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Chemical and physical analysis of the liquid fractions from soursop seed cake obtained using slow pyrolysis conditions

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A R T I C L E   I N F O

A B S T R A C T

This study analyzed the fractions obtained by applying slow pyrolysis to soursop (*Annona Muricata* L.) seed cake. The temperature employed was 400 °C because of the interest in the four products obtained at this temperature. The bio-oil, biochar, gas and aqueous fraction were obtained with yields 18.6%, 32.2%, 17.7% and 31.5% (w/w), respectively. The oil and aqueous fraction were analyzed by GCMS and showed a composition of phenol derivatives, furan, some acids and esters as main components and in the case of the oil, also hydrocarbons were observed. The profile of the fragments observed in the mass spectra of the compounds obtained in CGMS analysis were compared with the initial composition of biomass, lignin, cellulose, hemicellulose and extractives (fatty acids and proteins). The oil was further evaluated by FTIR, ^{1}H NMR, elemental analysis (C H N) and density, viscosity, moisture, acid content, calorific value, ash content and flash point. The oil showed to be a good fuel for industrial burners and when blended with ethanol this quality increase.

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1. Introduction

Agroindustry around the world generates a large amount waste material. However, this biomass has many potential applications, such as power generation, animal feed, erosion control, fertilizer and medicine [1]. Global production of fruit is estimated to be about 800 million metric tons per year. Brazil is in third place, after China and India. Very favorable growing conditions allow the country to produce a wide range of fruits throughout the year [2], the leading ones being orange, banana, pineapple, coconut and papaya.

Production of soursop or graviola, the fruit of the *Annona Muricata* L. tree (family Annonaceae), has been increasing in recent years. For example, in the state of Bahia, its production quadrupled in less than 10 years, going from 5.0 thousand tons to 20 thousand tons [3]. Native to tropical regions of Central and South America [4,5], it is currently now well distributed across the equatorial belt of the planet, with high economic importance in countries such as Venezuela, Puerto Rico, Mexico, Jamaica, Cuba, Spain, India, Suriname, Brazil, Senegal and others [5–7].

Soursop is an ovoid or heart-shaped fruit with dark green color, containing a creamy white edible pulp and black seeds. Due to its pleasant taste and smell, the pulp is consumed fresh and more so (due to perishability) in form of juice, candy and ice cream, among others [3,8]. Besides food use, studies show potential insecticidal activity of extracts of seeds [10]. Additionally, plant parts such as leaves and stems are used in folk medicine for the treatment of diseases such as hypertension and cancer, so studies have been performed to elucidate its medical potential [4]. These characteristics explain the growing interest in this plant.

Seeds left over from the commercial processing of soursop pulp, representing 5% by fruit mass, are usually discarded because they contain toxic substances, and therefore cannot be used as animal feed or sources of edible vegetable oil [9]. The analysis of their proximate composition showed on average (by mass), 20.5–40% oil (lipids), 8.5% protein, 34.1% total carbohydrates and 5.2% crude fiber, besides important minerals such as potassium, calcium, phosphorus, sodium and magnesium [11–13]. The high percentage of oil makes these seeds potentially attractive for producing chemical compounds. The oil consists of oleic acid (40.94%), linoleic acid (33.02%), palmitic acid (18.98%), stearic acid (5.28%) and palmitoleic acid (1.76%), with variations in content of fatty acids depending on the origin of the plant. In particular, the oil obtained from the seeds can be used as raw material for biodiesel production and the cake remaining after oil extraction can be subjected to pyrolysis to obtain new products.
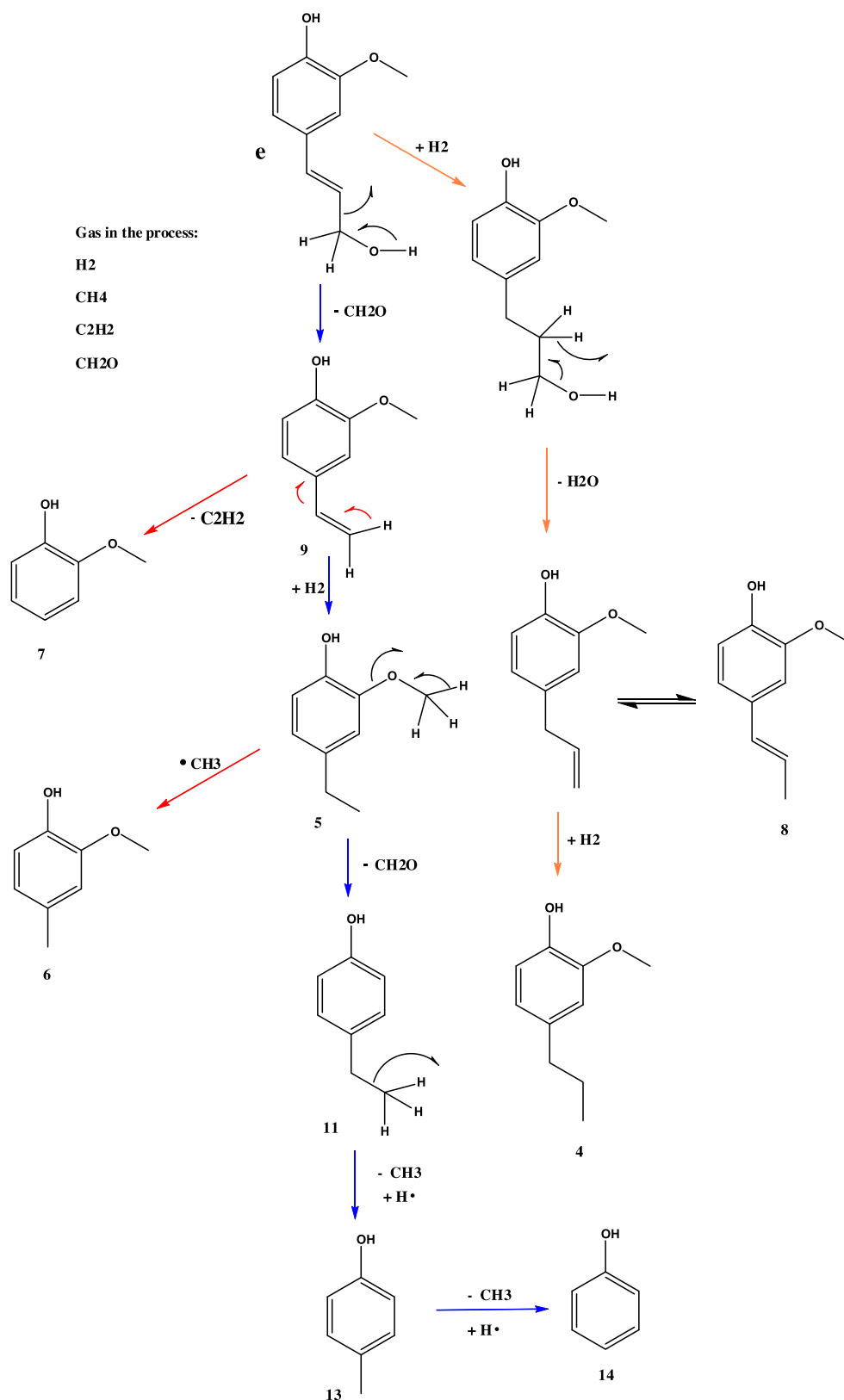
Scheme 1. Mechanisms of the decomposition of coniferyl alcohol in pyrolysis.

The need for alternative and renewable energy sources has led to the development of technologies able to convert this biomass into products of industrial and ecological importance. Among these techniques is pyrolysis, involving the thermochemical conversion of biomass at temperatures ranging from 300 to 900 °C in an inert atmosphere. The process generates three products: solid, liquid and gas [14].

