



Obtention of fatty acids and phenolic compounds from Colombian cashew (*Anacardium occidentale*) nut shells using pyrolysis: towards a sustainable biodiesel production

Luis J. Cruz-Reina^a, Juan Sebastián Flórez-Rojas^a, Gerson-Dirceu López^{b,c}, Israel Herrera-Orozco^d, Chiara Carazzone^b, Rocío Sierra^{a,*}

^a Product and Processes Design Group, Department of Chemical and Food Engineering, Universidad de los Andes, Carrera 1 No. 18A-10, Bogotá D.C. 111711, Colombia

^b Laboratory of Advanced Analytical Techniques in Natural Products, Department of Chemistry, Universidad de los Andes, Carrera 1 No. 18A-10, Bogotá D.C. 111711, Colombia

^c Faculty of Science and Humanities, Fundación Universidad de América, Avda. Circunvalar No. 20-53, Bogotá D.C., Colombia

^d Energy Systems Analysis Unit, Energy Department, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Av. Complutense 40, 28040, Madrid, Spain

ARTICLE INFO

Keywords:

Characterization
Pyrolysis
Cashew nut shell
Biofuel
Transesterification
Fatty acids
Phenolic compounds

ABSTRACT

Sustainable management of non-edible agricultural residues of cashew nut production is a concern in Colombia. Therefore, this study aimed to study the fatty acid content of a pyrolytic liquid obtained from cashew nut shells (CNSs) from the Vichada region in Colombia. Transesterification of pyrolytic liquid was conducted to obtain biodiesel at the micro-scale as the first approach for this valorization route. Proximal analysis of samples was carried out using advanced analytical techniques (UHPLC-MS and CG-MS) whereas phenolic content and antioxidant activity were determined. The production yield of pyrolytic liquid was $69.15 \pm 5.07\%$ weight (wt.), at 550°C and 2h of pyrolysis and the liquid was rich in fatty acids ($\sim 70\%$ wt.) and long-chain phenols ($\sim 18\%$ wt.). Among the phenolic compounds in liquid, mainly unsaturated C15:4 cardanol was identified (82.1 ± 5.5 mg/g), whereas the antioxidant activity of pyrolytic liquid was 0.714 ± 0.030 TE/g. Moreover, the biodiesel yield was 81% using catalyst sodium methoxide (12% v), and 50°C and 26 min for the reaction. The obtained biodiesel in the hexane fraction was rich in methyl *trans*-8-octadecanoate (20.9 % wt.) and methyl palmitate (14.3 % wt.), being the representative compounds in the biodiesel. Therefore, the results indicated that thermal conversion of CNSs for obtaining biodiesel on a one-step process is a suitable strategy for the management of toxic and non-edible cashew residues. Finally, this is the first work of its kind that propose in detail the composition of pyrolytic liquid obtained from Colombian cashew nut residues under the proximate analysis approach and using advanced analytical techniques.

1. Introduction

The demand for fuels is facing a growing trend, which is in concordance with population growth [1]. Energy is fundamental to

* Corresponding author.

E-mail address: rsierra@uniandes.edu.co (R. Sierra).

<https://doi.org/10.1016/j.heliyon.2023.e18632>

Received 15 December 2022; Received in revised form 14 July 2023; Accepted 24 July 2023

Available online 28 July 2023

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modern life and energy security is indispensable for human beings, e.g., manufacturing industry, transportation, and daily life requirements [1]. Nevertheless, declining fossil fuel reserves [2], the exploitation of traditional fuels [3], and the recent geopolitical instability [4] have placed energy security at risk. In addition, environmental concerns are on the rise for unstoppable environmental pollution. For this reason, it is necessary to develop alternatives focused on renewable energy sources to ensure the sustainable production of fuels.

Promising alternatives such as wind energy, solar energy, hydrogen, and biofuels from renewable biomass have been studied and represent a suitable solution for energy supply [5]. Nevertheless, renewable biomass such as agricultural residues and non-edible plant products, for obtaining biogas, char, and biodiesel has attracted the attention of industry and academic research [6]. Among the aforementioned products, biodiesel is an alternative to fossil fuels due to it is renewable, eco-friendly, and biodegradable nature. It can be obtained from raw materials that do not compete with food production. A wide variety of potential raw materials for biodiesel production are being studied, including lignocellulosic biomass, agricultural residues, and non-edible oils obtained from plants [2].

Biodiesel is defined as mono-alkyl esters of long-chain fatty acids derived from vegetable or animal fats. Several processes for biodiesel obtention have been developed, along with the catalyst and non-catalyst esterification and transesterification processes of fatty acids are the most used [1]. Obtaining biodiesel from residual biomass from agricultural residues is a sustainable strategy that increases the circularity of residues and maximizes the resources in use, reducing the environmental impact of human activities [7].

According to Food and Agriculture Organization (FAO) data, in 2020, the world cashew nut production was approximately 1.2 million tons [8], leaving about 3 million tons of cashew nut shells (CNSs) as agricultural residue. The nut grows attached to the cashew apple (pseudofruit), which is edible and easily degraded under natural conditions not representing an intensive hazard to the environment. On the other hand, the nut is covered by the CNS, which protects it from damage and predators. The extraction process of the nut is artisanal and demands several steps that include deshelling, peeling, and heating leaving the CNS as the agricultural residue of this processing step. This shell has a closed honeycomb structure, and it is very resistant. In addition, it is not edible and has corrosive effects on skin tissues, which difficult for its correct management. The composition of CNS has been described to be mostly cashew nut shell liquid (CNSL), which is trapped in the CNS structure and is rich in phenolic compounds of the alkyl phenol family associated with corrosive effects. Anacardic acids and cardanol are the most abundant phenolic compounds in natural CNSL [9–11]. Besides their adverse effects on living tissues, these substances have interesting bioactivities including antibacterial and antioxidant effects in low concentrations. Nonetheless, the natural degradation of CNS is slow because its phenolic compounds do not promote the proliferation of microorganisms [12]; additionally, the complexity of these compounds does not allow CNSs to be easily handled. Therefore, the accumulation of this residual biomass on farms is inevitable and becomes an environmental problem when the toxic substances alter the soils and water bodies.

