


# Production of Biochar, Bio-Oil and Synthesis Gas from Cashew Nut Shell by Slow Pyrolysis

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**Abstract** Cashew nut shell waste from northeast region of Brazil was characterized and slow pyrolyzed in a simple batch type reactor heated externally by liquefied petroleum gas as fuel. The experiments were performed using nitrogen or air as carrier gases. The properties of biochar, bio-oil and gases products were investigated and potential applications were proposed. Cashew nut shell showed a high heating value of 20.7 MJ kg<sup>-1</sup> that is among the highest found for different types of biomass. Pyrolysis under nitrogen flow showed a yield of solid, liquid and gas products of about 30, 40 and 30 wt%, respectively. Under air flow an increase of gas phase (46 wt%) was observed with a decrease in the production of biochar and, mainly bio-oil. The biochars have high contents of carbon (70–75 wt%) and high heating values in the range of 25–28 MJ kg<sup>-1</sup> presenting suitable properties for use as energy source. Biochars also contain significant quantities of K and minor amounts of Mg, Ca, Cu, Zn and Fe showing potential as fertilizer. The bio-oils showed high heating values of about 32 MJ kg<sup>-1</sup> and are not suitable for use in pure form, but can be used in mixtures with Diesel (42.5 MJ kg<sup>-1</sup>). The gas phase revealed the predominance of CO<sub>2</sub> and CO at temperatures lower than 400 °C and, above this temperature, there was a preferential formation of H<sub>2</sub> resulting in synthesis gas with different compositions

that could be burned to supply heat for the pyrolysis process and/or to produce organic chemicals.

**Keywords** Cashew nut shell · Slow pyrolysis · Bio-oil · Biochar · Syngas

## Introduction

Fossil fuels continue to be the primary form of energy supply worldwide as well as the main source of raw materials for the chemical industry. However, environmental and economical effects have stimulating the search for environmentally friendly renewable sources of energy and chemicals [1, 2]. Biomass has the potential to offer sources of energy and chemicals, with agricultural wastes posing as a better alternative than the use of biomass that can be consumed as food. Agricultural waste could be converted into chemicals by hydrolysis or thermochemical routes [3]. Pyrolysis is a thermochemical technique that converts biomass into solid (biochar), liquid (bio-oil) and gaseous fractions at moderate temperatures, either in the absence of air or when stoichiometric quantities of oxygen are diminished. In this process, the proportions of solid, liquid and gas products formed depend on the mode of pyrolysis and the type of the pyrolysis system used [4]. The liquid product is a complex mixture referred to as bio-oil, which is easily transportable and storable [4, 5]. This makes it an alternative approach to produce hydrogen for fuel cells since is possible to implement smaller-scale reforming of bio-oil at different locations or also to produce renewable transportation fuels [6]. The gas products were composed principally by CO, CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub> which could be used as combustible or in the production of organic chemicals [3, 7].

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Cashew nut shell (CNS) is an important agricultural by-product of the cashew nut and cashew apple industries [8]. The world's yearly production of cashew nut is estimated to be around 4 million tons and CNS represents 20 wt% (around 850 thousand tons). Brazil is responsible for 54 thousand tons of the world total [9]. After extraction of the cashew nut shell liquid (CNSL), a viscous reddish brown liquid used in the manufacture of resins and plastics [8] or used as a phenol antioxidants [10], the CNS are often disposed improperly in the environment. Although there are several studies on biomass pyrolysis [3, 6, 7, 11–16], only a few of them investigated slow [17–22] and fast [23] CNS pyrolysis. Recently, Doumer et al. [24] studied the slow pyrolysis of different Brazilian waste biomass such as water hyacinth, sugarcane bagasse, castor meal, coconut pericarp and *Eucalyptus* crop residues. They concluded that the produced bio-oils could compete as suitable raw materials for biofuel production or as feedstocks for the chemical industry. They also proposed that the resulting biochars could be used as soil conditioners.

