Industrial Crops & Products 139 (2019) 111485

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Transesterification of Pequi (*Caryocar brasiliensis* Camb.) bio-oil via heterogeneous acid catalysis: Catalyst preparation, process optimization and kinetics

Carlos Magno Marques Cardoso, Danilo Gualberto Zavarize*, Gláucia Eliza Gama Vieira

Department of Environmental Engineering, Federal University of Tocantins, Palmas, 77001-090, Brazil

ARTICLE INFO

Keywords:
Caryocar brasiliensis camb.
Alternative catalyst
Biomass valorization
Transesterification
Process optimization

ABSTRACT

The transesterification of Pequi (*Caryocar brasiliensis* Camb.) bio-oil was conduct with a heterogeneous acid catalyst prepared with the fruit's carbonized rinds. The newly-developed catalyst was characterized by TGA/DSC, XRD diffraction, and FTIR analysis. Experiments for process optimization of biodiesel production and catalyst reusability were carried out, also investigating the kinetics involved in bio-oil mass conversion. Crude FAME content was analyzed with GC-FID gas chromatographer and its fuel properties compared to worldwide standards. Main finds were a crude FAME majorly composed by methyl esters of palmitic acid, linoleic acid, and stearic acid, representing about 49.93, 13.24, and 10.16 wt.%, respectively. Optimized conditions for maximum FAME synthesis from Pequi bio-oil (99.4 ± 0.33%) were 18:1 M ratio of methanol to bio-oil, 60 °C of temperature, 100 min of reaction, catalyst load of 2.5 wt.%, and stirring speed of 600 rpm. Kinetics of the bio-oil mass conversion through transesterification presented reaction rates varying from 0.016 to 0.091 min^{-1}, 63.07 kJ kg^{-1} of activation energy (E_a), and pre-exponential value (A) of 11.4E10^5. Catalyst efficiency decreased to 34.9% after 10 reuse cycles. Fuel properties of the crude FAME met worldwide standards of biodiesel quality, thus indicate that Pequi bio-oil is a viable, sustainable, and widely available feedstock option in Brazil.

1. Introduction

The energy crisis and global warming caused by the continuous use of fossil fuels has been rapidly depleting oil reservoirs and leading to uncontrollable greenhouse emissions. Mutual efforts to explore alternative energy sources resulted in the appearance of biodiesel, a suitable option for diesel fuel replacement. Low greenhouse emissions, compatibility with current diesel engines, and simple obtaining process are some of the advantages of biodiesel (Nogueira, 2011). Unfortunately, some barriers such as feedstock availability and production costs still are key challenges (Marchetti et al., 2007). Feedstock options for low-cost biodiesel production currently available worldwide are animal fat, crude vegetable oil, and waste cooking oil, however, their high amount of free fatty acids (FFAs) and moisture content can be a drawback for their use (Foidl et al., 1996).

The presence of FFA in high quantities leads to uncontrolled formation of soap and reduces biodiesel yield and quality when the conversion process is conducted with conventional basic catalysts (Ahmad et al., 2014;Ogbu and Ajiwe, 2016 Yu et al., 2016). As an alternative approach, the biodiesel industry has been testing the pre-esterification of FFAs present in low-grade fatty oils via acid catalyzation, before the conduction of conventional base-catalyzed processes (Ahmad et al., 2014). Sulfuric acid (H_2SO_4) is one of the main homogeneous acid catalyst options for such pre-esterification processes. Even though highly efficient, its use in homogeneous form presents difficulties such as separation of residual acids after the reaction, environmental pollution, and corrosive effects (Yu et al., 2016).

Now, a new research field focusing on the reduction of biodiesel production costs and the minimization of environmental pollution has been testing the effectiveness of carbon-based heterogeneous acid catalysts, prepared from low-cost and recyclable materials. They are promising and differ from other heterogeneous catalysts by having high thermal stability and catalytic activity, robustness over various biodiesel feedstocks, and the possibility of preparation with low-cost waste

Abbreviations: TGA/DSC, thermogravimetric analysis/ differential scanning calorimetry; FAME, fatty acid methyl ester; XRD, X-ray diffraction; FTIR, Fourier-transform infrared spectroscopy; FFAs, free fatty acids; PRsulf, sulfonated Pequi rind; BRA, Brazil; ASTM, American Society for Testing and Materials; GC-FID, Gas Chromatography accoupled to Flame Ionization Detector; TG, triacylglycerides; ME, methyl ester; DG, diacylglycerides; MG, monoacylglycerides; G, glycerol

* Corresponding author.
E-mail address: profzavarize@outlook.com (D.G. Zavarize).

https://doi.org/10.1016/j.indcrop.2019.111485
Received 15 March 2019; Received in revised form 11 June 2019; Accepted 13 June 2019
0926-6690/ © 2019 Elsevier B.V. All rights reserved.

materials (Hara et al., 2004;Cheng and Fang, 2011 Lee et al., 2014). Their carbonic base can be obtained at different temperatures, forming polycyclic aromatic rings subsequently incremented or substituted by acidic functional groups from the activation agent (Zong et al., 2007). In their studies, Lee (2013); Liu et al. (2013); Arora et al. (2014); Wang et al. (2014); Bennett et al. (2016), and Zhou et al. (2016) evaluated carbon-based heterogeneous acid catalysts prepared from lignosulfonate, corn straw, rice husk, cassava stillage residue, seed cakes, and bamboo, respectively. They reported conversion efficiencies higher than 90% in the esterification of different biodiesel feedstocks.

Caryocar brasiliensis Camb., or popularly known as Pequi, is an endemic and multiuse fruit of the Brazilian Cerrado biome, available over 2 million km^2 across the country (Amorim et al., 2016). Culturally, the internal almond is the only consumed part of the Pequi fruit. It is rich in bio-oil (> 45%) and considered a promising biodiesel feedstock in Brazil, due to characteristics such as abundance and excellent fuel properties (Borges et al., 2012; Silva et al., 2014). On the other hand, studies have proven that its rinds possess several chemical and medicinal properties, representing about 60% of the whole fruit weight, which unfortunately are thrown away (Ribeiro et al., 2012; Bezerra et al., 2015). It means wasting a cheap, abundant, renewable, biodegradable, non-toxic, and biocompatible agroindustrial residue suitable for several purposes. With that said, there is an emerging possibility of using the whole Pequi fruit in the process of biodiesel production, since no research on the potential of its carbonized rinds as support material for the preparation of heterogeneous acid catalyst has been reported yet.

In this study, transesterification of Pequi (*Caryocar brasiliensis* Camb.) bio-oil was conducted with a heterogeneous acid catalyst prepared with the fruit's carbonized rinds. We performed the optimization of biodiesel production experiments, CG-FID analysis of crude FAME, investigation of the kinetics involved in bio-oil mass conversion, catalyst reusability, and determination of fuel properties in comparison to international standards.