The solid product obtained in the process, known as biochar, can be used directly in a variety of applications or as solid fuel. Its use in
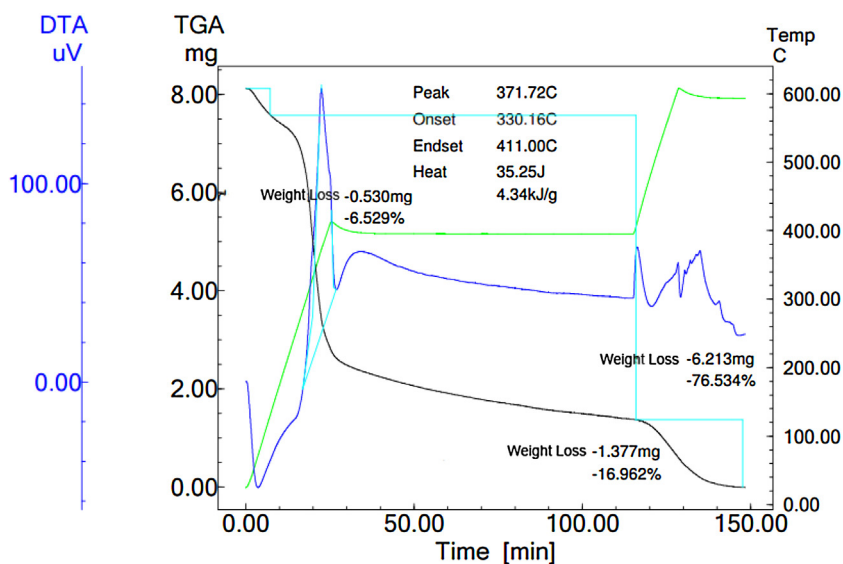
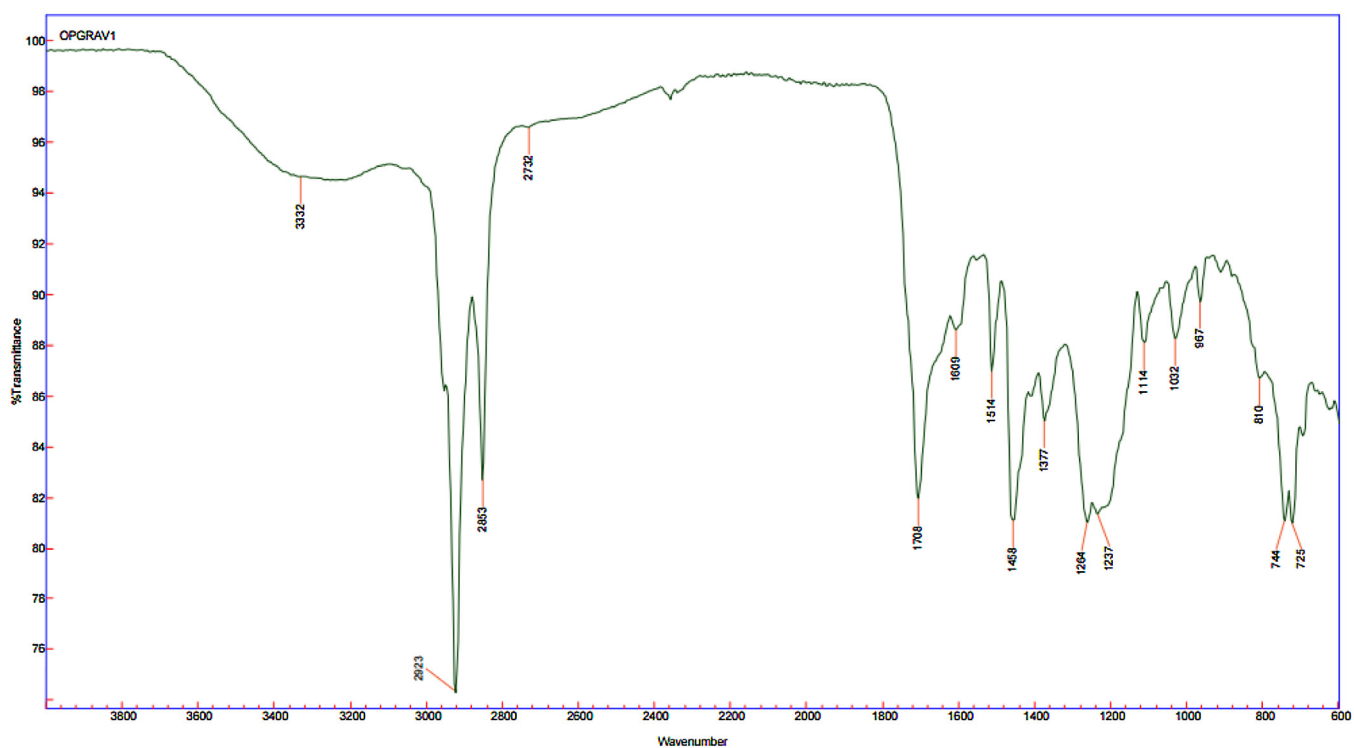Fig. 1. Thermogravimetric analysis of the soursop seed cake.

Fig. 2. Infrared spectrum of the oil from pyrolysis soursop seed cake.

soil reduces emissions of greenhouse gases and can help mitigate climate change problems [15–18].

The gaseous fraction is composed of CO, CO_2, H_2, CH_4, N_2 and other volatile compounds [1,19]. It can be used in internal combustion engines and industrial combustion processes [19]. The gas can also generate energy to power biomass pyrolysis plants, reducing processing costs [20].

The liquid product obtained from pyrolysis is the aim of this work. This is a fraction rich in organic compounds (bio-oil), which can be emulsified with the aqueous fraction or separated from it. Bio-oil has direct application as fuel in furnaces and boilers or it can be added to oil in refineries. However, the high water content and corrosive organic substances make its use as fuel quite limited. Nevertheless, its very complex composition makes it an important source of substances that can be used in fine chemicals, besides biofertilizers and other agro-industrial applications. Some substances identified in bio-oil are acids, alcohols, aldehydes, ketones, esters and phenols [14,19–23].

In recent decades, the use of pyrolysis has increased as a technological option in the exploitation of agroindustrial waste and byproducts, such as sugarcane filter mud [18], raspberry seed cake [24], castor seed cake [25], *Eucalyptus* crop residues, castor meal, coconut pericarp, sugarcane bagasse, and water hyacinth [26] and grugru palm seed residues [27].

Figueiredo et al. applied slow pyrolysis to castor seeds. The bio-oil obtained in the process was successfully mixed in differ-
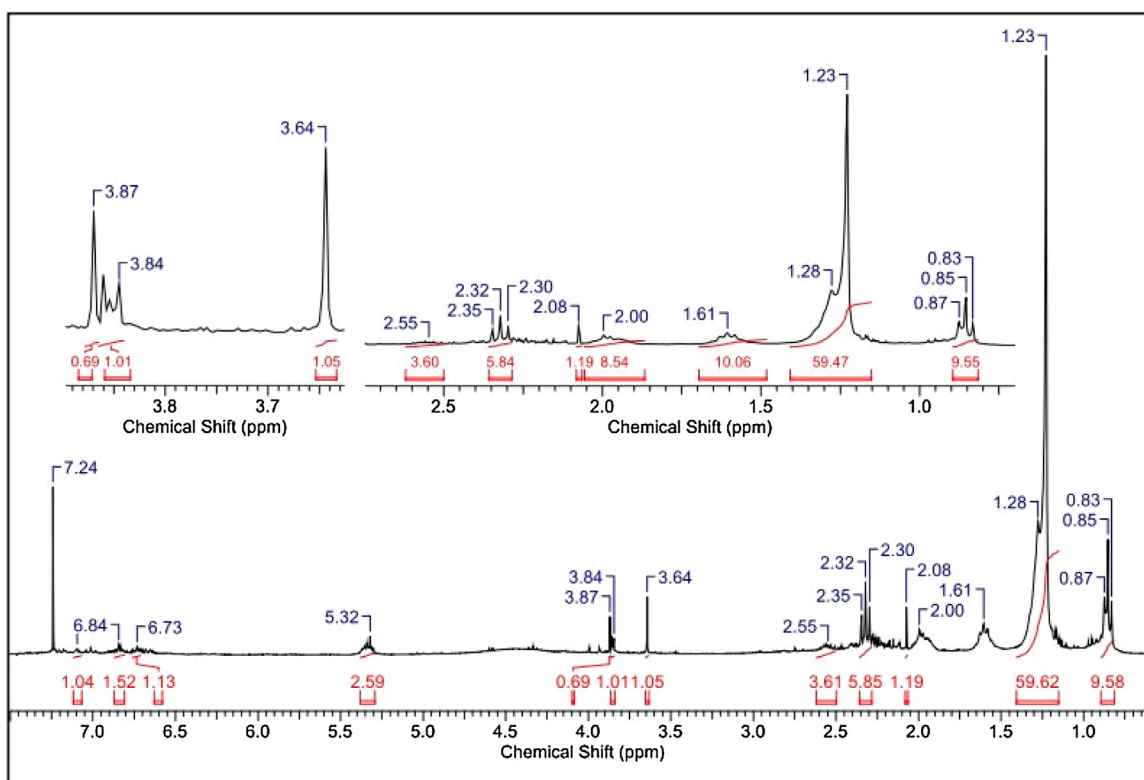
Fig. 3. ^{1}H NMR spectrum of the pyrolysis oil.

ent proportions with petroleum diesel [28]. Romeiro et al. applied slow pyrolysis to soluble coffee ground samples and found that the process can be a good alternative for the disposal of this waste since the bio-oil obtained showed calorific value higher than 34.3 MJ/kg and low water content, enabling its use as an alternative fuel [29].

The objective of the study presented in this paper was to determine the yields and the properties of the products obtained from slow pyrolysis, at fixed temperature (400 °C), of the residue generated after the extraction process of oil from pressing the soursop seeds, known as soursop seed cake.

2. Materials and methods

2.1. The sample

Soursop seed cake was obtained from the company "Extrair Óleos Naturais", Rio de Janeiro, Brazil. It is a solid waste from the extraction of oil from pressing the seeds. Prior to the pyrolysis process, the soursop seed cake was previously dried in an oven at 105 °C until reaching constant weight.

2.2. The slow pyrolysis process

The slow pyrolysis was carried out at 400 °C in a batch reactor consisting of a Heraeus R/O 100 oven, a temperature controller, operating timer, a fixed bed of Pyrex glass with dimensions of 10 mm × 1.40 cm, a liquid collection system consisting of a condenser, dropping funnel (500 mL) and gas washer bottle. The cake seed sample (500 g) was packed in the center of a cylindrical glass tube, which was then introduced into the reactor and coupled to the condensation system. Nitrogen gas was continuously injected into the system for 10 min before the heating process and continued until the end of the process. The initial temperature was 25 °C, heating 15 °C/min, during 25 min, until 400 °C, followed by isotherm of 90 min. After passage of the processing vapors through the con-

densation system, the liquid fractions were separated by density difference in a separating funnel. The biochar was retained inside the reactor and recovered after cooling. The non-condensable gas went through a gas scrubber system and was bubbled in water [28]. The experiment was repeated five times and the average yield was calculated.

2.3. Characterization of soursop seed cake and the liquid fraction obtained from pyrolysis

2.3.1. Proximate and ultimate analysis

The moisture content of the seed cake was calculated from the difference between the initial mass before heating and the final mass after heating in an electric oven at 105 °C to constant weight, according to the American Society for Testing and Materials (ASTM) method ASTM D1762–84 [30].

The bio-oil moisture content was determined by volumetric titration using the Karl Fischer method (ASTM D4928–11) [31], employing a Metrohm 836 Titrando potentiometric titrator.

The ash content and volatile content matter was determined in triplicate in a muffle furnace, according to ASTM D1762-84 [30].

The fixed carbon was determined as described in ASTM D3172-13 [32].

The elemental analysis of the raw material was conducted with a PerkinElmer series II C H N analyzer and the reference standard was acetanilide (C = 71.09%; H = 6.71%; N = 10.36%). For the bio-oil, the percentages of carbon, hydrogen and nitrogen were determined according to ASTM 5291-16 [33].