In this study, CNS obtained from the northeast region of Brazil (State of Sergipe, town of Carrilhos, city of Itabiana) was characterized and pyrolyzed on a simple batch type reactor heated by a combustion flame, which is an alternative for some regions that suffer for low rate of electrification or low quality of the electric supply service [25]. Additionally, we evaluated how nitrogen or air influenced on the yield of solid (biochar), liquid (bio-oil) and gas, all quantified and characterized using different techniques.

## Materials and Methods

### CNS Characterization

#### Biomass Feedstock

The CNS (from *Anacardium occidentale L. tree*) were ground in an industrial grinding mill Tokyo 500 GO and sieved to 60 mesh (0.250 mm).

#### Residual Moisture

The residual moisture was determined based on ASTM 1762/1964. It was first determined the moisture pre-drying (U) of fresh cashew nut shell. After pre-drying, it was determined the residual moisture content (u) of ground cashew nut shell with an approximate particle size of 60 mesh. After removing moisture from the biomass, the following procedures were carried out.

### Ash and Volatile Matter

The standard ash and volatile matter were determined based on ASTM E 1755 and ASTM D 1762, respectively.

### CHNS Analysis

Elemental Analyser Vario El Cube was used to determine the contents of C,H,N based on ASTM D 5291. The sulfur content was determined by LECO S-144 DR based on ASTM D 4239.

### High Heating Value (HHV)

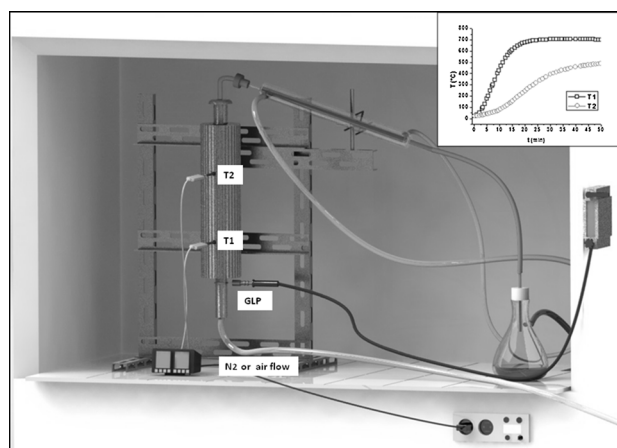
The 6400 Automatic Isoperibol Calorimeter Paar was used to determine the High Heating Values based on ASTM D 5865.

### Thermogravimetric Analysis

TG/DTG curves of CNS ground to 60 mesh were performed using the TG–DTA analyzer/DSC Setaram Instrumentation Labsys model with  $10\text{ }^{\circ}\text{C min}^{-1}$  heating rate and argon or synthetic air flow of  $50\text{ mL min}^{-1}$ .

### Slow Pyrolysis of CNS

The CNS slow pyrolysis was carried out in a simple batch type reactor, which is depicted in Fig. 1. The reactor in the form of a tube having an inlet at the bottom of which a gas flow (nitrogen or air) could be continuously flushed. The feedstock is fed at the top of the reactor falling on a perforated stainless steel screen; this part of the reactor was heated externally by a combustion flame produced by liquefied petroleum gas combustion (LPG) and air. At the top of the reactor was an outlet tube connected to a water



**Fig. 1** Pyrolysis batch reactor and a typical heating profile (*insert*)

cooled condenser, where the vaporized gas and the substances were cooled, the condenser outlet was, in turn, connected to a container where the condensed liquid was collected and separated from the produced gases. The pyrolysis reactor was fed with 50 g of crushed and sieved CNS. The temperature inside the reactor was measured using two thermocouples placed at different locations, one placed at the bottom (**T1**), near the screen used to support CNS bed, and another (**T2**) placed at the top of CNS bed. The flow rate ( $\text{mL min}^{-1}$ ) of the carrier gas (nitrogen or air) was controlled using a rotameter.

### Characterization of Pyrolysis Products

For bio-oil and biochar products the HHV and elemental analysis (C,H,N,S) were based on the same methodology used in the characterization of CNS. Some additional methodologies were used as described below.