2. Materials and methods

2.1. Materials

Samples of Pequi were collected in the Palmas campus of the Federal University of Tocantins. Sulfuric acid (H_2SO_4) and methanol were purchased from Synth® (Labsynth, Sao Paulo, BRA) in analytical grade.

2.2. Preparation and characterization of the carbon base and catalyst

The samples were initially washed with distilled water. The internal fruits were separated from the rinds and set aside for bio-oil extraction, and the rinds cut into small pieces (< 1 cm) to dry at 110 °C until constant weight. Dried rinds were ground in knife mill, screened to size 0.85 mm (mesh number 20), and calcinated at 800 °C. The catalyst was prepared by wet impregnation of the calcinated rinds. For that, 5 g were mixed with 10 mL of sulfuric acid placed into 250 mL conical flask, heated at 150 °C in oil bath for 3 h and, after cooling in room temperature, the mixture was gradually diluted with 150 mL of distilled water to avoid explosion risks. The catalyst was filtered and repeatedly washed with warm distilled water until neutral pH of the washing solution, proceeding with drying at 65 °C overnight. The final product was labeled PRsulf.

Pequi rinds were characterized by thermogravimetric analysis TGA/DSC (Perkin Elmer Pyris-1, heating rate of 10 °C min^{-1}, oxygen atmosphere, and temperature range from 15 to 1000 °C). Samples of catalyst (PRsulf) were characterized by XRD analysis (CubiX PRO Analytical X-Ray Diffractometer, equipped with a CuKα radiation source: 40 kV, 55 mA, 1.5406 Å, nickel as filter media, 1° min^{-1} goniometer, 1 cm min^{-1} chart speed, and 2θ angles ranging from 5 to 60° in 0.2° steps), and FTIR analysis (Cary 640 FTIR spectrophotometer, with finely divided KBr, at 10:100 ratio, and spectral resolution of 4 cm^{-1} with 16 scans per sample).

2.3. Pequi bio-oil extraction and purification

The procedures of oil extraction occurred via cell solvothermal disruption technique. Internal fruits were finely ground and dried at 110 °C overnight, then 10 *g* of the dried material was mixed with 150 mL of chloroform and methanol (2:1 v/v) solution, and placed into Teflon-based closed vessels. The operational conditions were 750 W microwaves at 60 °C for 45 min. The microwaved mixture was cooled at room temperature and centrifugated to separate solid from liquid. The layer of supernatant composed by the bio-oil and solvent was purified with double wash of distilled water (2:6 v/v) and centrifugated again at 3500 rpm for 3 min. After the second centrifugation, evaporation of the bottom layer containing bio-oil removed the residuals of chloroform. The average yield of bio-oil was 48.6% and measured gravimetrically. The acid value in bio-oil samples was determined as recommended by ASTM. All the bio-oil obtained from the extractions was kept in sealed recipients until biodiesel production experiments.

2.4. FAME synthesis

Direct transesterification of Pequi bio-oil (acid value: 0.41 mg g^{-1}) was conducted with 100 mL round-bottom tree-neck flasks. They were placed in a water bath with regulated temperature, also equipped with mechanical stirrer, thermometer, and condenser. Catalytic activity of PRsulf was initiated after mixing it with methanol (1:2 m/v) at 55 °C for 25 min, subsequently adding a stoichiometric amount of bio-oil. The reflux process was carried out by following these optimization conditions: molar ratio of bio-oil to methanol (from 1:6 to 1:21 M), catalyst dosage (from 1 to 3 wt.%), reaction time (from 20 to 120 min), temperature (from 45 to 65 °C), and stirring speed (from 200 to 700 rpm). When evaluating the effect of one variable, the others were kept at the maximum value, with exception to the molar ratio of oil to methanol. In this case, all the catalyst dosages were tested at the same time. The whole mixture was continuously stirred for homogenization of the temperature in the reaction system. After concluded, the mixture was transferred to a separating funnel for layers formation (upper: methyl ester, middle: glycerol, and lower: catalyst). The layer of methyl esters was removed and the excess of methanol and water was eliminated with a rotary evaporator and anhydrous Na_2SO_4, respectively. Each experiment was carried out in triplicate.

2.5. Characterization of synthetized FAME

Synthesized FAME was characterized with GC-FID gas chromatographer (Agilent 6890 N), equipped with a capillary column (Agilent DB-225) (30 m x25 mm i.d.; 0.25 μm) and a Flame Ionization Detector (FID). The column was configurated as follows: initial temperature of 160 °C maintained for 2 min, then ramping to 230 °C in 5 °C min^{-1} of heating rate, remaining still for 20 min. Nitrogen flow at rate of 1.5 mL min^{-1} was the carrier gas. Samples of synthesized FAME were injected in 50:1 ratio in split mode, while vaporizing the injection port at 250 °C. The 14 peaks in GC-FID analysis of synthesized FAME were compared to FAME standard mix (CRM 47885, Supelco®, Merck). Also, fuel properties (acid value, kinematic viscosity, density, carbon residue, calorific value, flash point, cloud point, pour point, peroxide index saponification, and ash and ester contents) of the synthesized FAME were analyzed as recommended by ASTM regulations.

2.6. Catalyst reusability

Sequential cycles of transesterification were carried out after the determination of optimal conditions for FAME synthesis. After every

cycle, PRsulf was washed with methanol to remove organic impurities and dried at 110 °C for 3 ± 2 h. The efficiency was calculated by comparison of yield.

2.7. Transesterification reaction kinetics

The relation between the rate constant and temperature has been evaluated in the kinetic transesterification reaction of Pequi oil. Consensually, kinetic behavior of transesterification reactions is characterized as a pseudo-first order event (Sahu and Mohanty, 2016). The activation energy (E_a) was obtained by variations in temperature of the process (45–65 °C), and also by varying the reaction time (20–120 min). Eqs. 1 and 2 were applied to determine the rate constant and the activation energy, respectively, related to the pseudo-first order reaction.

$$-\ln(1-BC) = k \bullet t \quad (1)$$

$$\ln k = \ln A - \frac{E_a}{R \bullet T} \quad (2)$$

Where BC is the biodiesel conversion yield at a time t, K is the rate constant of pseudo-first order reaction (min^{-1}), A is the pre-exponential factor (min^{-1}), R is the universal gas constant, and T is the temperature in Kelvin.

3. Results and discussion

3.1. Characterization of the catalyst

Fig. 1A presents the thermal behavior determined by TGA/DSC analysis of uncalcined Pequi rinds. The thermometric curve indicates three acceptable weight-loss stages. The first stage relates to moisture and carbohydrates contents degradation (15 to ~225 °C, representing a loss of 9.33%). The second stage, between 400 and 600 °C, represents about 3.59% of mass loss and corresponds to the thermal decomposition of volatile matter and other components such as cellulose, hemicellulose, and lignin. The third stage, after 600 °C and stable at nearly 830 °C, was attributed to the residual of organic content degradation, fiber decomposition, and the formation of ashes influenced by oxidation activity. It represented a weight loss of 28.6%. Total mass loss was 41.08% at nearly 1000 °C. From the DSC curve, it is noticeable that four endothermic peaks composed the thermal degradation of Pequi rinds. The first two peaks are related to the loss of water and general organic content. The third and fourth peaks correspond to oxidation events.