In Colombia, the Vichada region is experiencing growing cultivation of the cashew tree (*Anacardium occidentale*), seeking to develop this agricultural territory around the production of cashew nuts. Efforts of government and private investors focused the attention on cashew tree cultivation. The development of cashew tree varieties for its cultivation in the Vichada region resulted in the massive cultivation of *Mapiria*, *Yucao*, and *Yopare* varieties, which are resistant to plague and adverse environmental conditions. Additionally, it is reported that the *Mapiria* tree variety yields 1800 kg of cashew nuts (with shell) per hectare (ha) [13], being the most cultivated variety in this region. Currently, it is estimated that in Vichada about 4000 ha of cashew trees are cultivated, accounting for 52% of the total cashew cultivation in Colombia [14]. It is estimated that each year about 4.2 tons of CNSs can be produced in Vichada, and these values could increase intensively in the next ten years [15]. Nowadays, these residues are not being processed and they can become a problem that negatively impacts soils and water sources, so their correct management is a priority for the region. Moreover, Vichada has the potential for the expansion of agricultural production in Colombia and also the development of bioenergy solutions from agricultural residues [16]. This last, present an opportunity to generate knowledge about the valorization of cashew residues in the context of a country in South America.

Regarding the valorization of residues generated in the production of cashew nuts, the extraction of CNSL has focused the attention of researchers. Traditional hot mechanical pressing for the extraction of the CNSL is a suitable strategy, especially for obtaining the technical CNSL (rich in cardanol). This process converts the anacardic acids into cardanol through thermal decarboxylation (around 250 °C) [17]. Nonetheless, the purification, characterization, and transformation of CNSL into valuable products is still a challenge due to the low selectivity of mechanical pressing, the thermal interconversion of key compounds, and the poor available information about the fatty acid content of this substance. Similarly, extraction methods such as Soxhlet extraction, and supercritical fluid extraction (SFE) have been used to recover natural CNSL with interesting results that suggested the presence of fatty acids, diverse phenolic compounds, and sugars in the recovered extracts [18,19]. In addition to the mass transfer limitations due to the structure of CNS, the cost of these extraction technologies is inconvenient since require large amounts of solvents, high investment costs in equipment, and subsequent steps for refining and purification of extracts generally focused on food and pharmaceutical applications.

On the other hand, the CNSL has been studied for energy applications being a promising strategy for the management of this complex natural substance. Small quantities of CNSL without any modification were added to biodiesel mixtures for the stabilization of triglycerides with favorable results [20] probably related to the phenolic compounds of this substance. Moreover, the thermal cracking of technical CNSL has been tested for obtaining a biofuel that was used in blending in a diesel engine with promising results [21]. Recently, catalytic dehydrogenation to CNSL was performed to obtain C15 to C21 bio-hydrocarbons from the long-chain phenols of this substance to be used as biofuel [22]. The thermochemical processing of these residues seems to be a suitable technology for the management of CNS. Although promising results have been obtained, to the best knowledge of the authors, at the moment of writing this article, there are no available studies regarding the direct transformation of fatty acids from CNSL for producing biodiesel of second-generation with perspectives on energy applications.

Pyrolysis is a thermochemical conversion strategy used for residue management. With this technology, it is possible to obtain

pyrolytic products such as combustible gases, bio-oil, and biochar, all of them with applications in the energy sector [23]. This process is relatively simple and makes it possible to obtain products that can be directly valorized into energy solutions. Then, pyrolysis has been used for the thermochemical transformation of CNS to simplify its management [24]. It was obtained from this biomass mainly a pyrolytic liquid with yields up to 70% at temperatures above 400 °C; however, its chemical composition has not been discussed in detail. The pyrolysis of CNS in the context of Colombia is an open field of research that seeks to recover valuable substances, which could increase the circularity of this agricultural residue under the concept of biorefinery highlighting interesting possibilities for reducing reliance on fossil fuel, offset the carbon footprint of agroindustry and other sectors, enhancing energy security, and improve the management of cashew residues [25].

This work aimed to produce and characterize a pyrolytic liquid obtained from CNS generated in Vichada with perspectives in biodiesel production using this residual biomass. For that, pyrolysis of cashew nut shells was performed, followed by a transesterification process to obtain fatty acid methyl esters at a laboratory scale. The chemical characterization of samples was performed using both gas and liquid chromatography coupled with mass spectrometry to study the study of fatty acids and long-chain phenols, respectively. In addition, some attributes of pyrolytic liquid such as antioxidant activity were assessed. As the best knowledge of the authors, this is the first work that studied the rigorous chemical composition of phenolic compounds and fatty acids profiles in a pyrolytic liquid under a bio-fuel approach. The authors present this valorization perspective and characterization methodology to study oily agricultural residues with complex chemical compositions.

2. Materials and methods

2.1. Chemicals

Anacardic acid, gallic acid, ABTS (2,2'-azino-bis, 3-ethylbenzothiazoline-6-sulfonic acid) (all of them 99% of purity), and boron trifluoride-methanol (BF₃:MeOH) (~10% or ~1.3 M, for derivatization), and sodium methoxide were purchased from Sigma Aldrich (Saint Louis, MO, USA). Hexane, methanol, acetonitrile, ethanol, and Folin-Ciocalteu reagent were purchased from Merck (Darmstadt, Germany). Sodium carbonate was purchased from PanReac AppliChem (Chicado, USA).

2.2. Solid samples of cashew nut shells

The cashew nut shells were donated by a local farmer from Puerto Carreño, located in Vichada. The samples corresponded to the 2021 harvest, and they were obtained after the remotion of the nut without additional modification or transformation of the shells. Samples were stored at -20 °C to avoid degradation. For their use, the samples were defrosted until reaching room temperature (about 22 °C) and directly placed into the oven. The proximal characterization of samples is summarized in Table 1 in percentage of weight (% wt.).

2.3. Obtention of pyrolytic liquid

The pyrolytic liquid was obtained based on the experimental conditions reported by Javier Ábrego et al. [24]. In this research, the pyrolytic liquid yield was constant (about 60% wt.) at temperatures since 500 °C. Therefore, preliminary experiments of pyrolysis were carried out in the present work that confirmed these results using 550 °C, where the weight of obtained pyrolytic liquid did not change over time, and it was the parameter to establish the conditions of the following experiments.

For that, the CNS samples at room temperature were weighed (accurately 91.63 ± 0.01g of sample per run) and placed inside the reactor. Then, the sample was thermally converted using a tubular oven TF55035A-1 Lindberg-blue M (Thermo Scientific, Waltham, MA, USA) under a nitrogen atmosphere. The tubular oven was connected to a glass condenser with circulating water at 4 °C. The ultra-pure nitrogen flux was 100 mL/min, and the pyrolysis temperature was 550 °C with a heating ramp of 30 °C/min (Fig. 1). The pyrolysis was conducted for 2 h and the experiments were carried out in duplicate.

The yield of pyrolytic products was determined by weighing the liquid and solids obtained after the pyrolysis process and using Eq (1) for calculations.

$$\text{Yield}_{\text{pyrolytic product}} (\% \text{ wt.}) = \frac{m_{\text{product}}}{m_i} * 100\% \quad (1)$$

Table 1
Proximal analysis for raw CNS.