2.3.2. Higher heating value

The higher heating value (HHV) was calculated according to the equation:

$$[HHV (MJ/kg) = 0.335 \times C + H 1423 - 0154 \times O - 0.145 \times N] \text{ [34]}$$

(a)   Polimeric structure - Carbohydrate units

(b)   Monomeric unit of carbohydrate
(Pyranosidic ring)

(c)   (Furanosidic ring)

1

2

3

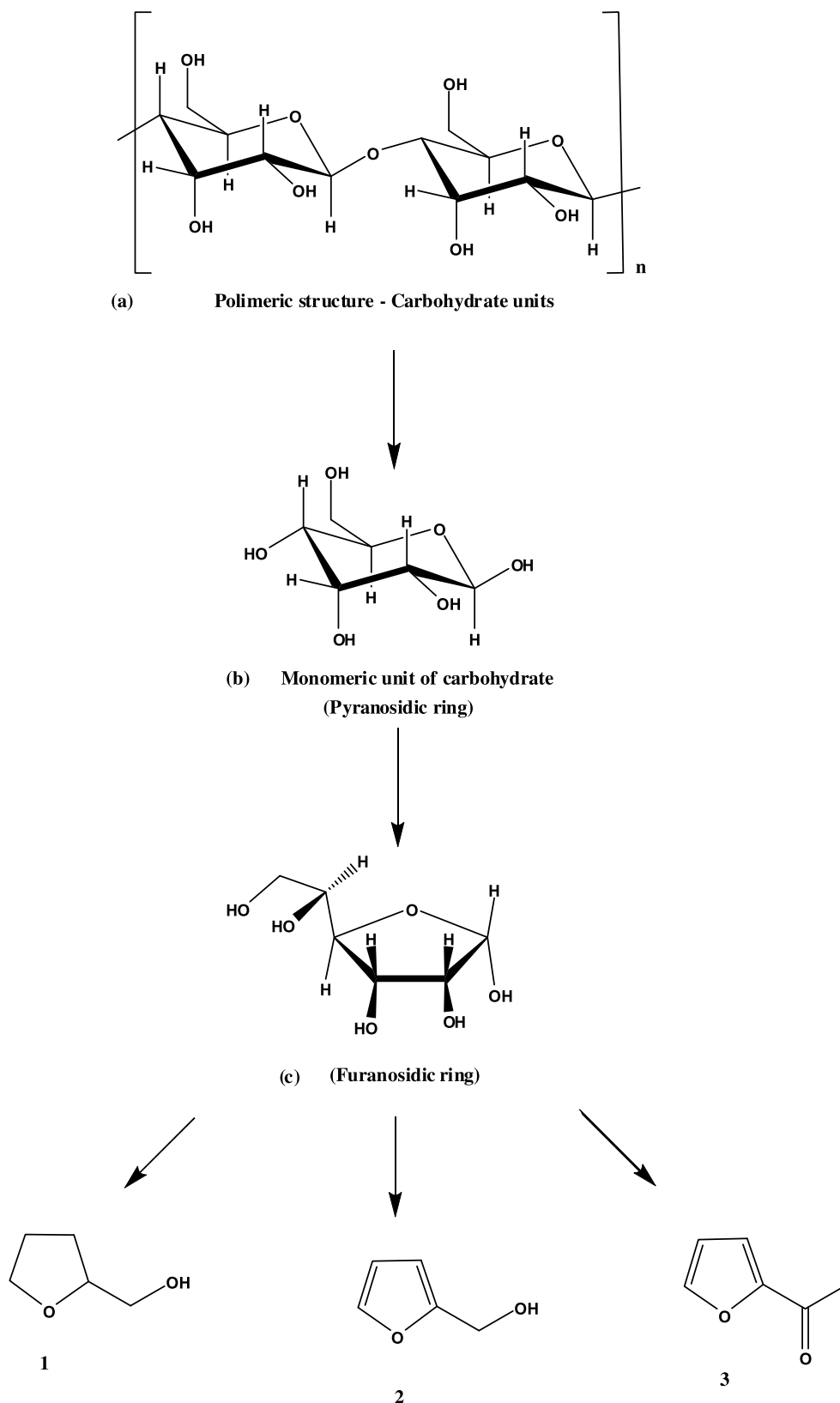**Fig. 4.** Origen of the furan derivatives: 1- 2-Furanmethanol, tetrahydro-; 2- 2-Furanmethanol; 3- Ethanone, 1-(2-furanyl)-.

2.3.3. Infrared spectroscopy and nuclear magnetic resonance

The soursop seed cake and bio-oil were subjected to spectroscopy in the infrared region using a Varian 7000e FT-IR spectrometer. The bio-oil was analyzed by ^{1}H NMR using a Varian Unity Plus 300 MHz spectrometer, $CDCl_3$.

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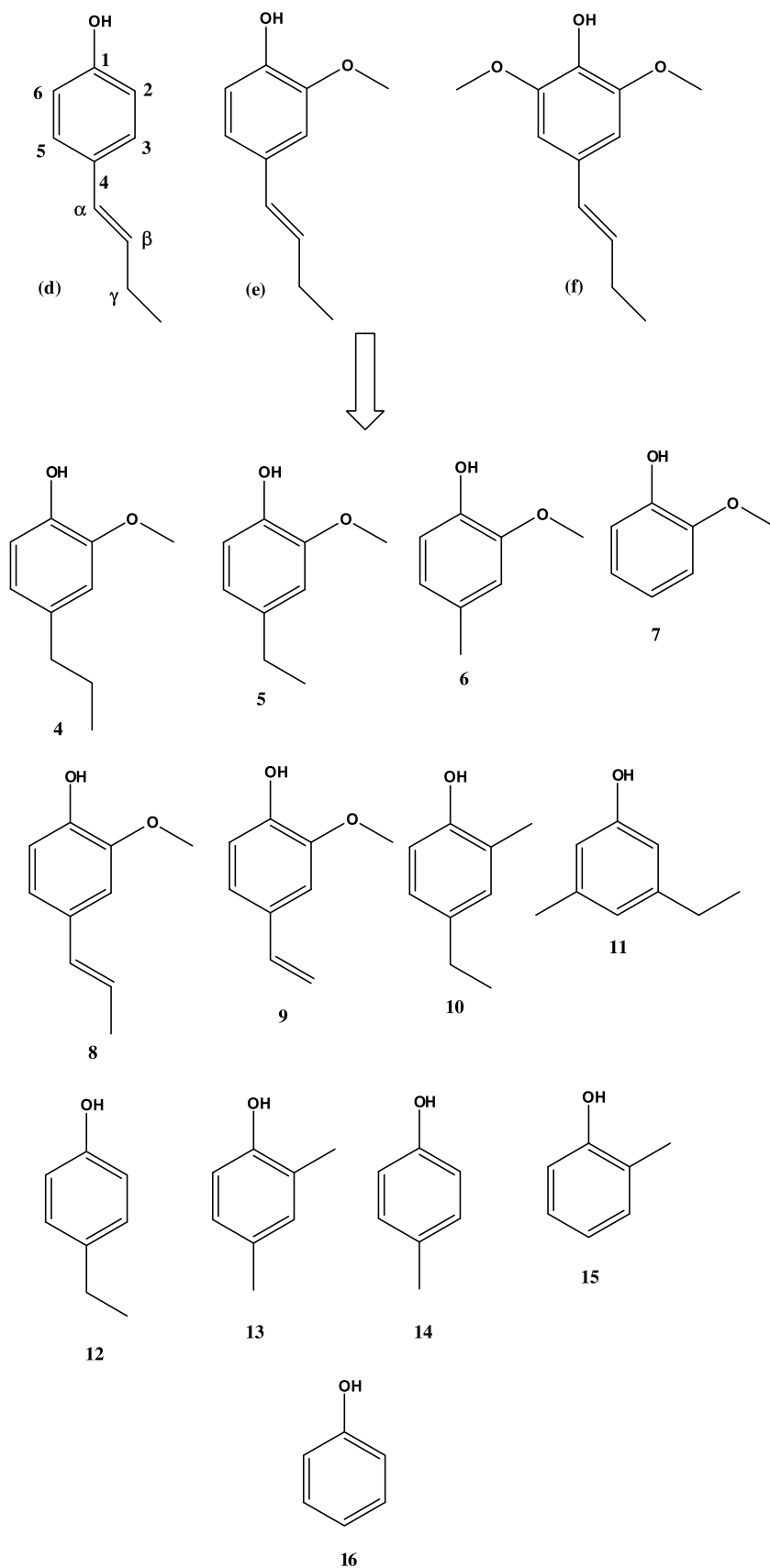
Fig. 5. Phenolic derivatives in the pyrolysis oil: (d) Cumarilic alcohol; (e) Coniferilic alcohol; (f) Sinapilic alcohol. 4- Phenol, 2-methoxy-4-propyl; 5- Phenol, 4-ethyl-2-methoxy; 6- Phenol, 2-methoxy-4-methyl; 7- Phenol, 2-methoxy; 8- Phenol, 2-methoxy-4-(1-propenyl)-(*E*); 9- Phenol, 2-methoxy-4-vinyl; 10- Phenol, 4-ethyl-2-methyl; 11- Phenol, 3-ethyl-5-methyl; 12- Phenol, 4-ethyl; 13- Phenol, 2,4-dimethyl; 14- Phenol, 4-methyl; 15- Phenol, 2-methyl; 16- Phenol.

Table 1
Replicates results of the slow pyrolysis process and standard deviations.

Slow Pyrolysis Replicates	Bio-oil	Biochar	Aqueous Fraction	GasFraction
1	18.0	30.0	33.0	19.0
2	18.0	37.2	32.4	12.4
3	19.0	30.4	32.8	17.8
4	17.4	30.8	31.6	20.2
5	20.8	32.4	27.6	19.2
Average	18.6	32.2	31.5	17.7
Standard deviation	1.34	2.96	2.22	3.09

Table 2
Comparison: ASTM D7544-12 with Bio-oil.

Property	ASTM D7544 −12	Bio-oil
Gross Heat of Combustion, MJ/Kg (min)	15	33.8
Water content, % mass (max)	30	3.0
Kinematic Viscosity at 40 °C, mm^2/s (max)	125	46.8
Density at 20 °C, Kg/dm^3	1.1–1.3	1.0
Ash Content, % mass (max)	0.15–0.25	0
pH	Report	3.0
Flash Point °C (min)	45	46.0

2.3.4. Thermogravimetric analysis

For thermogravimetric (TG) analysis, the raw material was analyzed using temperature range from 25 °C to 400 °C at a heating rate of 15 °C min^{-1}, followed by an isotherm at this temperature for 90 min and then further heating to 600 °C and maintenance at this temperature for 20 min. Nitrogen was used as carrier gas at a flow rate of 50 mL min $^{-1}$.

