2 shows the TGA/DTG profile of K-10 Montmorillonite. Two main regions of weight loss can be seen. The event between room temperature up to approximately 530°C can be associated with desorption of water, both physically adsorbed and present in the interlayer spaces. The second region goes from 530°C to near 790°C and is related to dehydroxylation of the crystal lattice, also releasing water [34].

The TGA/DTG profile of the TBD/MCM-41 catalyst is shown in figure S3. Again, three main regions of mass loss can be highlighted. The first goes from room temperature to approximately 190°C and is attributed to water desorption from the catalyst surface. The second region goes from 190°C to near 320°C and can be related to the degradation of the TBD moiety. The third mass loss event spans from

320°C to approximately 460°C and is associated with dehydroxylation of the MCM-41 support and release of water molecules.

The ^{29}Si and ^{13}C MAS/NMR spectra of the grafted catalysts are shown in figures S4 and S5. From the ^{29}Si MAS/NMR spectra one can see the success of the grafting procedure, with the decrease of the Q_2 , Q_3 and Q_4 peaks and appearance of T_2 , T_3 and T_4 peaks that correspond to the Si atom bonded to carbon atoms. The ^{13}C MAS/NMR also confirmed the grafting of the propyl sulfonic group. The peak at about 11.5 ppm is attributed to the C-Si bond, reinforcing the formation of the hybrid material. The peak at 18.2 ppm is related to the propyl chain, whereas the peak at 54.1 ppm can be related to the C-SO₃H group [24]. The spectrum also indicated that some molecules of the surfactant, which contains PEO poly(ethylene oxide) and PPO (poly(propylene oxide) blocks, are still present in the final material.

The ^{13}C NMR-MAS spectrum of TBD/MCM-41 agrees with previous published reports [29]. The peak at 10.1 ppm is associated to the C-Si bond, stressing the grafting of the organic moiety on the silica support. The peak at 26.3 ppm can be attributed to the carbon atoms of the propyl chain linked to the TBD moiety, but we cannot exclude some contributions from the surfactant that was not completely removed. The peak at 47.3 ppm can be associated to the C-N groups in the TBD molecule, whereas the peak around 150 ppm refers to the C = N bond of the TBD molecule.

Table 3 shows the textural properties of the catalysts measured by nitrogen adsorption. The BET area was reduced upon grafting of the propyl sulfonic moiety to the SBA-15 support. This was somewhat expected, since the grafting of the organic moiety may block part of the porous structure of the mesoporous silica. On the other hand, a more drastic decrease of the BET area was observed upon functionalization of the MCM-41 material with TBD, as previously reported [28, 29]. This may be explained by the porous structure of the MCM-41 material, which is mostly composed of straight tubes of mesoporous diameter. Thus, the grafting of TBD at the external surface may lead to severe blocking of the pores, consequently affecting the surface area. The K-10 Montmorillonite presents a BET area significantly lower than the area of the Pr-HSO₃/SBA-15 material, but it is within the normal values reported in the literature for this clay [35].

The base and acid properties of the catalysts can be obtained from the elemental analysis and Boehm titration, respectively. The TBD/MCM-41 showed 0.94 mmol of N atoms per gram of material, which is lower than previous reported synthesis of this material [28, 29]. In addition, the elemental analysis indicated that the surfactant was not completely removed. On the other hand, the Boehm titration indicated 1.05 and 0.35 mmol of acid sites per gram for the Pr-HSO₃/SBA-15 and K-10 catalysts, respectively.

Table 3
Textural properties of the catalysts.

Catalyst	Textural Properties		
	S_{BET} ($\text{m}^2.\text{g}^{-1}$)	$V_{\text{p-BJH}}$ ($\text{cm}^3.\text{g}^{-1}$)	$D_{\text{p-BJH}}$ (nm)
SBA-15	630	0.46	5.2
Pr- HSO_3 /SBA-15	443	0.43	4.4
K-10 clay	264	0.11	2.9
MCM-41	1134	1.02	2.0
TBD/MCM-41	9	0.01	5.2

3.3. Esterification of the vegetable oils

Table 4 shows the results of esterification of Babassu oil with the Pr- HSO_3 /SBA-15 catalyst, whereas Table 5 presents the results for Pequi oil with the same catalyst.