Analysis	Value (% wt.)	Method
Moisture	13.46 ± 0.64	ISO-589-1981
Total solids	86.54 ± 0.64	ISO-589-1981
Volatile solids	85.13 ± 0.68	ISO-5623-1974
Ashes (DB)	1.87 ± 0.13	ISO-1171-1976
Ashes (WB)	1.40 ± 0.08	ISO-1171-1976

DB = Dry Basis, WB= Wet Basis.

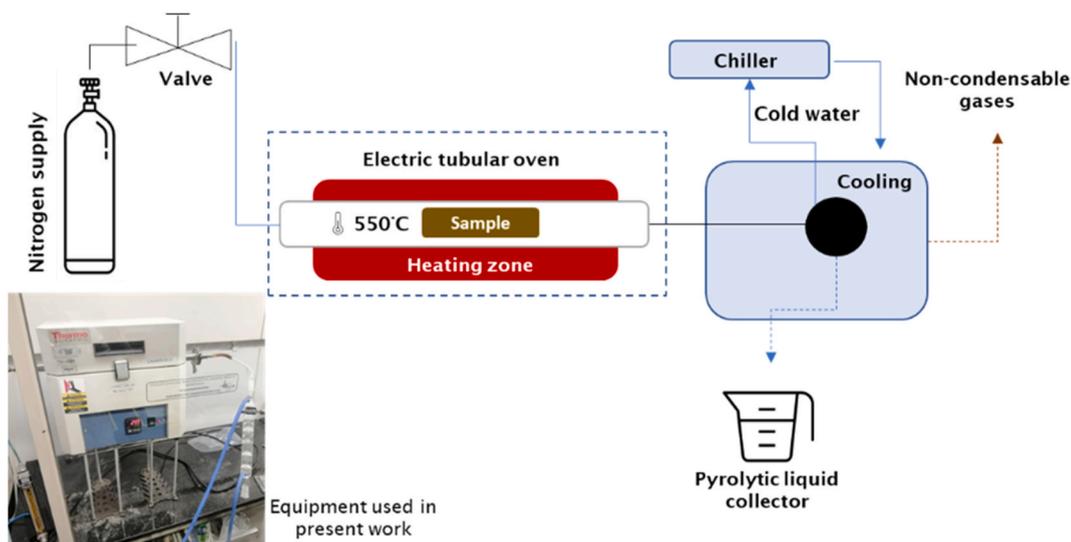


Fig. 1. Scheme for batch pyrolysis system.

Where m_i is the mass of CNS charged to the tubular oven, and m_{product} is the mass in grams of the recovered product after pyrolysis (including moisture). The obtained products and calculated yield of pyrolytic liquid are summarized in Table 2, where the yield of liquid reached 69.15 ± 5.07 % wt., being in the same order as the results reported by Abrego et al. [24] for pyrolysis of cashew nut shells.

The pyrolytic products that were obtained after the experiments are presented in Fig. 2. Regarding the liquid (Fig. 2 a), it had oily consistency, and its color was dark-brown. On the other hand, the obtained char (Fig. 2 b) was consistent in color, which indicated the sample was heated and transformed uniformly. The analysis of obtained biochar was not included in the present work since it was studied for addressing different applications in future work.

2.4. Pyrolytic liquid characterization

2.4.1. Total phenolic content (TPC)

The TPC was measured in the samples following the Folin-Ciocalteu method [26], with minor modifications. Using a micropipette, 250 μL of a diluted sample (1:50) was mixed with 500 μL of Folin reagent in a clean test glass tube. Then, 3750 μL of ultrapure water was added to the mixture, afterwards 750 μL of sodium bicarbonate (20% w/v) was transferred to the tube. The reaction was conducted in darkness for 1 h at room temperature. For determining the concentration of phenolic compounds, the absorbance of reacted samples was measured at 765 nm using the blank solution that used ultrapure water instead sample. The blank was processed at the same time as the samples. The absorbance was related to a concentration of gallic acid, which was used as standard in a calibration curve ranging from 50 to 400 ppm. Therefore, the results were expressed in gallic acid equivalents (GAE). The test was conducted in duplicate.

2.4.2. Long-chain phenols profiling

To determine the content of long-chain phenols the Ultra-High-Performance Liquid Chromatography (UHPLC) technique was conducted, using reported conditions for the identification of anacardic acids by the same technique [27]. The samples of pyrolytic liquid were diluted to a concentration of 1000 ppm and placed into vials. The UHPLC equipment was a Dionex UltiMate 3000, which has a binary pump, autosampler, and temperature-controlling compartment. The separation of long-chain phenols was performed using a Zorbax SB-C18 column (150 mm x 4,6 mm i. d., 3,5 μL particle size) (Agilent Technologies, CA, USA) in gradient flux as follows: i) mixture B 80% to 100% (8 min), ii) mixture B 100% (3 min), iii) B 100% to 80% (1 min), and iv) B 80% (3 min), for a total running

Table 2
Results for the pyrolysis in the present work.

Products	Mass (g)	Calculated yield (% wt.)
Sample	91.63 \pm 0.01	–
Pyrolytic liquid	63.36 \pm 1.28	69.15 \pm 5.07
Bio-char	16.93 \pm 0.69	18.48 \pm 1.12
Non-condensable gases*	4.38 \pm 0.41	4.79 \pm 0.45

*Determined by mass balance.

Values are expressed in means \pm standard deviation (n = 3).

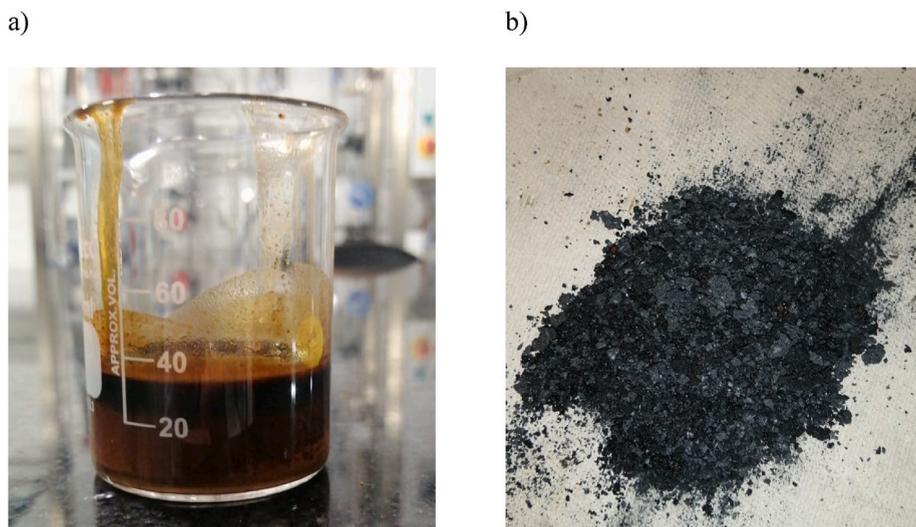


Fig. 2. Pyrolytic products from cashew nut shells, a) sample of pyrolytic liquid, b) sample of biochar.