2.3.5. Gas chromatography with mass spectrometry

The bio-oil produced during the pyrolysis process and the organic extracts of the aqueous fraction were analyzed by GCMS. The conditions used in the gas chromatograph were: column measuring 25 m × 200 μm × 0.33 μm; heating rate of 3 min^{-1} from 35 °C to 200 °C and then to 300 °C at a rate 8 min^{-1}, maintained at this temperature for 8 min; helium for gas entrainment at 0.6 mL min^{-1}; detector temperature of 280 °C; and injector temperature of 280 °C.

2.3.6. Analysis of viscosity at 40 °C, flash point, density at 20, 40 and 60 °C and acidity level of bio-oil

The kinematic viscosity analyses were performed as described in ASTM D445-15a [35]. Flash point analysis was performed according to ASTM D93-16a [36]. The density was determined using a Krüss K100 sphygmomanometer. The acid value was determined using a Metrohm 836 Titrando potentiometric titrator.

2.3.7. Bio-oil – ethanol

The bio-oil was added to ethanol in different concentrations (5%, 10%, 20% and 30%), and the following analyses were performed:

• kinematic viscosity at 40 °C according to ASTM D445-15a [35].
• pH determination according to ABNT NBR 10891:2013 [37].

2.3.8. Aqueous fraction extractions

The aqueous fraction was subjected, sequentially, to extraction using hexane, dichloromethane and ethyl acetate as solvents. The organic extracts were treated with anhydrous magnesium sulfate (MgSO$_4$), concentrated and analyzed by GCMS.

3. Results and discussion

Our group has particular interest in the products obtained using pyrolysis at the temperature of 400 °C, since at this tempera-

Table 3
Compounds identified in bio-oil with similarity index greater than 80%.

Compounds	Retention Time (min)	Quality (%)
2,5,5-Trimethyl-2-hexene	5.233	90
Cyclopentanone, 2-methyl-	6.067	81
Pentanenitrile, 4-methyl-	6.208	92
Ethylbenzene	6.775	96
2-Furanmethanol	7.133	90
1-Nonene	8.050	92
Acetic acid, chloro-, 2-phenylethyl ester	8.117	81
Nonane	8.400	95
2-Nonene, (E)-	8.783	94
2-Cyclopenten-1-one, 2-methyl-	9.050	93
Ethanone, 1-(2-furanyl)-	9.408	96
Benzene, propyl-	11.067	93
Benzene, 1-ethyl-3-methyl-	11.483	92
2-Cyclopenten-1-one, 3-methyl-	12.008	92
Benzene, 1-ethyl-2-methyl-	12.375	87
Pentanoic acid, 4-methyl-	12.525	87
1-Decene	12.983	95
Decane	13.375	95
Phenol	13.692	95
2-Furanmethanol, tetrahydro-	14.300	89
Benzene, 1-methoxy-4-methyl-	14.642	92
Limonene	14.792	81
1,2-Cyclopentanedione, 3-methyl-	15.342	93
2-Cyclopenten-1-one, 2,3-dimethyl-	15.650	84
Benzene, butyl-	16.242	91
Phenol, 2-methyl-	17.183	96
1-Undecene	18.058	96
Phenol, 4-methyl-	18.267	98
Phenol, 2-methoxy-	18.342	92
Undecane	18.433	90
Phenol, 4-ethyl-2-methyl-	19.317	88
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	19.875	92
Octanoic acid, methyl Ester	20.025	90
2-Methyl-7-exo-vinylbicyclo[4.2.0]oct-1(2)-ene	21.250	80
Phenol, 2,4-dimethyl-	21.625	92
Phenol, 4-ethyl-	22.633	94
1-Tridecene	22.908	89
Dodecane	23.258	90
Phenol, 2-methoxy-4-methyl-	23.325	96
2-Dodecene, (Z)-	23.583	90
Phenol, 3-ethyl-5-methyl-	25.767	93
Benzene, hexyl-	26.025	91
Benzene, (1,3-dimethylbutyl)-	26.342	81
Phenol, 4-ethyl-2-methoxy-	27.250	92
1-Dodecanol	27.475	91
Tridecane	27.800	96
2-Methoxy-4-vinylphenol	28.842	86
Phenol, 2-methoxy-4-propyl-	31.075	91
1-Tetradecanol	31.775	94
Tetradecane	32.075	93
7-Tetradecene	32.350	84
Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	34.525	93
1-Pentadecene	35.833	92
Pentadecane	36.117	97
8-Heptadecene	42.725	90
3-Heptadecene, (Z)-	42.958	91
Heptadecane	43.550	95
Hexadecanoic acid, methyl Ester	51.325	96
9-Octadecenoic acid (Z)-, methyl ester	56.617	96
8-Octadecenoic acid, methyl Ester	56.825	92
Octadecanoic acid, methyl Ester	57.400	93

ture we have previously achieved a reasonable yield of all the desired products (bio-oil, biochar, gas and water fractions). One of the biggest challenges is finding applications for these products. Their applications are directly associated with their chemical and physical-chemical properties [18,25,28,29].

Nevertheless, all these products have excellent possibilities for application. For this reason, we worked with slow pyrolysis at 400 °C. Here we report studies of the composition of the oil and the water fraction compared with the raw material. This elucida-
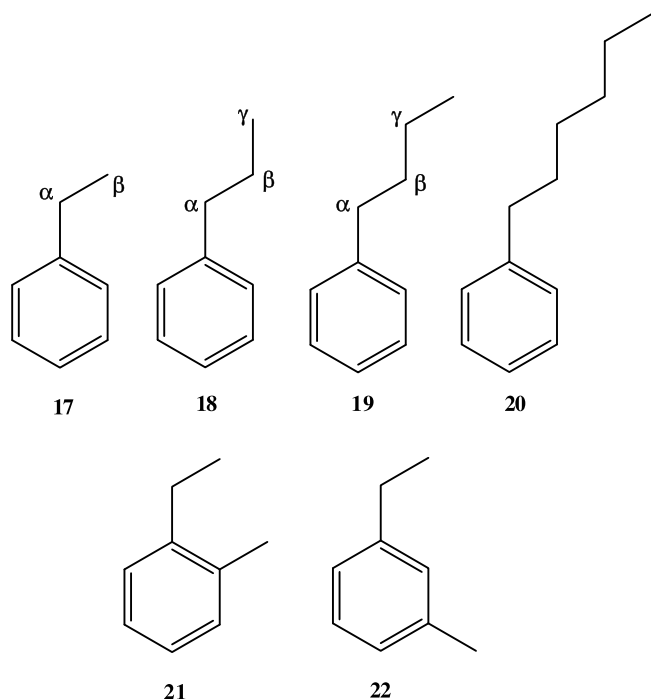
Fig. 6. Aromatic hydrocarbonsfound in the pyrolysis oil: 17- Ethyl benzene; 18- Propyl benzene; 19- Buthyl benzene; 20- Hexyl benzene; 21- 1-ethyl-2-methyl benzene; 22- 1-ethyl-3-methyl benzene.
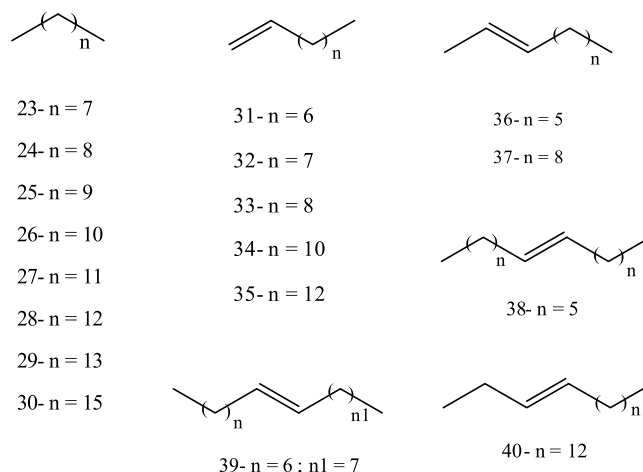

Fig. 7. Aliphatic Hydrocarbons found in the pyrolysis oil: 23- Nonane; 24- Decane; 25- Undecane; 26- Dodecane; 27- Tridecane; 28- Tetradecane; 29- Pentadecane; 30- Heptadecane; 31- Nonene; 32- Decene; 33- Undecene; 34- Tridecene; 35- Pentadecene; 36- 2- Nonene; 37- 2-Dodecene; 38- 7-Tetradecene; 39- 8-Heptadecene; 40- −Heptadecene.

3.1. Preliminary analysis of the sample

A good understanding of the chemical composition of the raw material, in this case soursop seed cake, will help to understand the formation of biochar, bio-oil, gas and aqueous fraction, in the gas phase, under the slow pyrolysis conditions.