Fig. 1B depicts the XRD patterns of calcined Pequi rinds and PRsulf. The peaks suggest amorphous material characteristics revealed by disorderly arranged graphitic plans. Both materials presented a broad range of diffraction peaks within the 2θ angles of 10 to 30° and of 30 to 50°, attributed to amorphous carbon faces (002 and 101) (Wang et al., 2014). Other studies regarding carbon-based acid catalysts presented similar behavior of diffraction peaks (Liu et al., 2010, 2013).

Fig. 1C shows spectrums of the FTIR analysis performed with samples of calcined rinds and PRsulf catalyst. The spectrums indicated that both materials had a similar response. However, as expected, PRsulf presented more prominent absorption bands. Strong absorption peaks between 3400 and 3600 cm^{-1} correspond to −OH stretching, and those between 2900 and 3000 cm^{-1} may represent vibrations of −COOH group (Silverstein et al., 1981). Peaks between 1000 and 1200 cm^{-1} represent asymmetric vibrations of O = S=O stretching and S-O binding. The shoulder-shape bands observed in both spectrums probably are intermolecular hydrogen bindings between hydrogen from the sulfonic (–SO_3H) and carbonyl (C=O) groups (Puziy et al., 2001). Formation of sulfur-oxygenated surface groups and structures containing N–O bonds from the thermal degradation of organic matter relate to 1300 and 900 cm^{-1} peaks, also suggesting oxygen species of discrete nature (El-Hendawy, 2003).

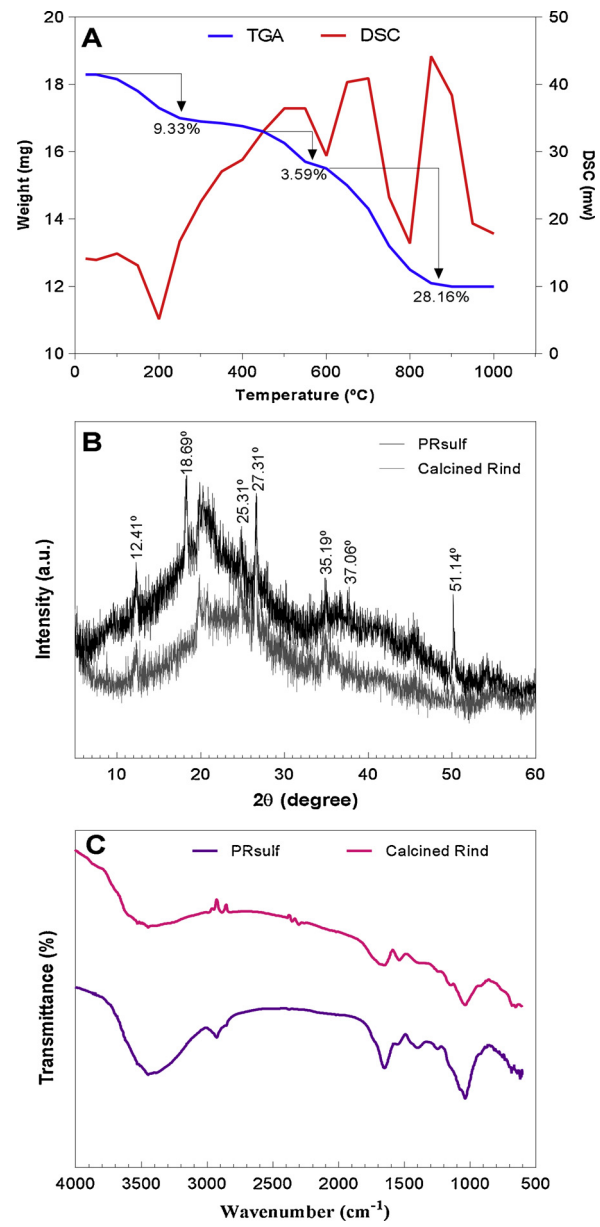

Fig. 1. Characterization of the carbon-based heterogeneous acid catalyst in terms of (A) TGA/DSC analysis, (B) XRD patterns, and (C) FTIR analysis.

Table 1
Composition of synthesized FAME from Pequi (*Caryocar brasiliensis* Camb.) bio-oil.

Retention Time (min)	Identified Compound	wt. %
1.63	Myristic acid methyl ester	1.59
2.49	Palmitic acid methyl ester	49.93
3.56	Palmitoleic acid methyl ester	2.17
3.79	Palmitoleic acid methyl ester	2.06
4.88	Heptadecanoic acid (IS) methyl ester	3.56
5.91	Stearic acid methyl ester	10.16
6.64	Oleic acid methyl ester	7.10
7.11	Linoleic acid methyl ester	13.24
7.76	Arachidic acid methyl ester	0.51
7.93	Gadoleic acid methyl ester	0.73
9.06	Behenic acid methyl ester	0.39
9.31	Erucic acid methyl ester	0.26
17.65	Lignoceric acid methyl ester	8.19
18.74	Nervonic acid methyl ester	0.11

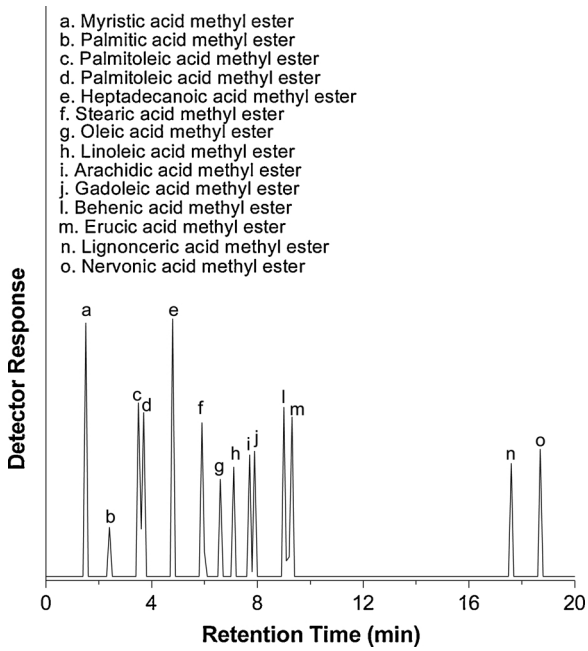

Fig. 2. GC-FID analysis of the synthesized FAME.