time of 15 min/sample. Mixture A was formic acid (0.1%, balance ultrapure water), and mixture B was formic acid (0.1%, balance acetonitrile). The column temperature was 30 °C and the injection volume was 5 µL. The UHPLC was coupled with an LCQ Fleet Ion Trap Mass Spectrometer (MS) using an electrospray (ESI) (Thermo Scientific, CA, USA) operated in negative polarity, sheath gas flowrate of 18 (arbitrary units), spray voltage of −3.5 kV, capillary temperature, voltage, and tube lens of 270 °C, −80 V, and −31 V, respectively. The mass spectra were acquired with full ion scanning (m/z 110–800), width 2, and depth 3. Metabolites were analyzed and processed using the Xcalibur 4.3 software to identify the molecular weight of long-chain phenols. The analytes were quantified using diode array detection (DAD) and compared with a calibration curve of C15:0 anacardic acid in a range of 5–500 ppm. The mass correction was done using the relation to the molecular weight of C15:0 anacardic acid (348.58 g/mol) with the identified compound based on the equation of the calibration curve. Results were reported in mg per g of samples, and the samples were analyzed in triplicate with two injections.

2.4.3. Antioxidant activity

The antioxidant activity was measured with the ABTS radical scavenging assay [28]. For that, the ABTS ion dissolved in ultrapure water (7 nM) was oxidized with potassium persulfate (0.45 nM). The mixture was stored in darkness overnight to obtain a dark-blue solution of oxidized ABTS. This solution was diluted in phosphate-buffered saline (PBS pH 7.4) until reaching an absorbance of 0.700 at 734 nm using ultrapure water as blank, then, the prepared solution was the working solution. The antioxidant assay was performed as follows: i) accurately 950 µL of the working solution was transferred to a spectrophotometer cell, and mixed with 250 µL of the diluted sample, ii) the mixture was vortex mixed for 5 s and allowed to react for 5 min in darkness, iii) the absorbance of the mixture was measured at 734 nm with a UV–vis spectrophotometer Genesys TM 10S (Thermo Scientific, CA, USA) using the working solution as a control. The absorbance was used to calculate the antioxidant activity using a calibration curve with Trolox in a range of 25–400 µM, therefore, the results were reported as Trolox Equivalents (TE), which corresponded to mmol Trolox/g of sample. The assay was done in duplicate.

2.4.4. Thermal decomposition

The thermal decomposition of pyrolytic liquid was measured using the thermogravimetric analysis under a nitrogen atmosphere. The test was conducted using a TA Instruments SDT Q600 thermogravimetric analyzer (New Castle, Denver, USA). The temperature ranged from 17 °C to 1000 °C, which was reached with a heating ramp of 20 °C/min. In addition, this test was used for determining the moisture of the sample.

2.4.5. Proximal analysis of the pyrolytic liquid

The chemical composition of pyrolytic liquid was proposed using the proximal analysis using the results obtained in the characterization of all phenolic compounds and fatty acids content. The mass balance was determined in the base of 1 g (1000 mg) and the non-identified fraction was established as others, closing the mass balance. In addition, the results were presented in mass percentages using Eq. (2).

$$\text{Percentage of component}_i (\% \text{ wt.}) = \frac{X_i \text{ mg}}{1000 \text{ mg}} * 100\% \quad (2)$$

Where X_i is the analyzed compound in mg/g concentration. The calculation was performed for each identified compound and the

results were presented in percentages.

2.5. Transesterification of pyrolytic liquid

The transesterification process was performed following the methodology framework described by Cruz-Reina L.J et al. [19] conducted in natural extracts CNSL obtained by SFE with effective results. This methodology for obtaining fatty acids methyl esters (FAMEs) was proposed by Yunyun Zou et al. [29] and applied to produce biodiesel from mixtures of diverse fats [30]. Additionally, the availability of chemicals and the catalyst used with this method were suitable and economical in the framework of the present work. The methodology for the obtention of FAMEs at the microscale using the pyrolytic liquid is detailed as follows.

The transesterification was performed by dissolving the sample at a concentration of 1000 ppm, also methyl nononate was added to the samples as an internal standard (IS) to a final concentration of 300 ppm. The sample (180 μ L) was transferred to an Eppendorf vial, and 100 μ L of sodium methoxide (0.5 N) was added and vortex mixed for 5 s. The mixture was heated (50 $^{\circ}$ C) for 10 min. Thereafter, 120 μ L of BF₃-MeOH (~10%) was added and then heated at 50 $^{\circ}$ C for 16 min. After, 200 μ L of water and 200 μ L of hexane were added and vortex mixed for 30. Then, the mixture was separated by centrifugation (10500 rpm, 5 min). The organic layer (hexane) was retrieved and transferred to amber vials with inserts and analyzed. The detailed method for the identification and characterization of fatty acids is presented in the following subsection.

2.6. Semi-quantitative fatty acid methyl esters identification by GC-MS

The analysis of fatty acids was performed using the Gas-Chromatography (GC) technique coupled with mass spectrometry (MS) following a reported method with minor modifications [19]. The GC-MS system consisted of Agilent 6890 equipment coupled with Agilent 5973 MS with an electron ionization (EI) source. The sample separation was achieved using a Phenomenex Zebron ZB-FAME column (30 m \times 250 μ m \times 0.25 μ m) using a flow rate of He at 12 mL/min as the carrier. The equipment was operated at an injection volume of 1 μ L (split mode) with a 10:1 ratio, 11.9 mL/min split-flow rate, and injector temperature of 250 $^{\circ}$ C. The temperature ramp in the GC was: i) 60 $^{\circ}$ C (3 min), ii) ramp of 10 $^{\circ}$ C until achieved 190 $^{\circ}$ C (2 min), and iii) ramp of 20 $^{\circ}$ C/min to achieve 260 $^{\circ}$ C (2 min). The mass detection was performed with the MS equipment operated in full-scan acquisition mode (m/z scan range 40–400 Da, 5 spectra/s). The temperatures for the transfer line, ion source, and quadrupole were set as 230 $^{\circ}$ C, 230 $^{\circ}$ C, and 150 $^{\circ}$ C, respectively. The mass fragmentation of compounds was analyzed with the NIST library of mass spectral data. To confirm the presence of identified FAMEs, the samples were compared with a standard mix of FAME Supelco 37 Component (Sigma Aldrich, MO, USA) consisting of FAMEs from C4 to C22. Samples were run in duplicate. Fig. 3 shows a chromatogram obtained with the described method.