#### Solid Product (Biochar) Analysis

*Scanning Electron Microscopy (SEM) and X-ray Energy-Dispersive Analysis (EDX)*

The SEM micrographs and EDX analysis were performed on a Jeol microscope (JSM-6010LA). EDX analyses were performed at different locations of the surface and the percentage of the elements corresponds to the average of these measurements.

#### Liquid Product (Bio-Oil) Analysis

*FTIR Spectroscopy*

The FTIR spectra of bio-oil were recorded in the region  $4000\text{--}800\text{ cm}^{-1}$  in a spectrometer Nicolet 6700 FTIR infrared using in attenuated total reflection (ATR) with a zinc selenide crystal (ZnSe).

#### Gas Products Analysis

Gas analyses were performed on a gas chromatograph (GC) from Agilent Technologies (model 7890A). The equipment was configured with two columns (column 1: HP Plot U, 30 m length and diameter 0.53 mm; column 2: HP Mol-Sieve 5A, 30 m length and diameter 0.53 mm), a methanizer, a thermal conductivity detector (TCD) and flame ionization detector (FID—detection limit of 0.1 %mol/mol for gases). The columns, methanizer, detectors and sample circuit were connected to a 6-way valve with pneumatic actuator. Argon 5.0 was used as the carrier gas. Programming oven temperature: 3.5 min at 35 °C, 35 °C/min to 150 °C, 13.2 min at 150 °C. Programming a 6-way valve:

3.2 min on, 16.8 min off. Elution order:  $\text{CO}_2$ ,  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{H}_2\text{O}$ , unknowns,  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{CO}$ .

## Results

### CNS Characterization

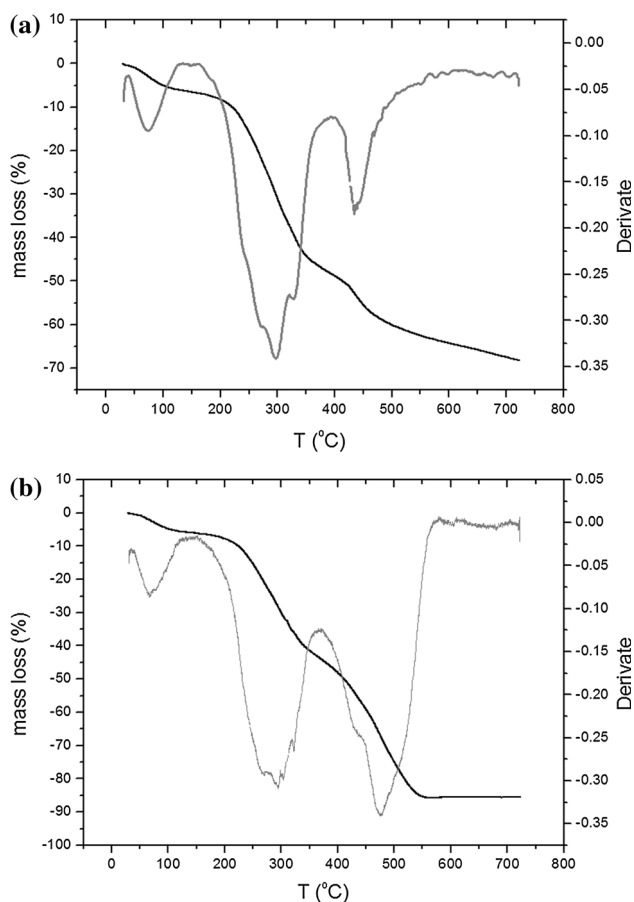
The properties of CNS are shown in Table 1. From proximate analysis it was observed that the water content was 8.9 wt% and the material contained 70.9 wt% of volatile matter and 23.8 wt% of fixed carbon. These values are similar to those already described for CNS samples from different geographical origins [12, 18, 20]. Only the ash content (5.3 wt%) was greater than in previous studies, which were in the range of 0.7–2.4 wt%. Additionally, the C, H, N, O and S contents as well as the HHV value were similar to the ones described in the literature [12, 18, 20]. Compared with other biomass materials [26], the CNS moisture content was similar to those reported for other types of biomasses (8.4 and 9.1 wt%). CNS contains a small amount of ash (5.3 wt%) and this makes it more favorable for thermochemical conversion. The amount of ash is a serious problem in the combustion process of biomass because of a high risk of slagging, bed agglomeration, fouling, and corrosion in the combustion devices [27]. It can be seen that CNS has a high content of volatile matter and a low content of nitrogen and sulfur, which is interesting with respect to their applications in gasification and pyrolysis. From all of these parameters, HHV is considered an important property of solid biofuels and CNS showed a value of  $20.7\text{ MJ kg}^{-1}$  that is among the highest found for different types of biomass [26].