3.2. GC-FID of the synthesized FAME

Table 1 lists and Fig. 2 shows the GC-FID retention times for synthesized FAME samples. As seen, the main components were methyl esters of palmitic acid (49.93 wt.%), linoleic acid (13.24 wt.%), and stearic acid (10.16 wt.%), at retention times of 2.49, 7.11, and 5.91 min, respectively. The composition of fatty acids in bio-oils depend on the source of extraction and, in the case of Pequi bio-oil, many studies reported components similar to those found in this study (Lima et al., 2007; Aquino et al., 2009; Oliveira et al., 2010; Aquino et al., 2011; Aguilar et al., 2012; Borges et al., 2012;Barra and Oliveira, 2013 Geőcze et al., 2013; Silva et al., 2014; Faria-Machado et al., 2015; Alves et al., 2017). For example, Borges et al. (2012) studied the methylic and ethylic conversion of Pequi bio-oil into FAME and they reported similar composition weights (wt.%). Oliveira et al. (2010) studied the chemical and physicochemical composition of Pequi bio-oil from cultivations distributed along the Chapada do Araripe, state of Ceara, Brazil. Oliveira and colleagues revealed that external factors such as soil type, distance among trees, water availability, and size of the fruit, directly influence the quality and amount of extractable bio-oil.

3.3. Optimization of transesterification experiments

PRsulf catalytic efficiency was tested with different experimental conditions such as bio-oil/methanol molar ratio (1:6 to 1:21), reaction time (20–120 min), stirring speed (200–700 rpm), temperature (45–65 °C), and catalyst loads (1–3 wt.%), aiming optimization of the Pequi bio-oil transesterification process. Reusability of the catalyst was also evaluated after determination of these optimum conditions. As previously mentioned, when testing a specific variable, the others were kept at maximum range with exception to the molar ratio experiments, in which all catalyst loads were tested at the same time. Fig. 3 shows the graphical response of each variable effects on the process.

3.3.1. Effect of molar ratio and catalyst dosage

Fig. 3-A depicts the effect of different molar ratios of bio-oil to methanol. Transesterification reactions usually require at least 3 mol of alcohol to convert 1 mol of triacylglyceride (Borges et al., 2012). However, the process is generally carried out with excess of alcohol to increase the reaction rate and also to limit backward reactions (Silva et al., 2014). In other words, transesterification with excess of alcohol shifts the equilibrium forwards and increases the amount of FAME. The experiments differed in molar ratios that varied from 1:6 to 1:21, and also in catalyst dosage (1 to 3 wt.%), while the temperature, reaction time and stirring speed were kept at 65 °C, 120 min, and 700 rpm, respectively. As seen from the graph, higher conversion percentage of FAME (97.2 ± 0.41%) was noticed at 1:18 M ratio and maximum PRsulf dosage of 2.5 wt.%. Any increase in molar ratio higher than 1:18 led to a decrease in FAME conversion, which probably was due to the dissolution of glycerol in excess of methanol, that reduced the reaction rate and shifted the equilibrium backwards. In the study of Sandouqa et al. (2019), waste vegetable oil was converted to biodiesel using a carbon-based heterogeneous acid catalyst prepared from olive cake. Three types of catalyst were prepared by varying the activation time in 1, 5 and 10 h. Sandouqa and colleagues evaluated different molar ratios (1:35, 1:45, and 1:55) and catalyst dosages (5, 7, 10 and 15 wt. %) for each of the three catalysts. Better results were noticed when applying the 1h-activated catalyst. They observed an increase in transesterification conversion (39.07 to 56.86%) when the load of this catalyst ranged from 5 to 10 wt.% and the molar ratio from 1:35 to 1:45, under the temperature of 65 °C and 6 h of reaction time. They attributed it to the multiplicity of active sites. On the other hand, they report that any increase in catalyst dosage or molar ratio did not positively influence on biodiesel conversion. Compared to our study, higher conversion percentages were achieved (97.2 ± 0.41%) requiring significantly less molar ratio of bio-oil to methanol (1:18).

3.3.2. Effect of reaction time

Fig. 3B illustrates the effect of different reaction times on the process of FAME synthesis. By knowing the ideal molar ratio and catalyst dosage, obtained from the previous experiment, the effect of reaction time was evaluated at 1:18 M ratio and 2.5 wt.% of PRsulf. The temperature and stirring speed were kept just as before (65 °C and 700 rpm, respectively). The highest yield of FAME at these conditions was 95.10 ± 0.81% after 100 min of reaction time. The graph indicates that any increase in reaction time did not affect FAME yield. Sani et al. (2015) prepared carbon-based heterogeneous acid catalyst with palm frond and spikelet as an environmentally benign alternative for biodiesel production. The catalysts differed in terms of carbonization temperature (300 and 400 °C) and homogenization with succinic acid (5 g). Sani and colleagues tested reaction times varying from 3 to 15 h, and catalyst dosage, molar ratio, and temperature of 1 wt.%, 1:5, and 100–200 °C, respectively. They report a 98.51% conversion efficiency achieved after 5 h of reaction time at these conditions, using the catalyst prepared from palm frond at 400 °C without homogenization by succinic acid. Compared to our study, the conversion efficiency was similar but required significantly less time (100 min).

3.3.3. Effect of temperature

Fig. 3C shows the temperature effect on transesterification. Conversion of bio-oils into FAME requires appropriated temperature to control the diffusion gradient among phases (oil, alcohol, and catalyst) (Nogueira, 2011). Silva et al. (2014) obtained 96% of FAME by converting Pequi bio-oil via transesterification with methanol and KOH as homogeneous catalyst (1 wt.%), 1:6 bio-oil/methanol ratio, at 40 °C for 40 min. As seen in the graph, maximum FAME conversion (99.4 ± 0.33%) was attained at 60 °C. At this temperature, there is more kinetic energy available for the reaction and thus transesterification is accelerated. This also reflects on the rate of mass transfer and solubility of the reactants (Sahu and Mohanty, 2016). For temperatures above 60 °C, a sharp decrease in FAME yield was observed, probably due to reductions on methanol availability since its boiling point is around 65 °C (Rashtizadeh et al., 2010). In the study of Ogbu et al. (2018), Hura crepitans seed pod was used as a support material for the production of an acid catalyst to convert vegetable oil with high FFA content. Four different types of catalyst were prepared by varying