2.6.1. Calculation of FAMEs production yield

The biodiesel yield of the transesterified pyrolytic liquid was calculated using Eq (3), based on the mass of the pyrolytic liquid that was initially used for the reaction.

$$\text{Yield}_{\text{biodiesel}} (\%) = \frac{\sum_{i=1}^n \text{mass of identified FAME (mg)}_i}{\text{mass of transesterified pyrolytic liquid (mg)}} \times 100\% \quad (3)$$

Where i refers to each identified FAME, and it is related to the total mass of the initial pyrolytic liquid sample. The units of mass were milligrams but can be changed depending on the scale of the process.

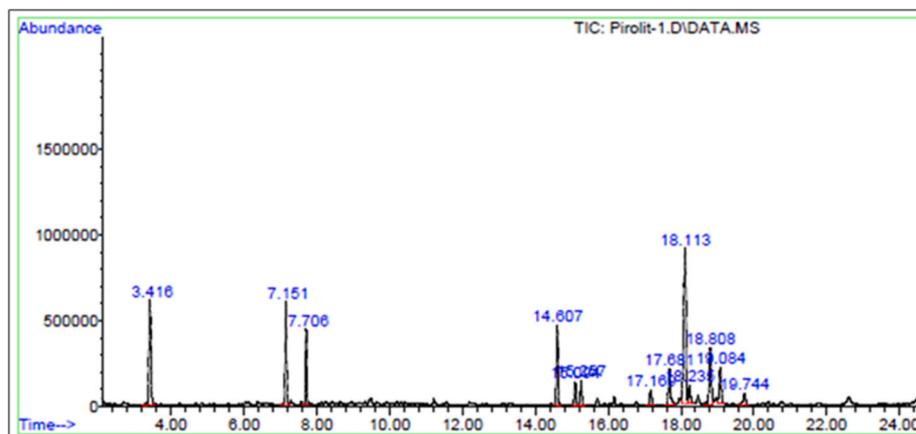


Fig. 3. Chromatogram obtained with transesterified samples (including the internal standard, peak 1).

2.6.2. Fatty acid content analysis

The fatty acid content of the pyrolytic liquid was related to the identified FAMES. The fatty acid without the methyl ester fragment was established as the probable compound in the pyrolytic liquid. The concentration of each fatty acid was estimated using the area of the chromatogram corrected with the internal standard. For the proximal analysis of pyrolytic liquid, the oily fraction was included using Eq (2), which was described in previous sub-sections.

2.7. Data treatment

Data obtained in the experiments were processed in Excel 2021 (Microsoft, Washington, USA), and calculations of media and standard deviation were performed.

3. Results and discussion

3.1. Pyrolytic liquid characterization

The TPC in pyrolytic liquid was 3.89 ± 0.37 mg/g. This result is near the range of phenolic compounds reported by Michael Melzer et al. [31], who determined the concentration of phenolic compounds in cashew nut shells. Results are in the range of 4.5 mg/g to 7.3 mg/g. These phenolic compounds can be phenol, phenol with methylations, and 4-dimethyl phenol, among others. Low-medium temperature extractions for obtaining natural CNSL showed values of TPC in the extracts ranging from 40.1 to 134.6 mg/mL [19]. Therefore, the temperature of pyrolysis promoted the degradation of these phenolic compounds reducing their concentration in the samples.

The results of long-chain phenols profiling in pyrolytic liquid are summarized in Table 3. These phenolic compounds have the particularity to be attached to an alkyl chain (known as long-chain phenols) with the random occurrence of one or more unsaturations. The main phenolic compound in the presence was the C15:4 cardanol, which was identified with a molecular mass of 312 g/mol through MS. Long-chain phenols are more resistant to temperature than other phenolics due to their thermal conversion at temperatures above 250 °C [20]. The decarboxylation of anacardic acids to cardanol explain the high presence of this compound in the pyrolytic liquid; therefore, this effect was also observed in pyrolytic liquid by Rajesh N. Patel et al. [32], who processed the CNSs at 500 °C. The second most abundant long-chain phenol in the liquid was the C15:3 anacardic acid followed by C15:1 anacardic acid and C15:2 anacardic acid, with a concentration of 40.1, 32.2, and 20.1 mg/g, respectively. This last suggests that the natural occurrence of unsaturated long-chain phenols is dominant in the analyzed samples. Contrarily, the saturated C15:0 anacardic acid was 4.9 mg/g, the lowest value among the identified long-chain phenols.

The identification of long-chain phenols by LC-MS prevents the interconversion between anacardic acid to cardanol, due to the heating (>200 °C) in the injection ports of the GC-MS, which has been used for the characterization of natural CNSL and pyrolytic liquids. Consequently, the results obtained in the present work can be considered reliable to describe the composition of these compounds in the analyzed samples.

Anacardic acids have been identified in natural CNSL using mass spectrometry. The occurrence of unsaturated anacardic acids reported by Petr Česla [36] was comparable to the profile observed in pyrolytic liquid. Similarly, CNSL extracted with hexane at room temperature showed a high relative occurrence of C15:3 and C15:2 anacardic acids with yields of 28% and 17.77%, respectively [37]. The isolation of long-chain phenols in heated CNSL revealed that the C15:3 anacardic acid is the predominant compound with a concentration of 153.50 mg/g followed by C15:2 anacardic acid (107.96 mg/g) in the fractions obtained by M.T.S. Trevisan et al. [33]. In addition, cardanols were observed in a total concentration of 218.29 mg/g, which can be related to the heating process performed on CNSL, also to yields obtained in each isolated fraction.

Compared with the results obtained in the present work, the total content of long-chain phenolics in the pyrolytic liquid was 179.2 mg/g of sample, which was lower than other reported results. Conversely, the variety of results in the literature can be attributed to the quantification methods employed for the characterization of the substances. The main advantage of the methodology used in the present work is the one-step quantitative characterization of samples by UHPLC-DAD-MS using a standard of anacardic acid. Then,

Table 3
Long-chain phenols profiling in pyrolytic liquid.

Peak No.	Ret. time (min)	[M – H] ⁻ (m/z)	MS ² and MS ³ product ions (-) (m/z)	Identification*	Concentration (mg/g) ^a
1	0.94	311.2	MS ² : 169, 125, 149.	C15:4 cardanol	82.1 ± 5.5
2	2.75	341.3	MS ² : 297, 281, 106. MS ³ [297]: 281, 203, 119, 107, 106.	C15:3 anacardic acid	40.1 ± 4.3
3	3.43	343.2	MS ² : 299, 297. MS ³ [299]: 203, 119, 107, 106.	C15:2 anacardic acid	20.1 ± 1.4
4	4.33	345.2	MS ² : 301. MS ³ [301]: 203, 119, 107, 106.	C 15:1 anacardic acid	32.2 ± 3.6
5	5.73	347.2	MS ² : 303. MS ³ [303] 189, 173, 107, 106.	C 15:0 anacardic acid ²	4.7 ± 0.3

Values are expressed in means ± standard deviation (n = 3). Identified compounds were supported with the following references: [18,33–35].