Thermogravimetric analyses (TGA) were performed to verify the behavior of CNS in the presence of nitrogen and air. TGA and DTG curves are shown in Fig. 2a, b, respectively. In Fig. 2a, the first mass loss occurred

**Table 1** The properties of cashew nut shell (CNS)

Proximate analysis (wt%)	
Total moisture	8.9
Ash	5.3
Volatile matter	70.9
Fixed carbon <sup>a</sup>	23.8
Ultimate analysis (wt%)	
Carbon	49.9
Hydrogen	6.0
Nitrogen	0.7
Sulfur	<0.1
Oxygen <sup>a</sup>	38.1
High heating value ( $\text{MJ kg}^{-1}$ )	
HHV	20.7

<sup>a</sup> Calculated by difference



**Fig. 2** TGA and DTG curves of raw cash nut shell in nitrogen (a) and air (b)

between 40 and 120 °C due to the release of moisture absorbed on shell residue and external water bounded by surface tension. The small shoulder in the DTG profile observed at approximately 270 °C is due to the decomposition of hemicellulose. The main decomposition of CNS occurred around 300 °C, which can be attributed to the decomposition of cellulose. The decomposition of lignin and other compounds occurred above 400 °C [23, 28]. The thermogram carried out in a nitrogen atmosphere revealed a total mass loss of about 70 wt%.

For the thermogravimetric analysis carried out in the presence of air (Fig. 2b) the DTG curve was of a similar profile until 350 °C. However, above this temperature it was observed a broad and more intense peak centered at around 470 °C showing that lignin are suffering a greater degradation in the presence of air leading to a total mass loss of 85 wt%.

### CNS Slow Pyrolysis

The CNS slow pyrolysis was carried out in a batch-type reactor. A typical heating profile is shown inside in Fig. 1.

The total process time took about 50 min, and a maximum temperature of about 700 °C was reached at around 30 min (T1) resulting in a heating rate of about 22.5 °C min<sup>-1</sup>. The liquid product (bio-oil + aqueous phase) was observed until the temperature reached 420–430 °C (approximately 12–14 min of operation); it ceased after that.

The CNS slow pyrolysis was studied using nitrogen or air as carrier gases at different flow rates. The yields of solid (biochar), liquid (bio-oil + aqueous phase) and gas products are shown in Table 2. When the CNS pyrolysis was performed under nitrogen flow a yield of solid, liquid and gas phases of about 30, 40 and 30 wt% was obtained, respectively, regardless of the nitrogen flow rate (mL min<sup>-1</sup>). These yields are characteristic of slow pyrolysis processes and long residence time (batch reactors), with similar results having described in the literature [3]. On the other hand, fast pyrolysis yields of 75, 12 and 13 wt% are reported for liquid, solid and gas products, respectively [11]. The obtained liquid product is composed of an aqueous phase, which normally contains a wide variety of oxygenated carbon compounds of low molecular weight, and a bio-oil, a liquid of dark brown color and irritating odor containing insoluble oxygenated carbon (mainly aromatics) compounds [11, 29]. The yield of bio-oil (10–11 %) did not change significantly with the variation of nitrogen flow. A yield of 30 % was observed for the solid product (biochar) and this value is similar to that observed in the TGA experiment (Fig. 2a) where a residue of 30 % was obtained under nitrogen flow.