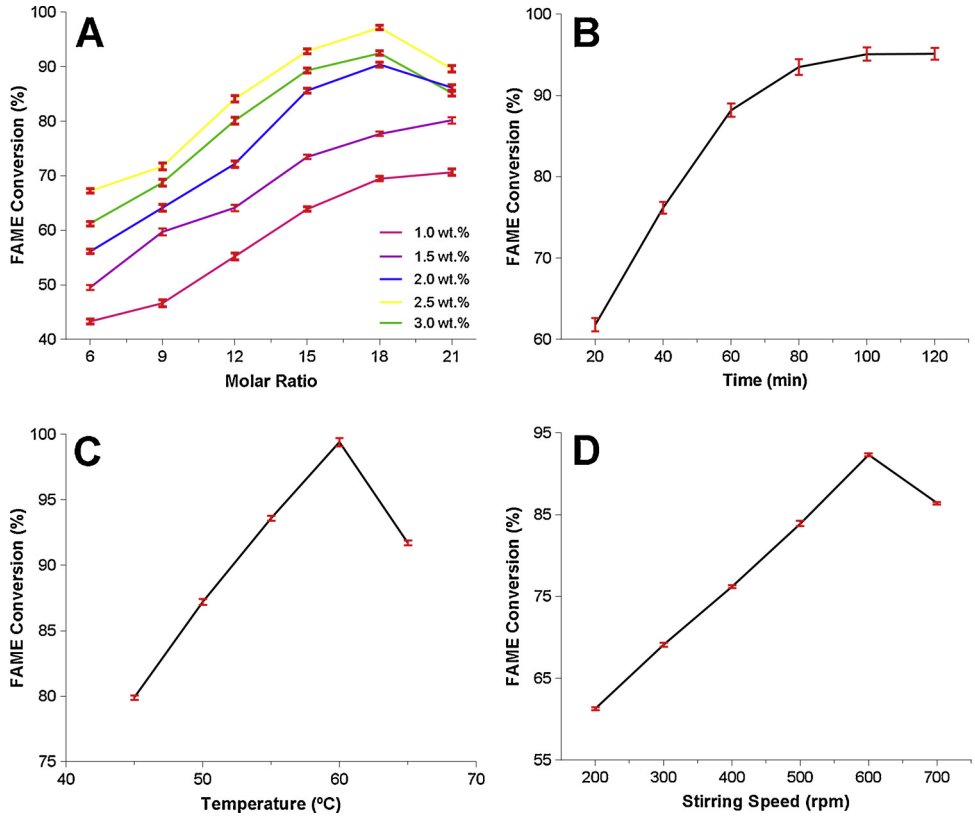

Fig. 3. Optimization of the transesterification process through analysis of (A) oil/methanol molar ratio, (B) reaction time, (C) temperature, and (D) stirring speed effects.

the carbonization time. Their experiments of biodiesel production were optimized by testing different catalyst loads (3, 5, and 10%), temperatures (60, 70, and 90 °C), molar ratio (1:6, 1:9, and 1:12), and reaction times (60, 90, and 150 min). They report that catalyst prepared at 60 °C carbonization was the most efficient for esterification of FFAs in vegetable oil. The highest conversion percentage (93.15%) was achieved at 90 °C, 60 min of reaction time, 1:9 M ratio, and 10% of catalyst load. Compared to our study, a similar conversion percentage was found but it required significantly less heat (60 °C).

3.3.4. Effect of stirring speed

Fig. 3D depicts the effect of stirring speed on the transesterification of Pequi bio-oil. An ideal stirring speed improves the contact among the mixture, as well as reduces the effect of mass transfer during the conversion (Ahmad et al., 2014). The graph shows that increase in the stirring speed up to 600 rpm led to higher yields of FAME (92.3 ± 0.19%). For higher speeds, the yield of FAME decreased considerably. To avoid any limitations by reaction rate due to mass transfer, all further tests were carried out at 600 rpm stirring speed. In the study of Rao et al. (2011), de-oiled canola meal was converted to a carbon-based heterogeneous acid catalyst. Oleic acid and high FFA canola oil (25:75 v/v) were mixed and used as a substrate for the catalyst evaluation in esterification reactions. Temperature, reaction time, catalyst load, and molar ratio were 65 °C, up to 48 h, 7.5%, and 1:65, respectively. Similar to our study, their experimental tests indicated 600 rpm as ideal stirring speed. So, among the four types of catalyst, the so-called "CAT 4″ activated by water steam and sulfuric acid presented the most efficient catalytic activity (~50% conversion) at that stirring speed. Their maximum conversion efficiency at that stirring speed was low compared to our study (92.3 ± 0.19%), even though there were similarities in the experimental approach regarding the other variables.

3.4. PRsulf reusability

One of the many advantages of using heterogeneous catalysts in transesterification reactions is the possibility of reuse. It is also essential in terms of industrial application and cost reduction (Joshi et al., 2016). In this study, after determining optimum conditions for the transesterification of Pequi bio-oil (1:18 M ratio, reaction temperature of 60 °C, reaction time of 100 min, catalyst load of 2.5 wt.%, and stirring speed of 600 rpm), sequential cycles of transesterification were performed by reusing the catalyst after washed with methanol to remove organic impurities and dried at 110 °C for 3 ± 2 h. The experiments stopped when the catalyst presented an efficiency below 40%. Reusability of the catalyst decreased by 58.3% after 10 cycles, as depicted in Fig. 4,

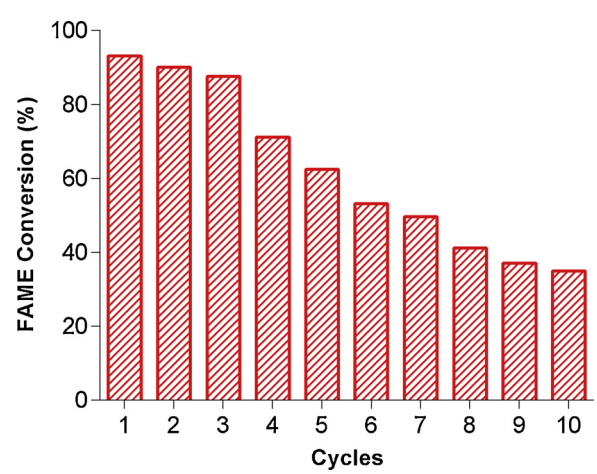

Fig. 4. Reusability of PRsulf under optimized conditions for transesterification reaction.

resulting in a final conversion efficiency of 34.9%. The integrity of the catalytic activity remained practically unchanged through the three first cycles, losing less than 5.5% of efficiency. Blockage of active sites by the formation of product layers may be one of the explanations for the low catalytic performance after 10 cycles since these layers reduce the contact of the catalyst with the alcohol (Zhou et al., 2016). Some authors attributed the decrease in efficiency to the leaching of -SO3H groups, which reduces the actives sites on the catalyst surface and thus its catalytic power (Liu et al., 2010, 2013; Sani et al., 2015; Ogbu et al., 2018).