^a Expressed as mg per g of pyrolytic liquid.

with the quantitative characterization a proximate analysis that describes the chemical composition of a substance can be proposed.

The antioxidant activity measured in the pyrolytic liquid was 0.714 ± 0.030 TE/g. The antioxidant activity is related to the presence of antioxidants in the sample, mainly phenolic compounds. The antioxidant activity of phenolic compounds in edible oils has been studied, being the lipophilic antioxidant capacity the interesting effect related to these substances that prevent the rancidity of fats [38]. In addition, it is known that unsaturated long-chain phenols are related to strong antioxidant effects [33], which is an interesting attribute of natural CNSL used in the stabilization of oils [39]. Antioxidant activities of natural CNSL extracts obtained with SFE, Soxhlet, and subcritical water extractions raised values in the magnitude from 59 to 2500 TE/mL of the sample [19], which are significant higher than observed in pyrolytic liquid. The antioxidant effect can be increased due to the synergy of phenolic compounds with sugars, organic acids, and fatty acids, which were identified in the natural CNSL extracts. Nonetheless, in the case of pyrolytic liquid, the thermal modification or degradation of phenolic compounds among others can explain the observed low antioxidant activity. Finally, it has been reported that derivatives of phenolic compounds such as alkylphenols phthalates chlorobenzenes are used for the coloration of textiles [40], which can be an application of phenolic compounds observed in pyrolytic liquid for the industry of pigments.

3.2. Thermal decomposition of pyrolytic liquid

The thermal decomposition behavior of pyrolytic liquid is presented in Fig. 4. The first weight loss is attributed to water evaporation and corresponded to about 4–5%. The second weight loss (up to 20%) that was observed in a range of 120–240 °C can be attributed to the decarboxylation reaction of anacardic acid to cardanol, where carbon dioxide is released. The production of a cardanol-rich liquid is conducted at this temperature using natural CNSL through thermal decarboxylation, which is the main process for obtaining the cardanol that is used in the synthesis of polymers [41], and biodiesel additive [17].

Following, the main sample degradation step occurred at around 300 °C, which can be attributed to the evaporation and decomposition of long-chain fatty acids [42]. The last weight loss was observed near 430 °C. Residual cardanol and other alkylphenols can be degraded at this temperature [43], which could explain the mass loss observed in the TG analysis. The obtained DTG curve is in concordance with the decomposition steps, and it was evident three main degradation peaks of the sample.

3.3. Obtention of FAMES from pyrolytic liquid

The results of FAMES profiling by GC-MS in the organic layer after transesterification of pyrolytic liquid are summarized in Table 4. The representative FAMES observed in the biodiesel fraction were the methyl *trans*-8-decanoate (20.9 % wt.), followed by methyl palmitate (14 % wt.) whereas the methyl octadeca-9,12-dienoate and methyl hexanoate were identified with concentrations of 11.7 % wt. and 11.4 % wt., respectively. Moreover, methyl oleate and methyl (*Z*)-pentadec-8-enoate were found in a smaller proportion among the others. Interestingly, methyl hexanoate is the shortest fatty acid identified in the samples with the C6 chain, which can be obtained from hexane.

The high presence of FAMES can be related to the oily nature of the CNSL; nevertheless, it has been suggested that the CNSL is

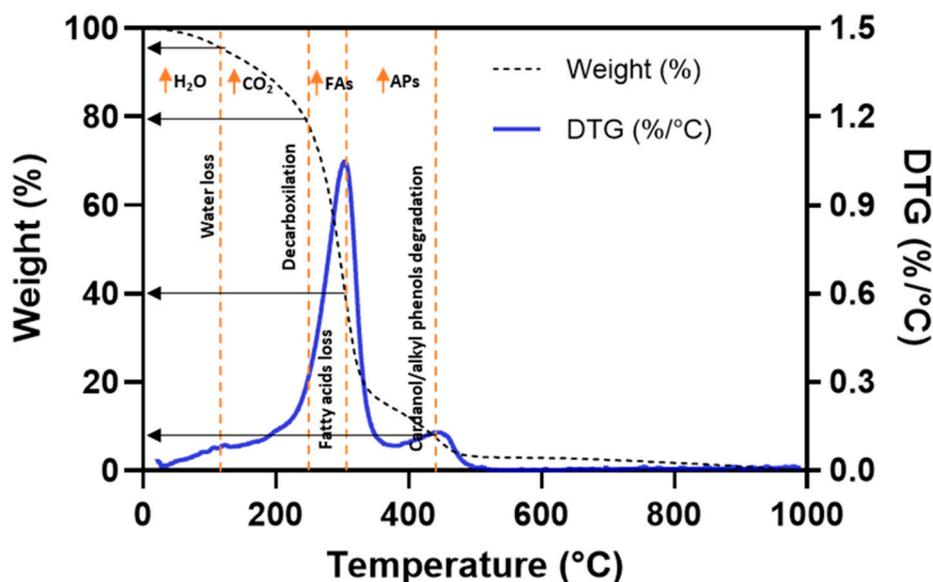


Fig. 4. Thermal analysis of pyrolytic liquid, TG curve (discontinuous black line), and DTG (continuous blue line). FAs=Fatty acids, APs = Alkylphenols (Long-chain phenols). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 4
Fatty acid methyl esters (FAMES) recovered in the organic layer.

Peak No.	Ret. time (min)	Name- (Methyl ester)	Common name	Fatty acid methyl ester formula	Match factor	Main fragments (<i>m/z</i>)	Molecular mass (g/mol)	Concentration ^b (% wt.)	Biodiesel yield _{FAME} ^c (%)
1	3.416	Hexanoic acid ^a	Methyl hexanoate	C ₇ H ₁₄ O ₂	90	74, 43	130.1	11.4 ± 0.7	12.9 ± 0.7
2	14.609	Hexadecanoic acid ^a	Methyl palmitate	C ₁₇ H ₃₄ O ₂	98	74, 87	270.4	14.3 ± 1.0	16.8 ± 1.0
3	15.095	9-Hexadecenoic acid ^a	Methyl (Z)-pentadec-8-enoate	C ₁₆ H ₃₀ O ₂	99	55, 69, 41	254.4	1.9 ± 0.1	2.0 ± 0.1
4	18.111	9-Octadecenoic acid ^a	Methyl oleate	C ₁₉ H ₃₆ O	99	55, 69, 41	296.4	8.7 ± 0.6	9.5 ± 0.6
5	18.234	8-Octadecenoic acid	Methyl <i>trans</i> -8-octadecanoate	C ₁₉ H ₃₆ O ₂	99	55, 69, 41	296.5	20.9 ± 1.1	26.5 ± 1.1
6	19.083	9,12-Octadecadienoic acid (Z,Z) ^a	Methyl octadeca-9,12-dienoate	C ₁₉ H ₃₄ O ₂	99	67, 81, 55	294.5	11.7 ± 12.3	13.3 ± 1.2

Values are expressed in means ± standard deviation (n = 3). Identified compounds were supported with the following references [19,30].