Table 4
Babassu oil esterification with methanol and Pr- HSO_3 /SBA-15 as catalyst.

Entry	Oil:MeOH	Cat (%)	Time (min)	Temp. ($^{\circ}\text{C}$)	Initial %FFA	Final %FFA	Yield (%)
1	1:8	none	120	110	1.16	0.93	20
2	1:6	0.5	60	110	1.16	0.72	38
3	1:6	0.5	120	110	1.16	0.68	41
4	1:8	0.5	60	90	1.16	0.77	33
5	1:8	0.5	120	90	1.16	0.45	61
6	1:8	0.5	60	110	1.16	0.46	61
7	1:8	0.5	120	110	1.16	0.47	60
8	1:8	1.0	120	110	1.16	0.24	79
9	1:8	5.0	120	110	1.16	0.07	94

Table 5
Pequi oil esterification with methanol and Pr-HSO₃/SBA-15 as catalyst.

Entry	Oil:MeOH	Cat (%)	Time (min)	Temp. (°C)	Initial %FFA	Final %FFA	Yield (%)
1	1:8	None	120	110	1.44	1.18	18
2	1:6	0.5	60	110	1.44	0.66	54
3	1:6	0.5	120	110	1.44	0.65	55
4	1:8	0.5	120	90	1.44	0.72	50
5	1:8	0.5	60	110	1.44	0.65	55
6	1:8	0.5	120	110	1.17	0.24	79
7	1:8	1.0	120	110	1.44	0.32	78
8	1:8	5.0	120	110	1.17	0.20	83

The reaction without catalyst presented 20% conversion at 110 °C, 120 minutes and 1:8 methanol to oil molar ratio (Table 4, entry 1). Because esterification is an acid-catalyzed reactions, the free fatty acids present in the Babassu oil may catalyze the reaction. Upon using 0.5% of catalyst loading, the conversion increased to 33%, even at 90 °C and 60 minutes, with 1:8 methanol to oil molar ratio (Table 4, entry 4). Doubling the reaction time increased the conversion to 61% (Table 4, entry 5). The temperature and methanol to oil molar ratio have great effects on the yield. At 110 °C and 1:8 molar ratio, the yield of methyl esters was 61% (Table 4, entry 6), whereas for 1:6 molar ratio, at the same temperature, the yield was 38% (Table 4, entry 2). The reaction time has a less significant impact on the yield when the reaction is carried out at 110 °C. For instance, the yield increased from 38 to 41% when the time was extended to 120 min (Table 4, entries 2 and 3), using 1:6 methanol to oil molar ratio. The effect is negligible with 1:8 molar ratio, where no appreciable change in the conversion was observed upon extending the reaction time (Table 4, entries 6 and 7). Since the esterification is a reversible reaction, it may have reached equilibrium within the first 60 minutes at these conditions. Nevertheless, to assure the best performance, we carried out the reaction varying the catalyst loading at 110 °C, 1:8 molar ratio and 120 minutes. The yield of methyl esters was 79% for 1% of catalyst loading (Table 4, entry 8) and 94% for 5% loading (Table 4, entry 9).

The same trends were observed in the esterification of Pequi oil with Pr-HSO₃/SBA-15 catalyst. The uncatalyzed reaction showed 18% yield in methyl esters (Table 5, entry 1), whereas the effect of temperature, methanol to oil molar ratio and reaction time followed the same pattern observed for Babassu oil. The highest yield, 83%, was achieved with 5% of catalyst loading, at 110 °C, 1:8 methanol to oil molar ratio and 120 minutes (Table 5, entry 8). Because of the acid value of Pequi oil was higher than the Babassu oil, the results may express this fact, suggesting that more severe conditions should have been employed to achieve higher yields of esterification.

It is worth mentioning that a leaching test was carried out to check if the Pr-HSO₃/SBA-15 material does not behave as a homogeneous catalyst within the reaction conditions used. A sample of the heterogeneous catalyst and methanol were heated at 110 °C for 120 minutes. At the end, the catalyst was separated by centrifugation and the methanol phase was mixed with the appropriated amount of Babassu oil at the same molar amount used in the blank reaction (1:8). The solution was heated to 110 °C for 120 minutes yielding 23% of methyl esters, which is close to the yield observed for the uncatalyzed reaction (Table 4, entry 1). This result indicates that leaching of the acid moiety is negligible under the reaction conditions used, stressing the role of Pr-HSO₃/SBA-15 as a true heterogeneous acid catalyst.