The analysis of the soursop seed cake showed 6.0% moisture and this is an advantage because the pyrolysis can be done without drying the material.
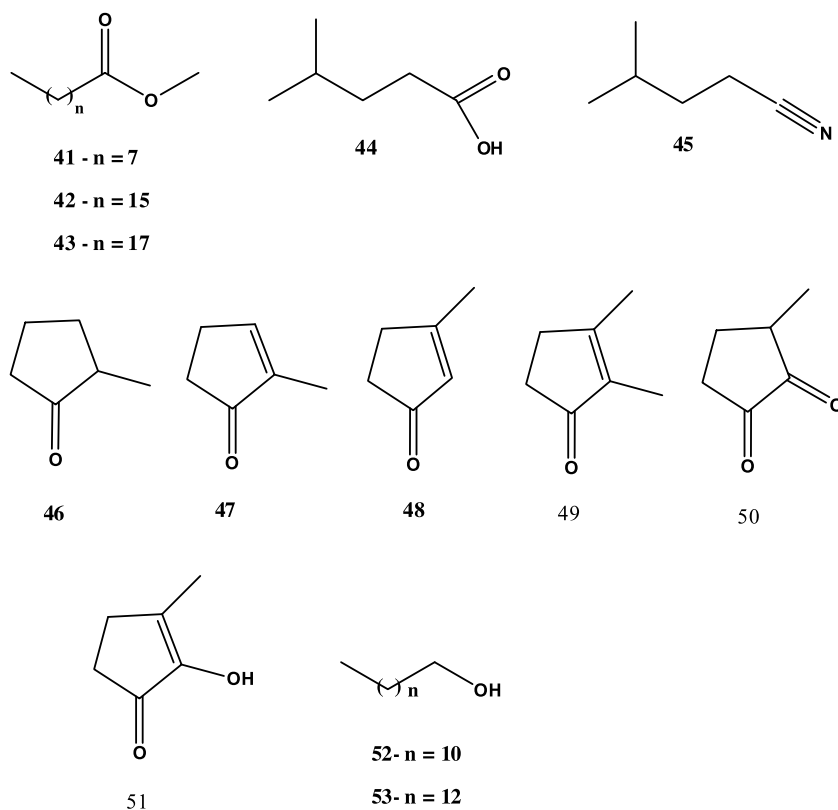
tion is very important to correlate the composition and activity of the product.

Fig. 8. Others compounds found in the pyroysis oil: 41- Octanoic acid, methyl esther; 42- Hexadecanoic acid, methyl esther; 43- Octadecanoic acid, methyl esther; 44- Pentanoic acid, 4-methyl; 45- Pentanenitrile, 4-methyl; 46- Cyclopentanone, 2-methyl; 47- Cyclopenten-1-one, 2-methyl; 48- Cyclopentanone, 3-methyl; 49- 2-Cyclopenten-1-one,2,3-dimethyl; 50- 1,2-Cyclopentanedione, 3-methyl; 51- 2-Cyclopenten-1-one, 3-ethyl-2-hydroxi; 52- Dodecanol; 53- Tetradecanol.
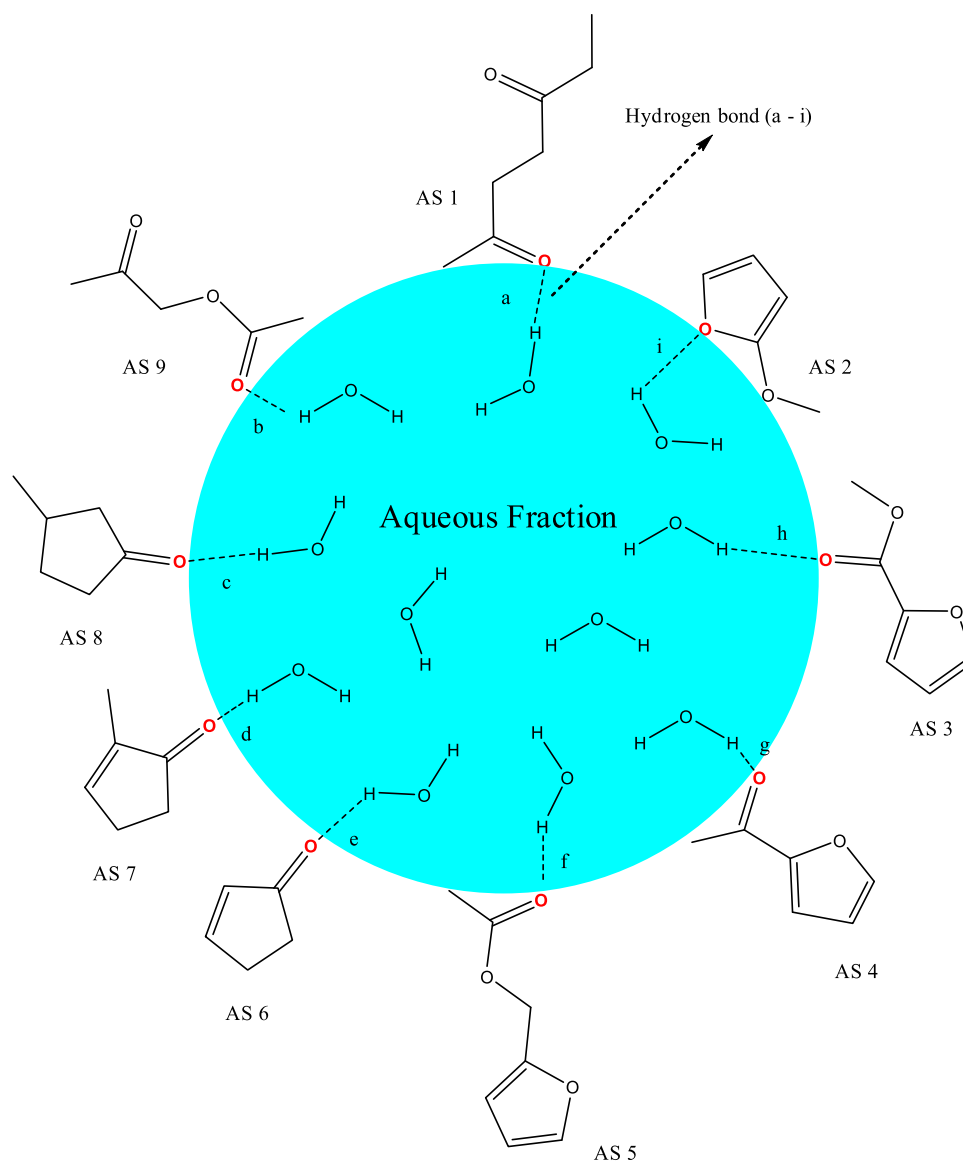
Fig. 9. Hydrogen bonds between carbonyl derivatives and water molecules.   AS: Aqueous solution

From the percentage of volatile material, 85.7%, it was possible to estimate a high yield of liquid and gaseous product from the pyrolysis process. Furthermore, the fixed carbon and ash concentrations (7.5% and 1.3%) should contribute to economic uses of the solid product. The elemental analysis showed as major elements: Carbon – 50.9%; Hydrogen – 5.9%; Nitrogen – 2.5%; and Oxygen – 39.4%, obtained by difference (100% − C% + H% + N%). The crude protein content, 15.6%, was estimated from the amount of Nitrogen (N × 6.25), while the High Heating Value, 19 MJ kg^{-1}, was determined by the elemental composition [HHV (MJ/kg) = 0.335 × C + H 1423 − 0154 × O − 0.145 × N] [34].

Thermal analysis of the seed cake was performed to verify the behavior of the biomass loss with increasing temperature. This analysis establishes a temperature range in which the sample decomposition process occurs. Fig. 1 depicts the mass loss as a function of time (black curve) and the temperature rise versus time (green curve). The analytic conditions simulate what happens within the pyrolysis reactor, with N$_2$ flow to generate an inert atmosphere and the same heating rate, but the converter temperature limit is 400 °C, while the analysis of the material reaches 600 °C.

The first mass loss, 6.529%, occurred at the beginning of the heating until 130 °C for 7 min due to loss of water and the volatile fractions contained in the material. The rest of the mass loss (76.534%) occurred between 130 and 400 °C (18 min), where the TG curve had greatest decline. DTG confirmed this loss (blue line). Together these losses amounted to 83.063%. A significant further mass loss, or 16.962%, occurred above 400 °C.

The profile in the infrared region of the soursop seed cake showed absorptions characteristics of a mixture of organic functions normally observed in all biomass. These absorptions are from cellulose, hemicellulose, lignin, fatty acids and proteins (extractives). The most relevant absorptions were the hydrogen bonds between 3200–3400 cm^{-1}; vibration of C—H bonds at 2853 and 2923 cm^{-1}; C=O group absorptions at 1743 cm^{-1} and other absorptions below 1600 cm^{-1}, characteristic of the axial deformation of C—O bonds, and C=C vibration of aromatic rings.

3.2. Slow pyrolysis

After preliminary analysis of the soursop seed cake, it was subjected to slow pyrolysis and the following average composition was
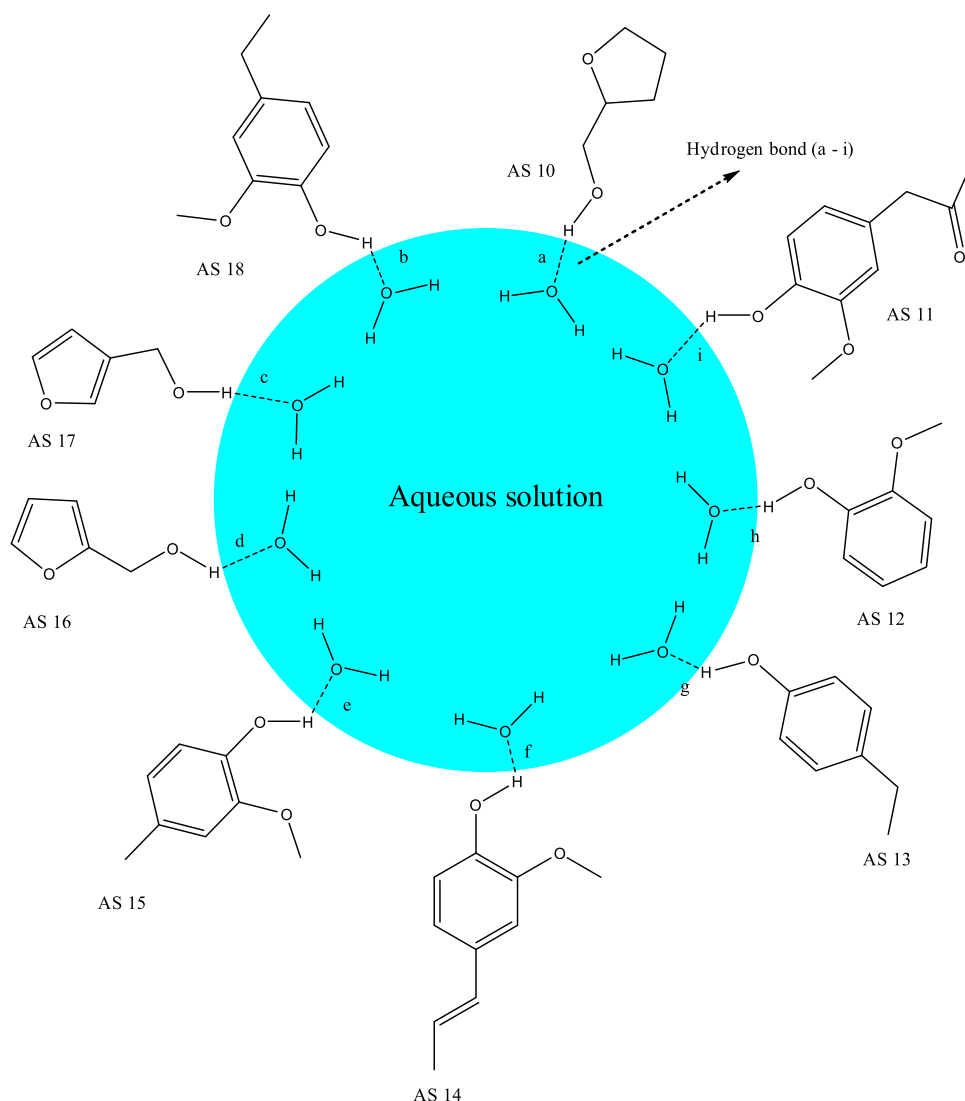
Fig. 10. Hydrogen bonds between hydroxylated derivatives and water molecules.   AS: Aqueous Solution