^a Identified with commercial standard mix FAME co-injection.

^b Reported as the concentration of FAMES in the organic layer.

^c Biodiesel yield was calculated with the mass of transesterified pyrolytic liquid.

mostly rich in long-chain phenols [44], but the results obtained in the present work suggest that high amounts of fatty acids can be easily obtained from CNSs through thermochemical conversion.

The natural CNSL extracted by supercritical carbon dioxide (CO₂) exhibited eleven fatty acids [45], where the four of which are related to the FAMES obtained in the present work as follows: hexanoic acid, methyl oleate, 9-octadecenoic acid, and methyl octadeca-9,12-dienoate. Although the thermochemical transformation of CNSL may promote the degradation of some fatty acids the similitude with natural CNSL was apparent. Comparing the results with the fatty acid composition of biodiesel from vegetable oils, the occurrence of fatty acids C16:0, C16:1, C18:1, and C18:2 was found similar to biodiesels obtained from soybean, palm, and rapeseed [46].

The total conversion yield of the FAMES after transesterification was 81%, indicating the high availability of fatty acids for the reaction in the pyrolytic liquid. Other substances such as phenolic compounds seemed not to interfere with the reaction of transesterification. This last presents an interesting finding that suggests that CNSL is mainly composed of fatty acids and the synergistic effect between the long-chain phenols and the stability of oils. This effect has been described in studies regarding the effect of

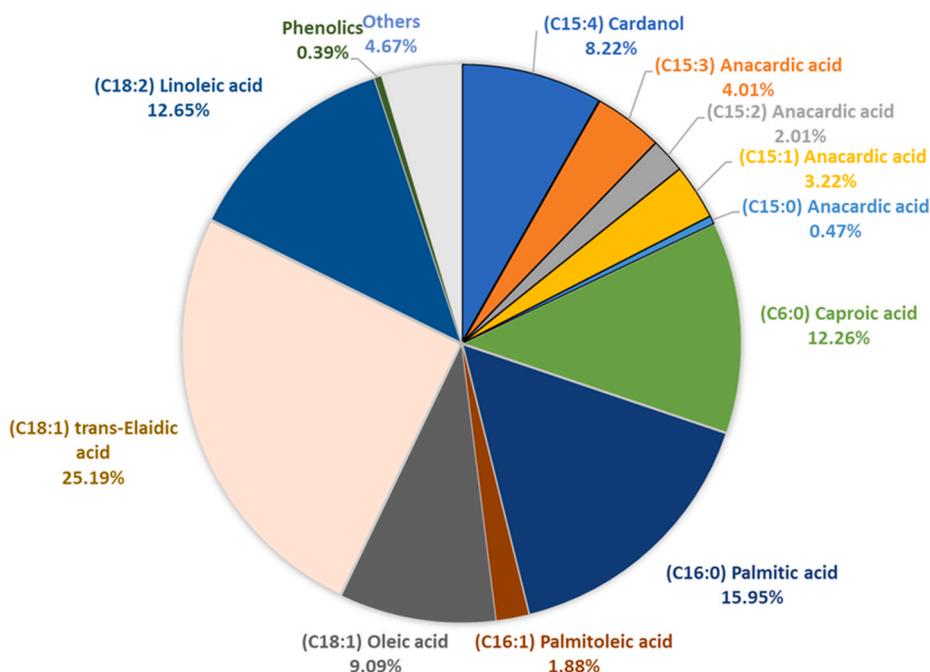


Fig. 5. Identified compounds (% wt.) of pyrolytic liquid obtained from cashew nut shells (estimated composition based on proximal analysis).

antioxidants in fatty acid mixtures [20,47].

The total fraction of FAMES recovered in the organic layer was 68.9 % wt., and the balance was expected to be hexane since glycerin is poorly soluble in this solvent. Then, the FAMES could be easily recovered in higher-scale transesterifications processes to obtain the biodiesel by the separation of the solvent; though, the scale-up of the process, and the optimization of transesterification variables concerning temperature, catalyst type/amount, and methanol ratio, among others, must be addressed in future work.

Finally, the pyrolytic liquid obtained from cashew nut shells under the conditions used in this work is a suitable feedstock for the obtention of FAMES from the perspective of biofuel production. Nevertheless, more studies about the physical properties of obtained biodiesel present an open investigation field. Since the CNS is a non-edible agricultural residue, the production of second-generation fuels can increase the circularity of these complex and toxic residues avoiding competition with edible feedstocks.

3.4. Perspectives and future work

The chemical characterization of the pyrolytic liquid analyzed in this work can explain the composition of the pyrolytic liquid before transesterification. Fig. 5 presents the diagram that schematizes the chemical composition of the pyrolytic liquid based on the proximal analysis. The long-chain phenols fraction corresponded to 17.9% of the total composition. Moreover, the representative fraction was the fatty acids, which reached 77% of the total composition which can be related to their efficient conversion to FAMES, described in the previous section.

Similarly, the profile of pyrolytic liquid fatty acids resembles that reported for Thailand cashew nuts (kernel) reported by Jitkunya Yuenyong et al. [48], where higher amounts of palmitic acid, palmitoleic acid, linoleic acid, and linolenic acid were detected. Nevertheless, the proportion and occurrence of these fatty acids can vary due to the differences between the vegetable tissues of cashew nuts and cashew nut shells. The 4.67% of the balance is related to moisture, which can be associated with the water loss observed in the TG analysis. Then, the proximal analysis conducted in this study explained the complete chemical composition of the pyrolytic liquid, being the first report regarding the rigorous characterization of liquid obtained by pyrolysis of CNSs.