The esterification of Babassu oil using K-10 Montmorillonite is reported in Table 6. Compared with the Pr-HSO₃/SBA-15 catalyst, the clay gives significantly lower yields of the esters. For instance, with 10% of catalyst loading, 110 °C, 120 min and 1:8 oil to methanol molar ratio the yield was 70% (Table 6, entry 5). Thus, we decided to carry out the esterification of Pequi oil with K-10 Montmorillonite with just 10% of catalyst loading. The yield of methyl esters was 75% at 110 °C, 120 minutes and 1:8 methanol to oil ratio. Thus, both oils are esterified within 70 to 75% yield under the best conditions studied for K-10 Montmorillonite.

The superior catalytic activity of Pr-HSO₃/SBA-15 compared to K-10 Montmorillonite may be explained by its higher acidity, as determined by Boehm titration. Although we did not specifically determine the acid strength distribution of the materials, a literature study [35] showed that the acid strength of K-10 montmorillonite is significantly lower than the strength of Amberlyst-15, which is a commercial sulfonic acid resin. Considering that the nature of the acid group is mostly the same on Amberlyst-15 and on the Pr-HSO₃/SBA-15 material, one would suppose that the acid strength is similar, supporting the present experimental findings.

Table 6
Esterification of Babassu oil with K-10 Montmorillonite as catalyst.

Entry	Oil:MeOH	Cat (%)	Time (min)	Temp. (°C)	Initial %FFA	Final %FFA	Yield (%)
1	1:6	0.5	120	110	1.16	1.20	0
2	1:6	1.0	120	110	1.16	1.01	13
3	1:6	5.0	120	110	1.16	0.69	41
4	1:8	5.0	120	110	1.16	0.49	57
5	1:8	10.0	120	110	1.16	0.35	70

3.4. Transesterification of the esterified oils

The Pequi and Babassu oils that were esterified with the Pr-HSO₃/SBA-15 heterogeneous catalyst, under the conditions that gave the highest yield of methyl esters, were subjected to transesterification with

methanol using the TBD/MCM-41 heterogeneous basic catalyst (Table 7).

Table 7
Transesterification of the esterified Pequi oil using TBD/MCM-41.

Entry	Oil:MeOH	Cat (%)	Time (min)	Temp. (°C)	Conv. (%)
1	1:8	1.0	60	90	2
2	1:8	1.0	120	110	3
3	1:8	15.0	120	110	39
4	1:8	20.0	120	110	89

At 1% of catalyst loading, the conversion was within 2 and 3% (Table 7, entries 1 and 2). Thus, we increased the catalyst loading to observe more significant conversion. Upon using 15% loading, the conversion was 39% (Table 7, entry 3), but only with 20% of catalyst loading the conversion achieved 89% (Table 7, entry 4). Table 8 shows the results with the esterified Babassu oil. The conversion is even lower when compared with the esterified Pequi oil. The highest conversion, 48%, was observed with 30% of catalyst loading (Table 8, entry 3).

Table 8
Transesterification of the esterified Babassu oil using TBD/MCM-41.

Entry	Oil:MeOH	Cat (%)	Time (min)	Temp. (°C)	Conv. (%)
1	1:8	1.0	60	90	0
2	1:8	20.0	120	110	23
3	1:15	30.0	120	110	48

The results may be associated with the low incorporation of the TBD moiety on the MCM-41 support, as determined by CHN analysis. Thus, significantly high loadings of catalyst were needed to achieve reasonable conversions. It is not completely clear why the results with Babassu oil were worse than with Pequi oil, as this later feedstock presented higher free fatty acid content than the Babassu oil after esterification. A possible explanation may be the presence of higher water content in the reaction medium. The Babassu oil presented almost twice water as the Pequi Oil (Table 1) and more water may be produced upon esterification. Although we heated the esterified oil prior to transesterification, we cannot rule out that traces of water were still present in the medium.