observed: bio-oil – 18.6% (+1.34); aqueous fraction – 31.5% (+2.22); biochar – 32.2% (+2.96) and gas – 17.7% (+3.09). All the replicates results of the slow pyrolysis process and standard deviations was show in Table 1.

The yield of the oil and aqueous fractions together was 50.1% of the total pyrolysis products. The investigation of the chemical composition of these fractions could help to understand the correlation of the composition and the chemical activity. Our recent research about the aqueous fraction and its applications in agricultural field are very promising and justify ours efforts in elucidate the components of these fractions.

3.2.1. Oil fraction

Initially we evaluated some parameters to use this oil as fuel. The low moisture content (3.0%), and the other values found for ash (0%), flash point (46.0 °C), kinematic viscosity at 40 °C (46.8 mm^2/s) and acid number (172.3 mg KOH/g) showed that the bio-oil meets the specifications described in the standard (ASTM D7544-12 – Standard Specification for Pyrolysis Liquid Biofuel). The elemental analysis (C – 70.8%, H – 9.2% N – 2.4%, O – 17.6%) revealed high carbon content in bio-oil and a large reduction in oxygen content relative to the feedstock. This difference occurs mainly due to loss of water, most of which is concentrated in the aqueous

fraction. These data allowed calculating the higher heating value, 33.8 MJ/kg, considerably higher than the starting biomass. Bio-oil has applications can be used in industrial power generation, commonly in boilers, furnaces and turbines for small- or large-scale (co-) combustion with natural gas, coal or heating oil. These systems are usually found in power plants where electricity, heat and steam are produced. Boilers, furnaces and turbines are also found at large factories to supply their demand for electricity, heat and steam. These data show that this oil has great potential for use as an optional fuel for industrial furnaces because it is in accordance with ASTM D7544–12 [38]. In Table 2 we can observe a comparison between the specification for pyrolysis oil and the data obtained for the bio-oil obtained under the conditions used in this work.

For a better understanding of the composition of this oil, we initially obtained the profile in the infrared region (Fig. 2), which showed absorptions very similar to the original biomass, due to the presence of the same types of organic functional groups. According to Brigdwater, the composition of bio-oil is very close to that of the original biomass, explaining the similarities found between infrared spectra [14].

The oil profile observed in the ^{1}H NMR spectrum (Fig. 3) shows different populations of aliphatic δ- 0.7–2.6 ppm; olefinic δ- 3.5–5.3 ppm and aromatic δ- 6.5–7.1 ppm regions (reduced signal
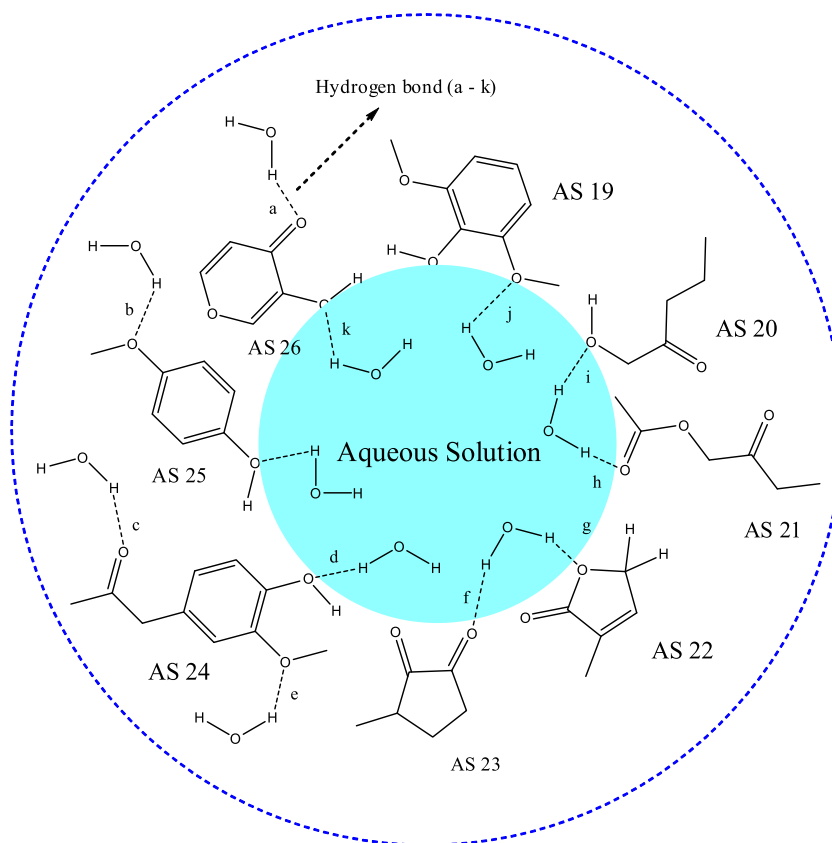
Fig. 11. Hydrogen interactions between compounds found in the extract in dichloromethane and water molecules.   AS: Aqueous Solution

in the last case due to the high population of aliphatic hydrogens). One can observe the large percentage of aliphatic hydrogens (sp^3), as shown in the gas chromatography-mass spectrometry results (Table 3).

Besides the information of the types of hydrogen, from the ^{1}H NMR, and organic functions found in IV spectrum, further data can be obtained from Gas Chromatography/Mass Spectrometry (GCMS) analysis. With this technique, it was possible to identify 59 compounds with similarity index greater than 80% (Table 3), listed according to their elutions. Comparative studies with the composition of the initial biomass (lignin, cellulose, hemicellulose, fatty acids and proteins) allowed drawing some conclusions about the origin of those compounds.

Three furan derivatives (1, 2, 3, Fig. 4), were observed by GCMS. These are likely associated with depolymerization of cellulose or hemicellulose (a) involving the monomer unit (b) with subsequent isomerization to a five-membered ring (c), followed by reactions such as dehydration, hydrogenation and decarbonylation (CH$_2$O) of the side chain (1 and 2).

Thirteen phenolic derivatives (4–16, Fig. 5) were identified, all originating from lignin, which is a very complex structure consisting of coumaryl (d), coniferyl (e) and sinapyl (f) alcohols. Several phenol derivatives were observed with alkyl, vinyl and methoxy substituents from reactions occurring in the substituent group in position 4 of the ring, carbons α, β, γ, involving homolytic cleavage and radical formation, as proposed in Scheme 1.

Six phenols found by GCMS showed one methoxyl group, suggesting presence of coniferyl alcohol. For this reason, in Scheme 1, the coniferyl alcohol (e) was used to study the mechanism that may be occurring in the gas phase. All mechanisms involve radical particles, suggesting the loss of H$_2$O and gases like H$_2$, CH$_4$, C$_2$H$_2$, CH$_2$O, along with some hydrogen migration, additions and

Table 4
Bio-oil/ethanol mixtures.

Analysis	0%	5%	10%	20%	30%
Kinematic viscosity 40 °C, (mm^2/s)	1.219	1.341	1.440	1.664	1.932
pH	6.8	6.2	6.2	6.0	6.0

isomerization. These mechanisms are classic and usually occur in mass spectrometry (EI – 70 eV), with the difference that in this case they formed positive ions. The molecular ions and the fragments according to their spectra are in perfect correlation with the proposed structures. In Scheme 1, nine of the thirteen phenols found were properly identified.

Six aromatic hydrocarbons, 17–22, with alkyl substituents have been identified, Fig. 6, as well as eighteen aliphatic hydrocarbons, 23–.40, Fig. 7. It was observed that the aromatic structures have similarities with the constituents of lignin, such as case of 18 that keeps the carbons of α, β and γ positins. Increased chain can be from free radical reactions between alkyl groups formed by homolytic cleavage.

Compounds 41–53 (Fig. 8) probably originate from fatty acids and proteins (extractives) which are commonly found in lignocellulosic biomass.

In the CGMS analysis, a predominance of hydrocarbons and phenols was observed. In order to improve the characteristics of the crude oil obtained for use as fuel, we tested the miscibility with ethanol at different concentrations. Ethanol was chosen because it is already widely used as a fuel in Brazil. The bio-oil/ethanol mixtures were analyzed for kinematic viscosity at 40 °C and pH. The results are shown in Table 4.