In the experiments performed under air flow, an increase in the gas products yield (45 wt%) was observed, compared to experiments under nitrogen flow (30 wt%). As expected, the presence of oxygen leads to combustion of the organic matter, and an increase in the formation of gases, mainly CO and CO<sub>2</sub>, thus resulting in a decrease in the values of the liquid and solid products. Furthermore, in these conditions, a drastic reduction of bio-oil yields was observed.

### Characterization of Solid Product (Biochar)

Elemental analysis (CHN), sulfur content and HHV values of the biochars are show in Table 3. The CNH composition and sulfur content of the biochars obtained under nitrogen or air flow rates did not change significantly being in the range of 70–80 wt% for carbon, 1.5–1.7 wt% for hydrogen, 0.2 wt% for nitrogen and 0.06 wt% for sulfur. Interestingly, the HHV values are in the range of 25–28 MJ kg<sup>-1</sup> and are greater than the raw CNS (20.7 MJ kg<sup>-1</sup>) being an option as coal fuel [15, 16]. The high carbon content is also an important parameter for using this biochar as activated carbon or to produce valuable chemicals [15, 16].

**Table 2** Products yields of CNS slow pyrolysis (50 g of CNS)

Carrier gas	Flow rate (mL/min)	Solid (wt%)	Liquid <sup>a</sup> (wt%)	Gas (wt%)	Bio-oil (wt%)
N <sub>2</sub>	100	30.4	38.6	31.0	10.7
	250	29.7	41.1	29.2	11.4
	500	29.0	40.8	30.2	10.1
Air	100	29.4	25.6	45.0	6.5
	250	22.0	31.0	47.0	3.6

<sup>a</sup> Aqueous phase plus bio-oil**Table 3** CHN analysis, sulfur content and high heating values of the chars obtained from CNS slow pyrolysis (50 g of CNS)

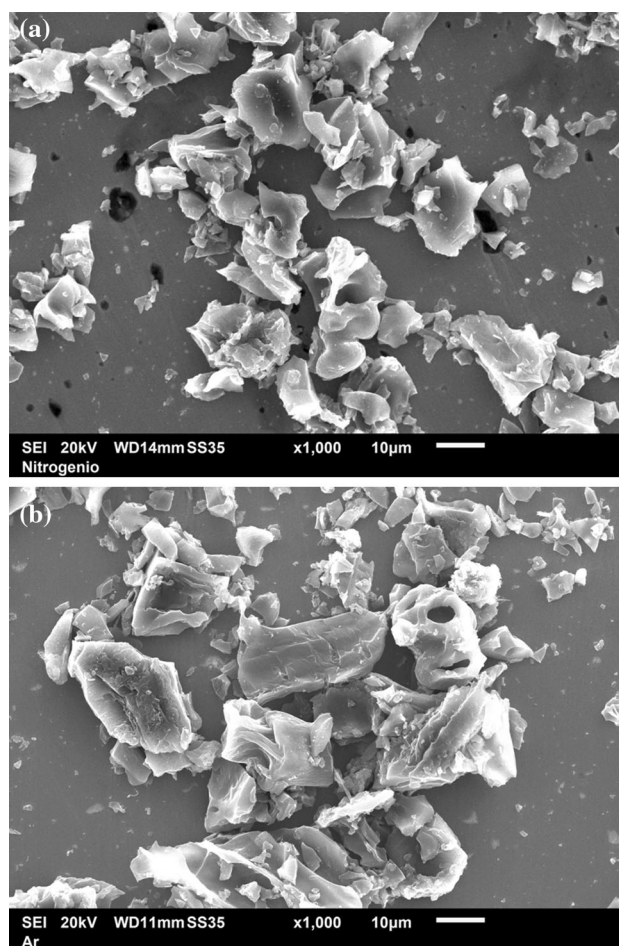
Carrier gas	Flow rate (mL min <sup>-1</sup> )	C (wt%)	H (wt%)	N (wt%)	S (wt%)	HHV (MJ kg <sup>-1</sup> )
N <sub>2</sub>	100	77.1	1.7	0.3	0.05	28.8
	250	73.5	1.6	0.2	0.07	26.6
	500	79.2	1.7	0.2	0.06	27.5
Air	100	67.0	1.4	0.1	0.07	25.0
	250	73.4	1.4	0.2	0.06	25.6