3.8. Reusability of the acid catalysts

Figure 3 shows the reuse of the Pr-HSO₃/SBA-15 acid catalyst in the esterification of Pequi oil. One can observe that the acid catalyst was effective in three consecutive runs, keeping the yield in methyl ester almost at the same level. The yield reduces in the fourth reuse and drop dramatically in the fifth consecutive reuse, indicating the almost complete deactivation of the acid catalyst.

Considering that previous tests did not show appreciable leaching of the catalyst, the abrupt loss of activity after the fourth reutilization suggests that the catalyst was severely poisoned by impurities present in the oil. It has been demonstrated that sulfonic acid-modified SBA-15 materials undergo deactivation upon ion-exchange with small amounts of metal ions present in the medium, as well as by antioxidants and phospholipids present in the oil [4]. The Pequi oil is rich in carotenoid compounds with antioxidant properties [8]. Thus, it is mostly probable that the observed loss of catalytic activity of the Pr-HSO₃/SBA-15 acid catalyst is due to poisoning of the active sites by carotenoid compounds present in the Pequi oil.

Since Babassu oil also presents high levels of carotenoid compounds [36], the reutilization of the Pr-HSO₃/SBA-15 acid catalyst was not explored with this oil but, instead, K-10 Montmorillonite was tested, although the yield of methyl esters was lower when this heterogeneous acid catalyst was used (Table 6). Figure 4 shows the results, which indicated a drastic deactivation upon the first reuse, with no conversion in the fourth consecutive reuse. Since the acidity of K-10 Montmorillonite is inferior to the Pr-HSO₃/SBA-15 acid catalyst, one may suggest that the deactivation by adsorbed carotenoids is more severe on K-10 Montmorillonite and might be the main cause of loss of catalytic activity on the clay heterogeneous catalyst.

In summary, both classes of heterogeneous acid catalysts deactivated upon reuse, but the functionalized silica was less severely affected compared with Montmorillonite.

4. Conclusions

The sequential esterification and transesterification of Babassu (*Attalea Speciosa* Mart. Ex Spreng.) and Pequi(*Caryocar brasiliense* Camb.) oils, of high acid values, was studied over different heterogeneous catalysts. The Pr-HSO₃/SBA-15 acid catalysts showed higher conversions in methyl esters for both oils, when compared to K-10 Montmorillonite. The results may be interpreted in terms of the higher acidity of the hybrid heterogeneous catalyst, in terms of total acidity and acid strength.

The Pr-HSO₃/SBA-15 acts as a truly heterogeneous catalyst, as leaching of the active phase was negligible under the reaction conditions used. The acid catalyst can be reused in three consecutive reactions without significant loss of activity. After the fourth reuse, the yield in methyl esters drops dramatically indicating the poisoning of the catalyst by impurities present in the oils, possibly carotenoid antioxidant compounds.

The sequential transesterification of the esterified oils with TBD/MCM-41 heterogeneous catalyst was effective, although satisfactory conversions were achieved only with high catalyst loadings and more severe reaction conditions. The reason may be due to the low grafting of the base on the silica support, as seen by the characterization results.

In summary, the sequential esterification and transesterification of Pequi and Babassu oils, of high acid value, could be carried out with hybrid heterogeneous catalyst. This strategy may be useful for biodiesel production in remote regions, where transportation of the homogeneous catalyst and the correct disposal of the wastes generated with the use of these type of catalysts cannot be properly addressed. Nevertheless, the heterogeneous acid catalysts may be poisoned by impurities in the oils and the reuse is drastically affected after the fourth cycle. The Pr-HSO₃/SBA-15 acid catalysts showed better performance than K-10 Montmorillonite, both in terms of activity and stability upon reuse.