There was considerable improvement in kinematic viscosity compared to the crude bio-oil, which was previously 46.8 mm^2/s. The viscosity of the diesel internationally (diesel cycle) is between

Table 5
Hexane extract of the aqueous fraction obtained from the pyrolysis

Compound	Retention time (min)	Quality (%)
2-Methyl pyrazine	5.492	94
2-Furfuryl methyl ether	5.783	91
2-Cyclopenten-1-one	5.892	94
Pentanenitrile, 4-methyl	6.158	91
(R)-(+)-3-Methylcyclopentanone	6.283	89
2-Furanmethanol	7.175	97
3-Furanmethanol	7.283	94
2-Propanone, 1-(acetyloxy)-	7.725	89
2-Cyclopenten-1-one, 2-methyl-	9.017	95
Ethanone, 1-(2-furanyl)	9.408	90
2-Butanone, 1-(acetyloxy)	12.442	94
Methyl 2-furoate	12.767	96
2-Cyclopenten-1-one	13.592	96
2-Furanmethanol, acetate	13.842	96
2-Furanmethanol, tetrahydro-	14.308	92
Phenol, 2-methoxy-	18.600	95
Phenol, 4-ethyl	22.817	93
Phenol, 2-methoxy-4-methyl	23.483	96
Phenol, 4-ethyl-2-methoxy	27.350	92
Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	34.567	91
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)	37.917	90

Table 7
Ethyl acetate extract from the aqueous solution from pyrolysis.

Compound	Retention Time (min)	Quality (%)
Propanoic acid	5.392	92
2,3-Butanediol	5.625	98
Formic acid, 1-methylethyl Ester	5.717	92
Pyrazine, methyl-	6.025	96
Propanoic acid, 2-methyl	6.192	96
2-Cyclopenten-1-one	6.283	90
2-Furanmethanol	7.917	93
Butanoic acid, 4-hydroxy-	10.092	93
2(5H)-Furanone	10.250	96
1,2-Cyclopentanedione, 3-methyl-	16.025	95
Maltol	19.958	96
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy	20.175	91
1,2-Benzenediol	25.425	90
1,2-Benzenediol, 3-methoxy	26.842	91
Hydroquinone	29.617	92
1,4-Benzenediol, 2-methyl-	31.817	94
Benzeneethanol, 4-hydroxy	34.967	90
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)	38.058	91
Dodecanoic acid, ethyl Ester	40.000	95
Tetradecanoic acid, ethyl Ester	47.033	94

2 and 4 mm^2/s, close to the 1.932 mm^2/s found with the addition of alcohol (30%). This parameter is very important because it determines the storage temperature, economical pumping and spraying (atomization) for combustion. The influence of viscosity on the fuel spraying process is very significant. The higher the viscosity, the greater will be the average size of the fuel spray droplets within the combustion chamber. High viscosity results in bad mixtures and slower burning, which affect ignition and combustion efficiency [39,40]. Therefore, reducing the kinematic viscosity greatly enhances the quality of biofuel. Another advantage observed in the ethanol/bio-oil mixture was pH. The presence of ethanol changes the value of pH and the kinematic viscosity of the bio-oil. Thus, mixture of bio-oil with ethanol causes a considerable improvement in the characteristics of the fuel.

3.2.2. Aqueous fraction

We usually devote many studies involving chemical, physicochemical and applications of the bio-oil and biochar. The aqueous phase has been spreading our interest more and more because of its potential applications.

In several conversions, at 400 °C, of different types of biomass, we isolated the separate oil and water fractions. At higher temperatures, these two phases are miscible and difficult to separate.

The aqueous fraction obtained from slow pyrolysis of the soursop seed cake had an average yield of 32.16% and pH 3. The aqueous fraction was subjected to extraction using hexane, dichloromethane and ethyl acetate as solvents. The organic extracts

were treated with anhydrous magnesium sulfate (MgSO$_4$), concentrated and analyzed by GCMS.

The main compounds identified in the three extracts, 52 compounds, compared with the mass spectra of NIST27 and NIST147 libraries are listed in Tables 3–5, revealing mainly ketones, alcohols and phenols.

Table 5 shows 21 compounds found in the hexane extract, in ascending order of retention time. Several of these compounds were also found in the oil phase.

Figs. 9 and 10 show the structures of the compounds found in the hexane extract and the hydrogen bonds involved in some interactions of the carbonyls, alcohols, phenols and water molecules. We believe these interactions are responsible for the miscibility of these compounds in the aqueous phase.

The second extraction, in dichloromethane, of the aqueous fraction (Table 6) revealed 11 compounds containing groups which can perform hydrogen interactions in different ways, as shown in Fig. 11.

In this case, several compounds also appeared in the oil and water phases. Like in other oxygenated compounds, there are different points (carbonyl, hydroxyl and methoxyl) where hydrogen bonds with water molecules can occur (Fig. 11).

The third extraction, in ethyl acetate (Table 7), yielded the most polar compounds found in the aqueous solution.

This extraction produced some short-chain carboxylic acids and esters as well as cyclic ketones and phenols (Fig. 12). In addition, in all cases these hydrogen bonds can occur with water molecules.

Table 6
Dichloromethane extract of the aqueous fraction from pyrolysis.

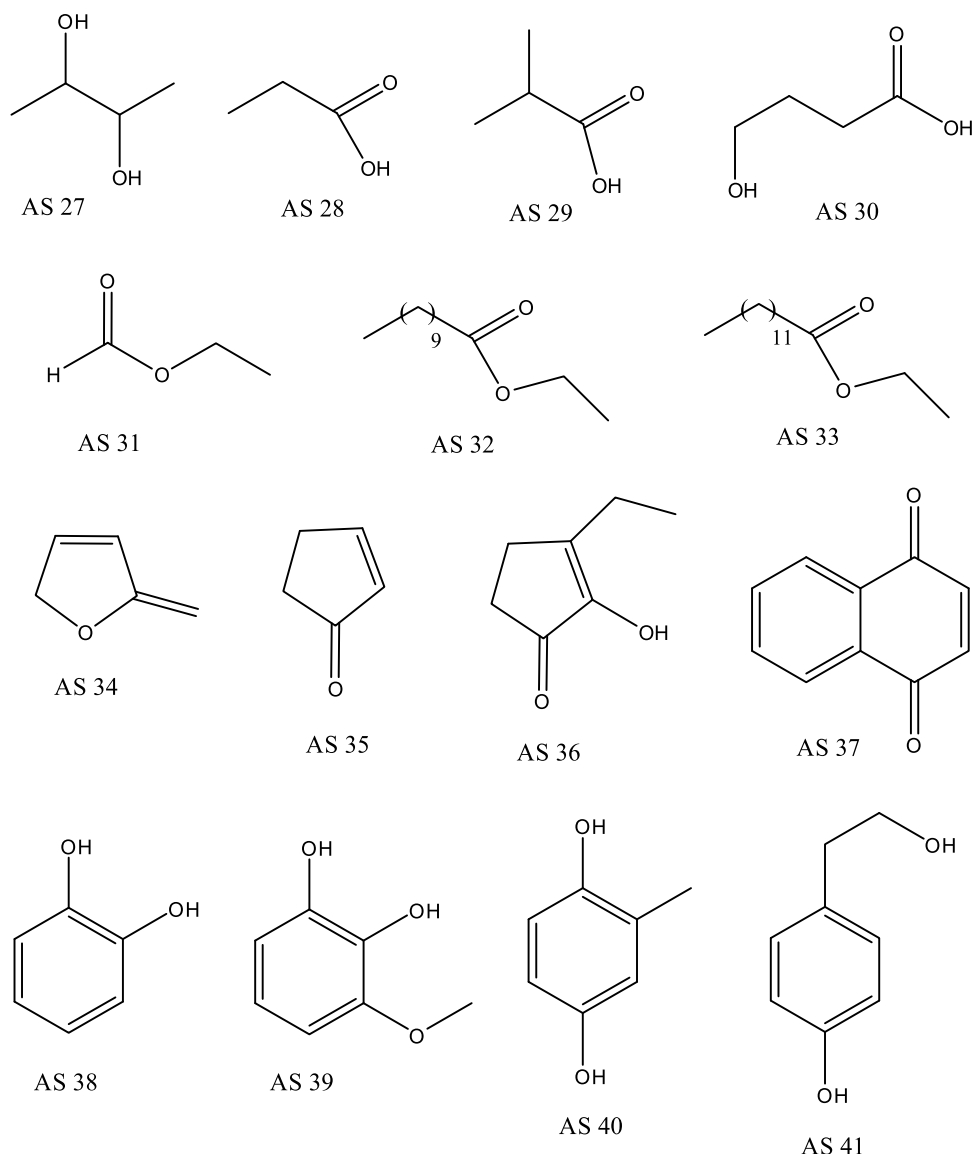| Compound	Retention Time (min)	Quality (%)
Pyrazine, methyl-	6.033	94
1-Hydroxy-2-pentanone	7.225	92
2-Furanmethanol	8.425	89
2-Butanone, 1-(acetyloxy)	13.283	93
2(5H)-Furanone, 3-methyl-	13.942	91
1,2-Cyclopentanedione, 3-methyl-	17.667	93
Mequinol	19.192	93
Maltol	21.242	86
Phenol, 2,6-dimethoxy-	31.333	93
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)	38.825	90
5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a;1′,2′-d]pyrazine	52.617	91

Fig. 12. Compounds found in ethyl acetate extract from the aqueous solution from pyrolysis.

The greatest difference between the composition of the oil phase and the aqueous solution were the aliphatic and aromatic hydrocarbons, which were found only in the oil, due to its apolar characteristic. So, we can propose that a number of substances present in the aqueous fraction form a network of hydrogen interactions and cause acid pH, and a number of protonations can occur, causing these substances to be soluble in water.

4. Conclusions

The slow pyrolysis conditions applied to the soursop seed cake leading to oil, char, aqueous fraction and gas in god yields and in accordance with our purposes of using all fractions of the pyrolyzed raw material.

The oil and aqueous fractions were analyzed by GCMS and the different compounds identified and correlated with the initial biomass composition, lignin, cellulose, hemicellulose, fatty acids and proteins. The composition of the oil fraction differed from the aqueous fraction, especially in the series of aromatic and aliphatic hydrocarbons, compared to many oxygenates, which appear in two fractions.

The oil can be used as fuel, because presented the limits established in the ASTM D7544-12 – Standard Specification for Pyrolysis Liquid Biofuel. The mixture with ethanol showed an improvement in quality with fuel.

The aqueous fraction showed several phenolics compounds and others containing oxygen and probably associated with the numerous hydrogen bond interactions leading to their miscibility.

The elucidation of the composition of the oil and aqueous solution helps to determine the best applications for the substances obtained.