The SEM micrographs of the biochars obtained under nitrogen and air flows are shown in Fig. 3a, b, respectively. The micrographs showed no defined morphology and the absence of pores on both materials. From SEM images is possible to obtain details about the pore structure of biochars that is often related to the specific surface area and determine the adsorption capacity of the material [30]. Semi-quantitative analysis of the obtained chars by EDX showed carbon contents of about 80 wt%, the presence of significant amounts of K (8 wt%) and minor amounts (about 1 wt%) of Mg, Ca and transition metals like Cu, Zn and Fe.

### Characterization of the Liquid Product (Bio-Oil)

Elemental analysis (CHN), sulfur content and HHV values of the bio-oils are shown in Table 4. The CHN composition and sulfur content of the obtained chars did not change significantly at different conditions of carrier gas and stream. HHV values were in the range 31–34 MJ kg<sup>-1</sup> and are similar to those obtained for other biomass [31]. These values, however, are lower than those reported for the commercial Diesel (42.5 MJ kg<sup>-1</sup>) and it is not suitable for use them in pure form. Mixtures with Diesel can be used in modern engines, though [31].

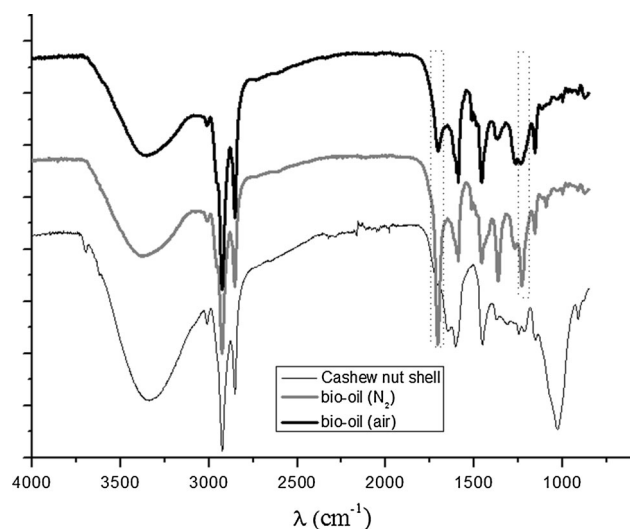
The bio-oils obtained from CNS slow pyrolysis were characterized for the presence of functional groups and FTIR spectra are shown in Fig. 4. The spectra were similar to those described in the literature [18], showing bands and peaks at approximately: 1150 and 1230 cm<sup>-1</sup> (ν C–O), 1360 and 1450 cm<sup>-1</sup> (ν C–H), 1600 cm<sup>-1</sup> (ν C=C), 1700 cm<sup>-1</sup> (ν C=O), 2850 and 2920 cm<sup>-1</sup> (ν C–H) and 3300 cm<sup>-1</sup> (ν O–H). The main difference observed in the FTIR spectrum of raw CNS when compared with the spectra obtained for the bio-oils was the presence of a

**Fig. 3** Scanning electron micrographs of chars obtained in nitrogen (a) and air (b) flow rate of 250 mL min<sup>-1</sup>

broad band at 1028 cm<sup>-1</sup> related to the stretching of the C–O bond on primary alcohols, secondary or tertiary and a less intense band at 911 cm<sup>-1</sup> related to the deformation

**Table 4** CHN analysis, sulfur content and high heating values of the bio-oils obtained from CNS slow pyrolysis (50 g of CNS)

Carrier gas	Flow rate (mL min <sup>-1</sup> )	C (wt%)	H (wt%)	N (wt%)	S (wt%)	HHV (MJ kg <sup>-1</sup> )
N <sub>2</sub>	100	72.7	8.4	0.7	0.03	32.1
	250	70.3	8.4	0.7	0.03	33.7
	500	69.5	8.3	0.6	0.03	32.8
Air	100	74.7	8.6	0.7	0.04	31.6
	250	76.3	8.7	0.7	0.04	33.5