Declarations

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Schemes

Scheme 1 is available in the Supplementary Files section

Figures

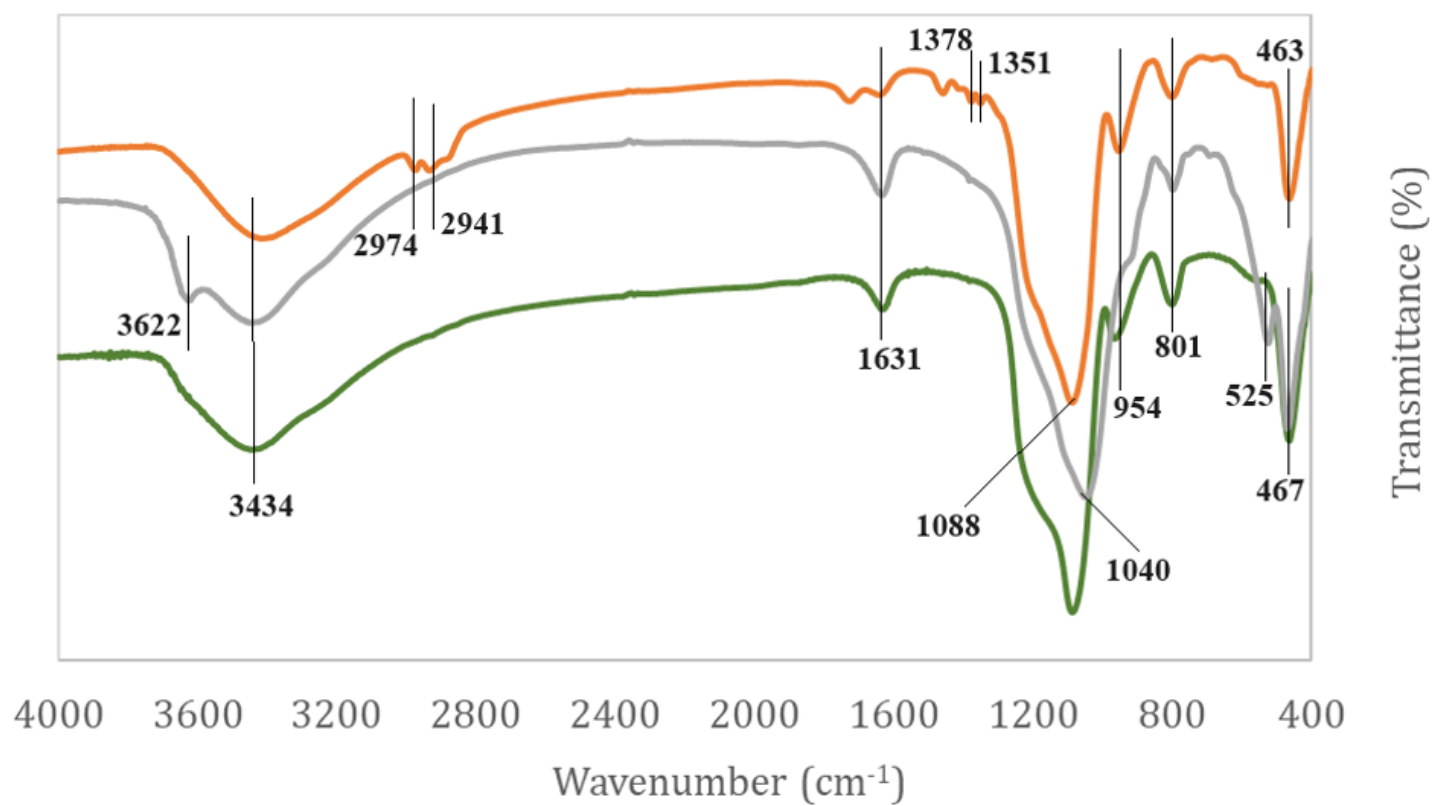


Figure 1

FTIR spectra of SBA-15 (green), Pr-HSO₃/SBA-15 (orange) and K-10 (gray).