Vegetable oils are important feedstocks for biodiesel production, being cheap and available biomass with renewable origin. The transesterification of vegetable oils is a common technique for the obtention of biodiesel and various conditions and types of catalysts have been used and reported in the literature (Table 5). The main challenge in the transesterification process of CNSL is the presence of higher amounts of phenolic compounds compared to other oils; however, sodium methoxide was observed to be effective for the transesterification of CNSL, the conditions used in the present work required a short reaction time and lower temperature at the scale it was performed. The use of an internal standard in the analysis of FAMES provided a semiquantitative analysis of these compounds, effective for the chemical analysis of the samples. This work can be considered the first approach for the direct conversion to biodiesel from a pyrolytic liquid obtained from CNSs. The fatty acid content of the CNS becomes this biomass into an interesting and renewable source of second-generation fuels.

Nevertheless, it is important to mention that transesterification conditions of pyrolytic liquid were based on reports for the fatty acid derivatization specifically for CNSL since this liquid has a complex chemical composition. The high relation of methanol to the oil used in the present work can be inconvenient in terms of cost efficiency and methanol requirement. Therefore, it is convenient to address studies to evaluate parameters such as the type of catalysts, the relation of methanol to oil, temperature, and process scale-up, which is an open field of investigation for pyrolytic liquids obtained from CNSs.

The pyrolytic liquid is also an alternative source of phenolic compounds that can be used in diverse applications in the materials field similar to the technical CNSL [41]. Also, blends of diesel that include biodiesel obtained from CNS pyrolytic liquid should be studied. This work provides a guide for the thermal transformation and characterization of complex oily vegetable biomass obtained from non-edible agricultural residues such as CNS. The CNSL is a renewable feedstock for the obtention of biofuel due to its high content of fatty acids; nevertheless, more investigation is needed to scale up the process and the optimization of transesterification reaction for its obtention.

In future work, it is suggested to develop the concept of biorefinery for the management of cashew residues for the obtention of a wide range of valuable substances and products. The implementation of a circular economy productive model is necessary to reduce residue generation and promote natural resource conservation. In addition, the development of new business models based on the circularity of residues presents economic opportunities and social benefits to the society around agribusiness. In this sense, according to J.F. Velasco-Muñoz et al. [55], it is needed that the life cycle of agricultural residues is extended to ensure its circularity in the economy seeking the goals of decarbonization of the economy and environmental sustainability.

4. Conclusions

In conclusion, this study provides valuable insight into the energetic valorization of CNS through thermal conversion and following transesterification for the obtention of biodiesel. Through advanced analytical techniques used in the methodological framework, it was possible to describe quantitatively the chemical composition of the pyrolytic liquid and the biodiesel, being fatty acids and long-chain phenols the representative fractions with concentrations of 77% wt. and 17% wt., respectively. The common fatty acids such as palmitic acid, oleic acid, and linoleic acid were identified in the pyrolytic liquid amounting to 37.69 % wt., which proved the oily nature of CNSL. These results contribute to understanding the composition and valorization perspectives of hard management cashew residues through the thermal transformation of this biomass.

The importance of increasing circularity of cashew agricultural residues has important perspectives for the energetic security of agricultural regions in developing countries. The obtention of biofuels from non-edible cashew agricultural residues demonstrate the

Table 5
Reported data about transesterification of vegetable oils.

Oil source	Catalyst	Conditions	Relevant results	Yield (%)	Ref.
<i>Ricinus communis</i> seed oil	1-(2,3-dihydroxy)-propyl-3-methylimidazolium hydroxide	10.51:1 M of methanol to oil ratio, 57.87 °C for 61.01 min.	Optimized conditions 6.26% w/w of catalyst	97.83	[49]
Linseed/marula bi-oil	Bio-composite	15:1 methanol to oil ratio, 65 °C, 60 min	Optimized conditions 3.6% of catalyst	95.03	[50]
Pithecellobium dulce seed oil	NaOH	6:1 methanol to oil ratio, 3 h	Optimized conditions 0.5% of catalyst	96.6	[51]
<i>Citrus maxima</i> seeds	Sodium methoxide	6:1 methanol to oil ratio, 70 °C, 120 min	Optimized conditions 1.25% w/w of catalyst	93.61	[52]
<i>Reutealis trisperma</i> oil	NaOH	12:1 methanol to oil ratio, 60 °C, 60 min	Optimized conditions 5% of catalyst	97.95	[53]
Palm oil	NaOH	9:1 methanol to oil ratio, 65 °C, 45 min	Optimized conditions 0.75% of catalyst	92.05	[54]
Pyrolytic liquid from CNSs	BF ₃ :MeONa (10%)	21:1 methanol to oil ratio, 50 °C, 26 min	Included internal standard	81	Present study

potential for strengthening the production chain of cashew, reducing its environmental impacts. Nonetheless, the present study is limited to the micro-scale of transesterification and the use of one catalyst. Therefore, future research should focus on the optimization of transesterification reactions for biodiesel production at a pilot scale for the valorization of large amounts of CNSs.

The findings of this study have important implications for the use of non-traditional oily feedstocks of renewable origin for the obtention of biofuels. This research sets the stage for future studies in the chemical characterization of vegetable materials and energetic solutions for further exploration and innovation in the field of chemical engineering.

Declarations

Author contributions

Luis J. Cruz Reina: conceived and designed the experiments; performed the experiments; analyzed and interpreted the data; contributed reagents, materials, analysis tools or data; wrote the paper; Sebastián Flórez: conceived and designed the experiments; performed the experiments; analyzed and interpreted the data; Gerson-Dirceu López: analysis tools or data; Israel Herrera-Orozco: analyzed and interpreted the data; materials, analysis tools or data; Chiara Carazzone: conceived and designed the experiments; analyzed and interpreted the data; contributed reagents, materials, analysis tools or data; Rocío Sierra: conceived and designed the experiments; analyzed and interpreted the data; contributed reagents, materials, analysis tools or data.

Funding statement

Part of this research was financed by the Ministry of Science, Technology, and Innovation of Colombia (MinCiencias) and Vichada Local Government through the Bicentennial Doctoral Excellence Scholarship Program. Additionally, University of Los Andes, Colombia, financed the publication of this article through the internal funding “*Publica tus conocimientos 2023*”.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Rocío Sierra reports financial support was provided by University of the Andes. Luis Jorge Cruz Reina reports financial support was provided by Colombia Ministry of Science Technology and Innovation. Part of this research was financed by the Ministry of Science, Technology, and Innovation of Colombia (MinCiencias) and Vichada Local Government through the Bicentennial Doctoral Excellence Scholarship Program. Additionally, University of Los Andes, Colombia, financed the publication of this article through the internal fund “*Publica tus conocimientos 2023*”

Acknowledgments

Our sincerely acknowledgments to Laura Ibarra for supporting the operation of the equipment for the FAMES analysis conducted in Department of Chemistry of University of los Andes. Also, our acknowledgments to Santiago Correa for his assistance for the FAMES analysis.

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