3.5. Kinetics of pequi bio-oil transesterification

As reported by Verma et al. (2017), the conversion of triacylglycerides (TG) in alkyl esters generally occurs in three main steps, and in each one of them there is the formation of 1 molcule of methyl ester (ME) by using 1 molcule of methanol. In the first step, TG is converted into diacylglycerides (DG) under effect of methanol (Eq. 3). Subsequently, DG react with methanol and is converted to monoacylglycerides (MG) (Eq. 4). Then, in the third step, MG react with methanol and form ME plus glycerol (G) (Eq. 5).

$$TG + Methanol \leftrightarrow DG + ME \quad (3)$$

$$DG + Methanol \leftrightarrow MG + ME \quad (4)$$

$$MG + Methanol \leftrightarrow ME + G \quad (5)$$

A drawback of studying 3-step transesterification reactions kinetic behavior is its complexity. However, it can be avoided if overlooked the intermediate reaction (Eq. 4) (Al-Sakkari et al., 2017). In this way, the rate constant and activation energy of the process can be defined from describing the whole reaction in a single step, as presented in Eq. 6.

$$TG + 3\,Methanol \leftrightarrow 3\,ME + G \quad (6)$$

In reference to the experiments performed at optimum conditions, the maximum yield of FAME occurred at 2.5 wt.% and 1:18 M ratio of oil:methanol. Thus, a linear relationship was plotted considering the interaction of – ln (1 – BC) vs. time (t) (Eq. 1), assuming the viability of the reaction as a pseudo-first order event (Fig. 5-A). This relation was determined at our variated experimental temperatures (45, 55, and 65 °C).

The rate constants increased in higher temperatures, and presented values of 0.016, 0.044, and 0.091 min^{-1}, respectively. By analyzing the data, a gain of 20 °C in temperature led to an increase in the rate constants by nearly 6 folds. Determination of the activation energy (E_a) and pre-exponential factor (A) was in accord to the Arrhenius model (Eq. 2). Fig. 5-B illustrates the plot of ln k vs. 1/T where E_a and A correspond to 63.07 kJ mol^{-1} and 11.4E10^5, respectively. An activation energy value greater than 25 kJ mol^{-1} indicates that PRsulf catalytic activity did not limit the mass transfer during transesterification of Pequi bio-oil (Kaur and Ali, 2014). Studies of Tan et al. (2001); Chen et al. (2011); Chen and Luo (2011), and Borsato et al. (2014) reported similar values regarding kinetic behavior.

3.6. Fuel properties of Pequi oil synthesized FAME

Table 2 summarizes the parameters of acid value, viscosity, density, carbon residue, calorific value, flash point, cloud point, pour point, peroxide index saponification, and ashes and esters contents of the synthesized FAME, determined in accord to ASTM regulations. Also, these fuel properties were compared to biodiesel quality standards of Brazil, the European Union, and the USA. Studies of Borges et al. (2012) and Silva et al. (2014) reported similar fuel properties for FAME produced of Pequi bio-oil. As seen from Table 2, the physicochemical characteristics represented by these parameters are in accord to the worldwide standards for biodiesel quality, thus indicate that Pequi bio-oil is a viable, sustainable, and widely available feedstock option in Brazil.

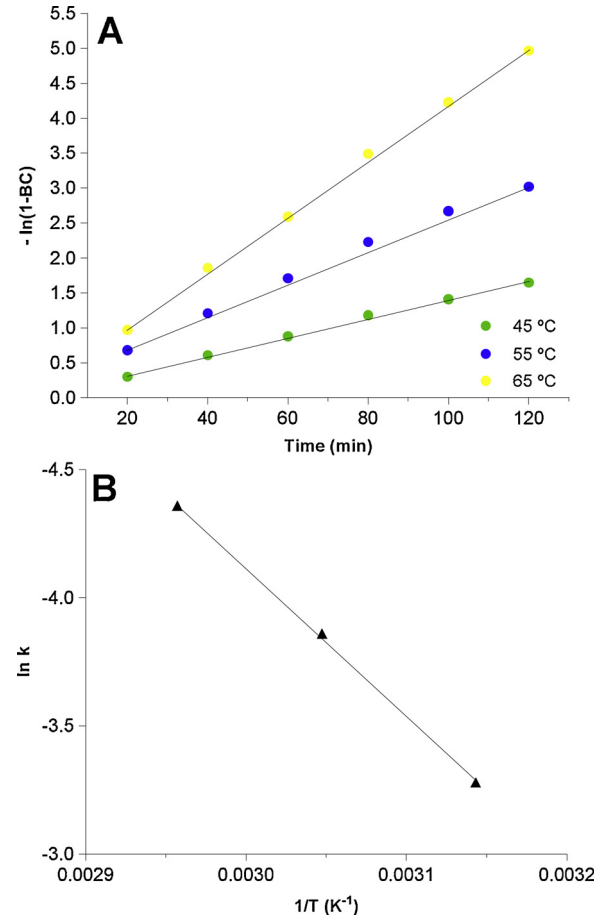

Fig. 5. Kinetics of the transesterification with PRsulf under optimized conditions where (A) plot between – ln (1 - BC) vs. time (t) at different temperatures, and (B) Arrhenius plot between ln k versus 1/T.

Table 2
Physicochemical properties of synthesized FAME compared to worldwide standard values.

Properties	This Study	Biodiesel Standards		
		Brazil[a]	EU[b]	USA[c]
Density at 15 °C (kg m^{-3})	890	850-900	860-900	870-900
Viscosity at 40 °C (mm^2 s^{-1})	4.8	3.0-6.0	3.5-5.0	1.9-6.0
Flash point (°C)	94	100	120	130
Acid value (mg of KOH g^{-1})	0.41	0.80	0.50	0.80
Copper Strip corrosion at 50 °C	1a	1a	1a	N. º 3 max
Calorific value (mJ kg^{-1})	34.11	37.27	35	–
Pour point (°C)	5.37	−6 to 6	0	−15 to 10
Cloud point (°C)	7.41	–	–	−3 to 12
Carbon residue (% mass)	Nil	0.05	0.30	0.020
Peroxide index (mEq kg^{-1})	1.12	–	–	–
Saponification (mg of KOH g^{-1})	56.77	–	–	–
Ash content (%)	Nil	0.010	0.020	0.050
Ester (%)	96.8	96.5	96.5	96.5

[a] ANP (National Agency of Oil, Natural Gas and Biofuels) – Regulation n.° 07 (2008).
[b] EN – 14,213 (2003) and EN – 14,214 (2003).
[c] ASTM D7467-17 (2018) and ASTM D6751-15ce1 (2007).

4. Conclusions

In this study, transesterification of Pequi (*Caryocar brasiliensis* Camb.) bio-oil was conducted with a heterogeneous acid catalyst

prepared with the fruit's carbonized rinds. FAME composition was majorly by methyl esters of palmitic acid, linoleic acid, and stearic acid, which represented 49.93, 13.24, and 10.16 wt.%, respectively. Optimized conditions for maximum conversion of Pequi bio-oil (99.4 ± 0.33%) were 18:1 M ratio of methanol to bio-oil, 60 °C of temperature, 100 min of reaction, catalyst load of 2.5 wt.%, and stirring speed of 600 rpm. Kinetics of the bio-oil mass conversion through transesterification presented reaction rates varying from 0.016 to 0.091 min^{-1}, 63.07 kJ kg^{-1} of activation energy (E_a), and pre-exponential value (A) of 11.4E10^5. Catalyst efficiency decreased to 34.9% after 10 reuse cycles. Fuel properties of the crude FAME met worldwide standards of biodiesel quality, thus indicate that Pequi bio-oil is a viable, sustainable, and widely available feedstock option in Brazil.