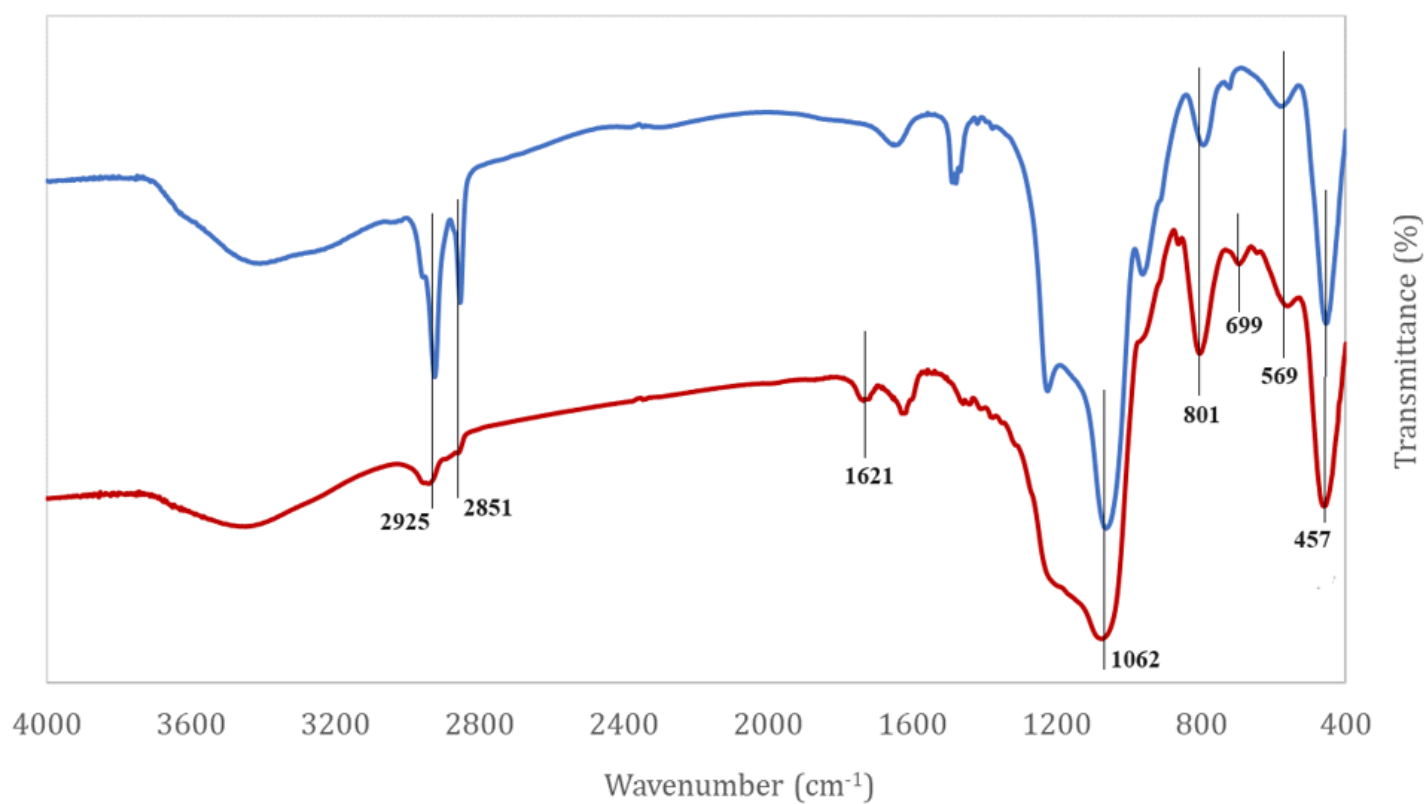


Figure 2

FTIR spectra of MCM-41 (blue) and TBD/MCM-41 (red).