References

[1] L.A.B. Cortez, E.E.S. Lora, E.O. Gómez, Biomassa Para Energia, Ed. Unicamp, 2008, pp. 1–734, 8526807838.

[2] E.R. Reetz, B.B. Kist, C.E. dos Santos, C. de Carvalho, M. Drum, Anuário Brasileiro da Fruticultura, 2014, Ed. Gaz., 2015, pp. 104.

[3] E.E.P. de Lemos, A Produção de Anonáceas no Brasil, Rev. Bras. 36 (2014) 77–85, http://dx.doi.org/10.1590/S0100-29452014000500009.

[4] G.A.R. Kelmer, N. Nascimento, P.V. Oliveira, I. De Química, U.D.S. Paulo, S. Paulo-sp, Determination of essential, non-essential, and potentially toxic elements in graviola (Annona muricata L.) Pulp by ICP OES and GF AAS, J. Braz. Chem. Soc. 26 (2015) 1981–1987, http://dx.doi.org/10.5935/0103-5053.20150177.

[5] M.A. Coêlho de Lima, R.E. Alves, Soursop (Annona Muricata L.), Woodhead Publishing Limited, 2011, http://dx.doi.org/10.1533/9780857092618.363.

[6] R.B. Sobrinho, Potencial De Exploração De Anonaceas No Nordeste Do Brasil, in: 17a Sem. Int. Da Frutic. Floric. E Agroindústria, Embrapa Agroindústria Tropical, Fortaleza, 2010, p. 27.

[7] A.R. São José, A.L.G.E. de Freitas, D.P. Ribeiro, L.A.A. Perez, Atualidades e perspectivas das Anonáceas no mundo, Rev. Bras. Frutic. 36 (2014) 86–93, http://dx.doi.org/10.1590/S0100-29452014000500010.

[8] M.A.C. de Lima, O cultivo da gravioleira, Rev. Bras. Frutic. 26 (2004) 0 http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0100-29452004000300001&nrm=iso.

[9] J.A. Leatemia, M.B. Isman, Insecticidal activity of crude seed extracts of Annona spp., Lansium domesticum and Sandoricum koetjape against lepidopteran larvae, Phytoparasitica 32 (2004) 30–37, http://dx.doi.org/10.1007/bf02980856.

[10] M.J. Rieser, Z.M. Gu, X.P. Fang, L. Zeng, K.V. Wood, J.L. McLaughlin, Five novel mono-tetrahydrofuran ring acetogenins from the seeds of Annona muricata, J. Nat. Prod. 59 (1996) 100–108, http://dx.doi.org/10.1021/np960037q.

[11] F.A. de Castro, G.A. Maia, L. Flavio, F. Holanda, Z.B. Guedes, D.E.A. Moura, Características Físicas e químicas da graviola, Pesq. Agropec. Bras. 19 (1984) 361–365 https://seer.sct.embrapa.br/index.php/pab/article/viewFile/15472/9410.

[12] I.A. Onimawo, Proximate composition and selected physicochemical properties of the seed, pulp and oil of soursop (Annona muricata), Plant Foods Hum. Nutr. 57 (2002) 165–171, http://dx.doi.org/10.1023/A:1015228231512.

[13] A. Kimbonguila, J.M. Nzikou, L. Matos, B. Loum, C.B. Ndangui, N.P.G. Pambou-Tobi, Proximate composition and physicochemical properties on the seeds and oil of annona muricata grown In Congo-Brazzaville, Res. J. Environ. Earth Sci. 2 (2010) 13–18.

[14] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass Bioenergy 38 (2012) 68–94, http://dx.doi.org/10.1016/j.biombioe.2011.01.048.

[15] D. Mohan, A. Sarswat, Y.S. Ok, C.U. Pittman, Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – a critical review, Bioresour. Technol. 160 (2014) 191–202, http://dx.doi.org/10.1016/j.biortech.2014.01.120.

[16] Y. Lee, J. Park, C. Ryu, K.S. Gang, W. Yang, Y.K. Park, J. Jung, S. Hyun, Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500 °C, Bioresour. Technol. 148 (2013) 196–201, http://dx.doi.org/10.1016/j.biortech.2013.08.135.

[17] M. Ahmad, A.U. Rajapaksha, J.E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S.S. Lee, Y.S. Ok, Biochar as a sorbent for contaminant management in soil and water: a review, Chemosphere 99 (2014) 19–23, http://dx.doi.org/10.1016/j.chemosphere.2013.10.071.

[18] C.A.R. Bernardino, C.F. Mahler, M.C.C. Veloso, G.A. Romeiro, Preparation of biochar from sugarcane by-product filter mud by slow pyrolysis and its use like adsorbent, Waste Biomass Valorization (2016), http://dx.doi.org/10.1007/s12649-016-9728-5.

[19] M.I. Jahirul, M.G. Rasul, A.A. Chowdhury, N. Ashwath, Biofuels production through biomass pyrolysis- a technological review, Energies 5 (2012) 4952–5001, http://dx.doi.org/10.3390/en5124952.

[20] D. Meier, B. Van De Beld, A.V. Bridgwater, D.C. Elliott, A. Oasmaa, F. Preto, State-of-the-art of fast pyrolysis in IEA bioenergy member countries, Renew. Sustain. Energy Rev. 20 (2013) 619–641, http://dx.doi.org/10.1016/j.rser.2012.11.061.

[21] R. Xu, L. Ferrante, C. Briens, F. Berruti, Bio-oil production by flash pyrolysis of sugarcane residues and post treatments of the aqueous phase, J. Anal. Appl. Pyrolysis 91 (2011) 263–272, http://dx.doi.org/10.1016/j.jaap.2011.03.001.

[22] Q. Zhang, J. Chang, T. Wang, Y. Xu, Review of biomass pyrolysis oil properties and upgrading research, Energy Convers. Manag. 48 (2007) 87–92, http://dx.doi.org/10.1016/j.enconman.2006.05.010.

[23] S. Xiu, A. Shahbazi, Bio-oil production and upgrading research: a review, Renew. Sustain. Energy Rev. 16 (2012) 4406–4414, http://dx.doi.org/10.1016/j.rser.2012.04.028.

[24] K. Smets, S. Schreurs, R. Carleer, J. Yperman, Valorization of raspberry seed cake by flash and slow pyrolysis: product yield and characterization of the liquid and solid fraction, J. Anal. Appl. Pyrolysis 107 (2014) 289–297, http://dx.doi.org/10.1016/j.jaap.2014.03.014.

[25] R.V.S. Silva, A. Casilli, A.L. Sampaio, B.M.F. Ávila, M.C.C. Veloso, D.A. Azevedo, G.A. Romeiro, The analytical characterization of castor seed cake pyrolysis bio-oils by using comprehensive GC coupled to time of flight mass spectrometry, J. Anal. Appl. Pyrolysis 106 (2014) 152–159, http://dx.doi.org/10.1016/j.jaap.2014.01.013.

[26] M.E. Doumer, G.G.C. Arízaga, D.A. Da Silva, C.I. Yamamoto, E.H. Novotny, J.M. Santos, L.O. Dos Santos, A. Wisniewski, J.B. De Andrade, A.S. Mangrich, Slow pyrolysis of different Brazilian waste biomasses as sources of soil conditioners and energy, and for environmental protection, J. Anal. Appl. Pyrolysis 113 (2015) 434–443, http://dx.doi.org/10.1016/j.jaap.2015.03.006.

[27] C.A.L. Cardoso, M.E. Machado, E.B. Caramão, Characterization of bio-oils obtained from pyrolysis of bocaiuva residues, Renew. Energy 91 (2016) 21–31, http://dx.doi.org/10.1016/j.renene.2015.11.086.

[28] M.K.K. Figueiredo, G.A. Romeiro, L.A. ĎAvila, R.N. Damasceno, A.P. Franco, The isolation of pyrolysis oil from castor seeds via a Low Temperature Conversion (LTC) process and its use in a pyrolysis oil-diesel blend, Fuel 88 (2009) 2193–2198, http://dx.doi.org/10.1016/j.fuel.2009.05.025.

[29] G.A. Romeiro, E.C. Salgado, R.V.S. Silva, M.K.K. Figueiredo, P.A. Pinto, R.N. Damasceno, A study of pyrolysis oil from soluble coffee ground using low temperature conversion (LTC) process, J. Anal. Appl. Pyrolysis 93 (2012) 47–51, http://dx.doi.org/10.1016/j.jaap.2011.09.006.

[30] ASTM D1762-84(2013), Standard Test Method for Chemical Analysis of Wood Charcoal, ASTM, International, West Conshohocken PA, 2013 www.astm.org.

[31] ASTM D4928-11, Standard Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration, ASTM International, West Conshohocken PA, 2011 www.astm.org.

[32] ASTM D3172-13, Standard Practice for Proximate Analysis of Coal and Coke, ASTM, International, West Conshohocken, PA, 2013 www.astm.org.

[33] ASTM D5291-16, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants, ASTM, International, West Conshohocken PA, 2016 www.astm.org.

[34] A. Demirbas, Calculation of higher heating values of biomass fuels, Fuel 76 (1997) 431–434, http://dx.doi.org/10.1016/S0016-2361(97)85520-2.

[35] ASTM D445-15a, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity), ASTM, International, West Conshohocken PA, 2015 www.astm.org.

[36] ASTM D93-16a, Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester, ASTM, International, West Conshohocken PA, 2016 www.astm.org.

[37] ABNT NBR 10891:2013 Etanol hidratado combustível — Determinação do pH — Método potenciométrico, ABNT – Associação Brasileira de Normas Técnicas, 2013, http://www.abntcatalogo.com.br.

[38] ASTM D7544-12, Standard Specification for Pyrolysis Liquid Biofuel, ASTM, International, West Conshohocken PA, 2012 www.astm.org.

[39] X. Yang, W. Li, A novel theoretical approach to the temperature-viscosity relation for fluidic fuels, Fuel 153 (2015) 85–89, http://dx.doi.org/10.1016/j.fuel.2015.02.115.

[40] S. Bair, The pressure and temperature dependence of volume and viscosity of four Diesel fuels, Fuel 135 (2014) 112–119, http://dx.doi.org/10.1016/j.fuel.2014.06.035.