Acknowledgements

This research was carried out in the Laboratory of Test and Development on Biomass and Biofuels at Federal University of Tocantins, Palmas, Brazil. The authors thank all laboratory staff for help.

References

Aguilar, E.C., Jascolka, T.L., Teixeira, L.G., Lages, P.C., Ribeiro, A.C.C., Vieira, E.L.M., Peluzio, M.C.G., Alvarez-Leite, J.I., 2012. Paradoxical effect of a pequi oil-rich diet on the development of atherosclerosis: balance between antioxidant and hyperlipidemic properties. Braz. J. Med. Biol. Res. 45, 601–609.

Ahmad, J., Yusup, S., Bokhari, A., Kamil, R.N.M., 2014. Study of fuel properties of rubber seed oil-based biodiesel. Energy Convers. Manage. 78, 266–275.

Al-Sakkari, E.G., El-Sheltawy, S.T., Attia, N.K., Mostafa, S.R., 2017. Kinetic study of soybean oil methanolysis using cement kiln dust as a heterogeneous catalyst for biodiesel production. Appl. Catal. B Environ. 206, 146–157.

Alves, A.A., Rodrigues, M.Z., Pinto, M.R.M.R., Vanzela, E.S.L., Stringheta, P.C., Perrone, I.T., Ramos, A.M., 2017. Morphological characterization of pequi extract microencapsulated through spray drying. Int. J. Food Proper. 20, 51298–51305.

Amorim, D.J., Rezende, H.C., Oliveira, E.L., Almeida, I.L.S., Coelho, N.N.M., Matos, T.N., Araújo, C.S.T., 2016. Characterization of Pequi (*Caryocar brasiliense*) shells and evaluation of their potential for the adsorption of Pb (II) ions in aqueous systems. J. Braz. Chem. Soc. 27, 616–623.

Aquino, L.P., Borges, S.V., Queiroz, F., Antoniassi, R., Cirillo, M.A., 2011. Extraction of oil from pequi fruit (*Caryocar brasiliense* Camb.) using several solvents and their mixtures. Grasas Y Aceites 62, 245–252.

Aquino, L.P., Ferrua, F.Q., Borges, S.V., Antoniassi, R., Correa, J.L.G., Cirillo, M.A., 2009. Influence of pequi drying (*Caryocar brasiliense* Camb.) on the quality of the oil extracted. Ciênc. Tecnol. Aliment 29, 354–357.

Arora, R., Kapoor, V., Toor, A.P., 2014. Esterification of free fatty acids in waste oil using a carbon-based solid acid catalyst. 2Nd International Conference on Emerging Trends in Engineering and Technology (ICETET'2014) 1–10.

ASTM D6751-15ce1, 2007. Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International, West Conshohocken, PA, 2015, www.astm.org. Accessed in: December 2018.

ASTM D7467-17, 2018. Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20), ASTM International, West Conshohocken, PA, 2017, www.astm.org. Access in: December 2018.

Barra, P.M.C., Oliveira, M.A.L., 2013. Simultaneous analysis of saturated and unsaturated fatty acids present in pequi fruits by capillary electrophoresis. Quim. Nova 36, 1430–1433.

Bennett, J.A., Wilson, K., Lee, A.F., 2016. Catalytic application of waste derived materials. J. Mater. Chem. A Mater. Energy Sustain. 4, 3617–3637.

Bezerra, N.K.M.S., Barros, T.L., Coelho, N.P.M.F., 2015. The effect of the Pequi oil (*Caryocar brasiliensis* Camb.) in the healing of skin lesions in mice. Rev. Bras. Pl. Med. 17, 875–880.

Borges, K.R., Batista, A.C.F., Rodrigues, H.S., Terrones, M.H., Vieira, A.T., Oliveira, M.F., 2012. Production of methyl and ethyl biodiesel fuel from pequi oil (*Caryocar brasiliensis* Camb.). Chem. Technol. Fuels Oils 48, 83–89.

Borsato, D., Galvan, D., Pereira, J.L., Orives, J.R., Angilelli, K.G., Coppo, R.L., 2014. Kinetic and thermodynamic parameters of biodiesel oxidation with synthetic antioxidants: simplex centroid mixture design. J. Braz. Chem. Soc. 25, 1984–1992.

Cheng, G., Fang, B.S., 2011. Preparation of solid acid catalyst from glucose–starch mixture for biodiesel production. Bioresour. Technol. 102, 2635–2640.

Chen, Y.H., Chen, J.H., Luo, Y.M., Shang, N.C., Chang, C.H., Chang, C.Y., Chiang, P.C., Shie, J.L., 2011. Property modification of jatropha oil biodiesel by blending with other biodiesels or adding antioxidants. Energy 37, 4415–4421.

Chen, Y.H., Luo, Y.M., 2011. Oxidation stability of biodiesel derived from free fatty acids associated with kinetics of antioxidants. Fuel Proc. Technol. 92, 1387–1393.

El-Hendawy, A.N.A., 2003. Influence of HNO_3 oxidation on the structure and adsorptive properties of corncob-based activated carbon. Carbon 41, 713–722.

European Committee for Standardization. Standard EN 14213, 2003. Available in: https://www.ds-bremen.com/tl_files/media/pdf/eng_biodiesel.pdf. Access in: December 2018.

European Committee for Standardization. Standard EN 14214, 2003. Available in: < http://cdn.intechweb.org/pdfs/23666.pdf > . Access in: December 2018.

Faria-Machado, A.F., Tres, A., van Ruth, S.M., Antoniassi, R., Junqueira, N.T.V., Lopes, P.S.N., Bizzo, H.R., 2015. Discrimination of pulp oil and kernel oil from pequi (*Caryocar brasiliense* Camb.) by fatty acid methyl esters fingerprinting, using GC-FID and multivariate analysis. J. Agric. Food Chem. 63, 10064–10069.

Foidl, N., Foidl, G., Sanchez, M., Mittelbach, M., Hackel, S., 1996. *Jatropha curcas* L. As source of production of biofuel in Nicaragua. Bioresour. Technol. 58, 77–82.

Geőcze, K.C., Barbosa, L.C.A., Fidêncio, P.H., Silvério, F.O., Lima, C.F., Barbosa, M.C.A., Ismail, F.M.D., 2013. Essential oils from pequi fruits from the Brazilian Cerrado ecosystem. Food Res. Int. 54, 1–8.

Hara, M., Yoshida, T., Takagaki, A., 2004. A carbon material as a strong Protonic acid. Angew. Chem. Int. Ed. 43, 2955–2958.