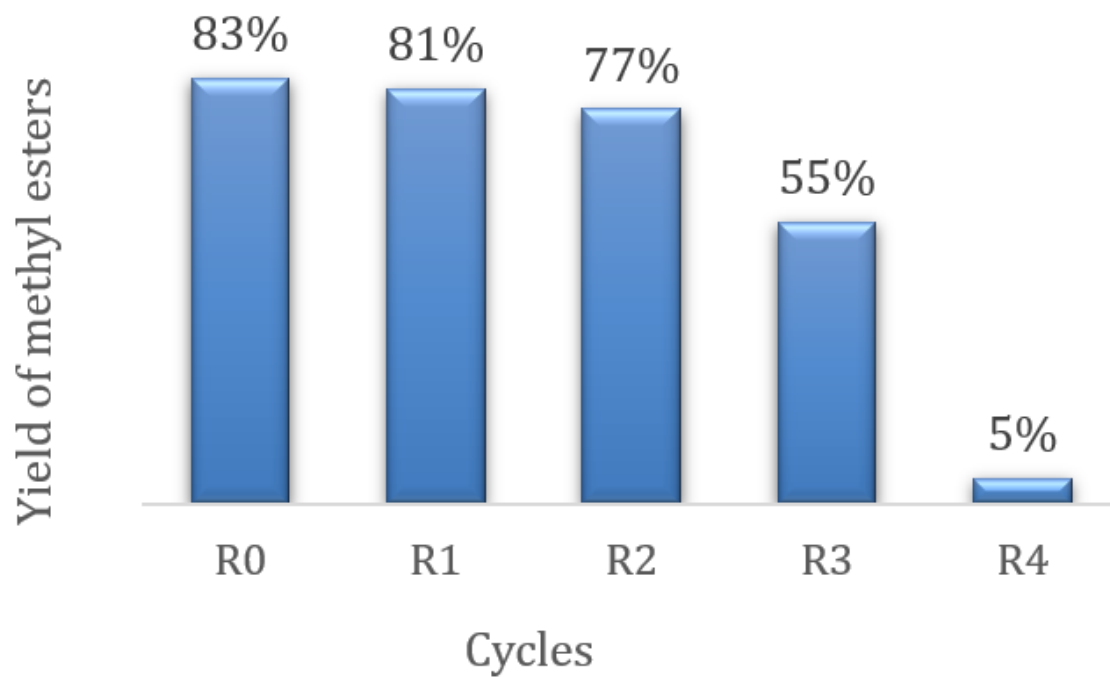


Figure 3

Reusability of the Pr-HSO₃/SBA-15 catalyst in the esterification of Pequi oil.

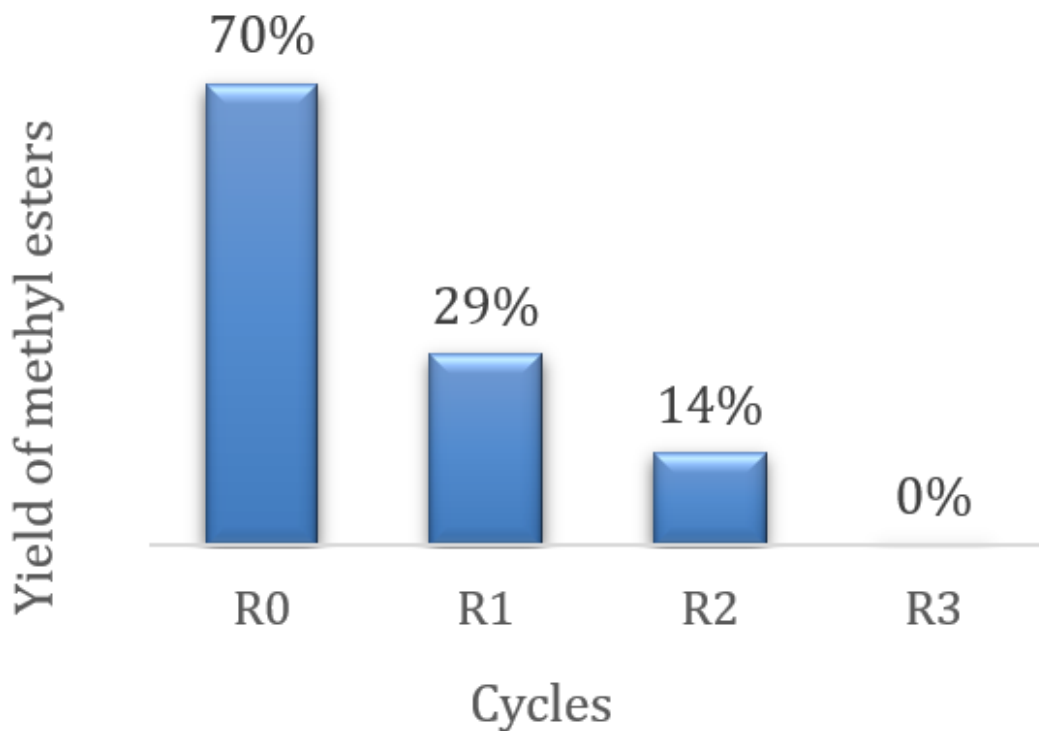


Figure 4

Reusability of K-10 Montmorillonite in the esterification of Babassu oil.

Supplementary Files

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