Joshi, G., Rawat, D.S., Sharma, A.K., Pandey, J.K., 2016. Microwave enhanced alcoholysis of non-edible (algal, jatropha and pongamia) oils using chemically activated egg shell derived CaO as heterogeneous catalyst. Bioresour. Technol. 219, 487–492.

Kaur, N., Ali, A., 2014. One-pot transesterification and esterification of waste cooking oil via ethanolysis using Sr-Zr mixed oxide as solid catalyst. RSC Adv. 4, 43671–43681.

Lee, A.F., Bennet, J.A., Manayil, J.C., Wilson, K., 2014. Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification. Chem. Soc. Rev. 43, 7887–7916.

Lee, D., 2013. Preparation of a Sulfonated carbonaceous material from Lignosulfonate and its usefulness as an esterification catalyst. Molecules 18, 8168–8180.

Lima, A., Oliveira e Silva, A.M., Trindade, R.A., Torres, R.P., Mancini-Filho, J., 2007. Chemical composition and bioactive compounds in the pulp and almond of pequi fruit. Rev. Bras. Frutic. 29, 695–698.

Liu, T., Li, Z., Wei, L., Shi, C., Wang, Y., 2013. Preparation and characterization of biomass carbon-based solid acid catalyst for the esterification of oleic acid with methanol. Bioresour. Technol. 133, 618–621.

Liu, X.-Y., Huang, M., Ma, H.-L., Zhang, Z.-Q., Gao, J.-M., Zhu, Y.-L., Han, X.-J., Guo, X.-Y., 2010. Preparation of a carbon-based solid acid catalyst by Sulfonating activated carbon in a chemical reduction process. Molecules 15, 7188–7196.

Marchetti, J.M., Miguel, V.U., Errazu, A., 2007. Heterogeneous esterification of oil with high amount of free fatty acids. Fuel 86, 906–910.

National Agency of Oil, Natural Gas and Biofuels – ANP. Regulation Nº 07 of 2008. Available in: < http://www.anp.gov.br/brasil-rounds/round1/HTML/Winning_pt.htm > . Accessed in: December 2018.

Nogueira, L.A.H., 2011. "Does biodiesel make sense?". Energy 36, 3659–3666.

Ogbu, I.M., Ajiwe, V.I.E., 2016. Fuel properties and their correlations with fatty acids structures of methyl- and butyl-esters of *Afzelia africana*, *Cucurbita pepo* and *Hura crepitans* seed oils. Waste Biomass Valoriz. 7, 373–381.

Ogbu, I.M., Ajiwe, V.I.E., Okoli, C.P., 2018. Performance evaluation of carbon-based heterogeneous acid catalyst derived from *Hura crepitans* seed pod for esterification of high FFA vegetable oil. Bioenerg. Res. 11 (4), 772–783.

Oliveira, M.E.B., Guerra, N.B., Maia, A.H.N., Alves, R.E., Santos, N.M., Sampaio, F.G.M., Lopes, M.M.T., 2010. Características químicas e físico-químicas de pequis da Chapada do Araripe – CE. Rev. Bras. Fruticult. 32, 114–125.

Puziy, A.M., Poddubnaya, O.L., Ritter, J.A., Ebner, A.D., Holland, C.E., 2001. Elucidation of the ion binding mechanism in heterogeneous carbon-composite adsorbents. Carbon 39, 2313–2324.

Rashtizadeh, E., Farzaneh, F., Ghandi, M., 2010. A comparative study of KOH loaded on double aluminosilicate layers, microporous and mesoporous materials as catalyst for biodiesel production via transesterification of soybean oil. Fuel 89, 3393–3398.

Rao, B.V.S.K., Chandra Mouli, K., Rambabu, N., Dalai, A.K., Prasad, R.B.N., 2011. Carbon-based solid acid catalyst from de-oiled canola meal for biodiesel production. Catal. Commun. 14 (1), 20–26.

Ribeiro, M.C., Vilas Boas, E.V.B., Riul, T.R., Pantoja, L., Marinho, H.A., Santos, A.S., 2012. Influence of the extraction method and storage time on the physicochemical properties and carotenoid levels of pequi (*Caryocar brasiliense* Camb.) oil. Ciênc. Tecnol. Aliment. 32, 386–392.

Sahu, H., Mohanty, K., 2016. Pseudo-first order reaction kinetics and thermodynamic properties study of neem oil esterification using MgO grafted natural hydroxyapatite. RSC Adv. 6, 8892–8901.

Sandouqa, A., Al-Hamamre, Z., Asfar, J., 2019. Preparation and performance investigation of a lignin-based solid acid catalyst manufactured from olive cake for biodiesel production. Renew. Energy 132, 667–682. https://doi.org/10.1016/j.renene.2018.08.029.

Sani, Y.M., Raji, A.O., Alaba, P.A., Abdul Aziz, A.R., Wan Daud, W.M.A., 2015. Palm frond and spikelet as environmentally benign alternative solid acid catalyst for biodiesel production. BioResour. 10 (2), 3393–3408.

Silva, T.A., Assunção, R.M.N., Vieira, A.T., Oliveira, M.F., Batista, A.C.F., 2014. Methylic and ethylic biodiesels from pequi oil (*Caryocar brasiliense* Camb.): production and thermogravimetric studies. Fuel 136, 10–18.

Silverstein, R.M., Bassler, G.C., Morrill, T.C., 1981. Spectrometric Identification of Organic Compounds. John Wiley and Sons, New York.

Tan, C.P., Che Man, Y.B., Selamat, J., Yusoff, M.S.A., 2001. Application of Arrhenius kinetics to evaluate oxidative stability in vegetable oils by isothermal differential scanning calorimetry. J. Am. Oil Chem. Soc. 78, 1133–1138.

Verma, P., Dwivedi, G., Sharma, M.P., 2017. Comprehensive analysis on potential factors of ethanol in Karanja biodiesel production and its kinetic studies. Fuel 188, 586–594.

Wang, L., Dong, X., Jiang, H., Li, G., Zhang, M., 2014. Preparation of a novel carbon-based solid acid from cassava stillage residue and its use for the esterification of free fatty acids in waste cooking oil. Bioresour. Technol. 158, 392–395.

Yu, H., Niu, S., Lu, C., Li, J., Yang, Y., 2016. Preparation and esterification performance of sulfonated coal-based heterogeneous acid catalyst for methyl Oleate production. Energy Convers. Manage. 126, 488–496.

Zhou, Y., Niu, S., Li, J., 2016. Activity of the carbon-based heterogeneous acid catalyst derived from bamboo in esterification of oleic acid with ethanol. Energy Convers. Manage. 114, 188–196.

Zong, M.H., Duan, Z.Q., Lou, W.Y., Smith, T.J., Wu, H., 2007. Preparation of a sugar catalyst and its use for highly efficient production of biodiesel. Green Chem. 7, 434–437.