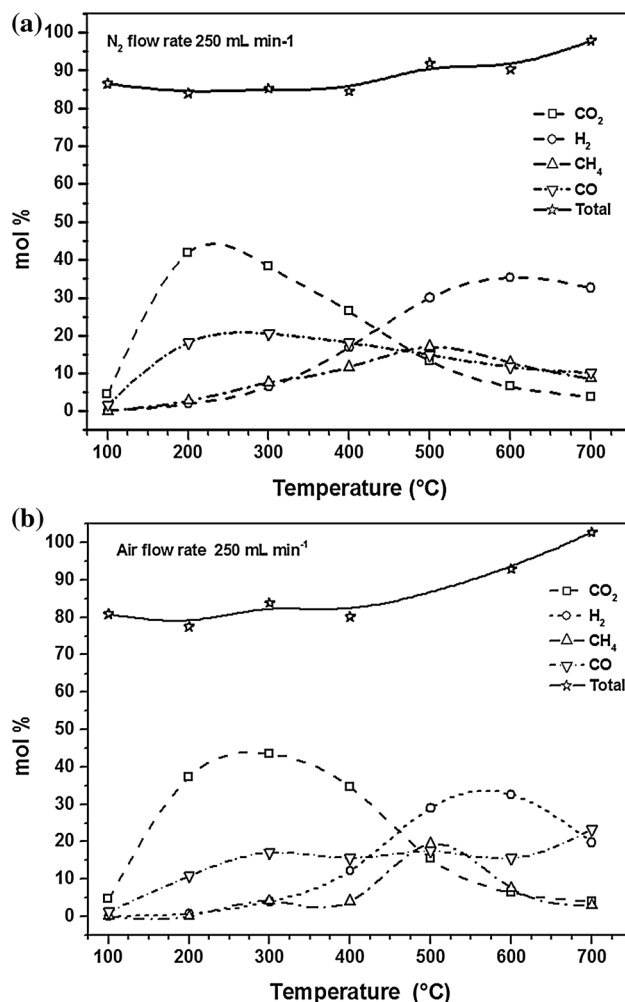
**Fig. 4** FTIR spectra of raw CNS and the bio-oils obtained in nitrogen and air flow rate of 250 mL min<sup>-1</sup>

O–H present in aromatic compounds, which were not observed in the spectra of the bio-oils. This suggests that the phenolic aromatic compounds present in raw CNS, which is dominated by anacardic acid [17], are decomposed during pyrolysis leading to the formation of new compounds. The main differences observed in the FTIR spectra of the bio-oils obtained under nitrogen and air flows were the increase of the relative intensity of the bands at about 1700 cm<sup>-1</sup> ( $\nu$  C=O) and 1230 cm<sup>-1</sup> ( $\nu$  C–O) for the bio-oil obtained under nitrogen flow. This indicates the production of a bio-oil containing major quantities of oxygenated carbon compounds like aldehydes, ketones ( $\nu$  C=O) and alcohols ( $\nu$  C–O) [18]. The oxygen content of bio-oil prevents its utilization as a fuel since the high oxygen content causes high viscosity, poor thermal and chemical stability, corrosivity and immiscibility with hydrocarbon fuels [32].

### Characterization of Gas Products

The pyrolysis experiments were performed under nitrogen and air flow (250 ml min<sup>-1</sup>) and the gas products were collected at different temperatures and analyzed by GC. In the experiment performed under nitrogen flow (Fig. 5a) the following gases were identified and quantified: H<sub>2</sub>, CO<sub>2</sub>,

CO, CH<sub>4</sub>. Figure 5a also shows that the sum of the gases and the difference noted corresponds to other gases or volatile components that have not been identified. The amount of unidentified products decreased as the temperature increased. At 100 °C, it was observed that small amounts of CO<sub>2</sub>, CO, H<sub>2</sub> and CH<sub>4</sub> were formed. From 200–400 °C, it was observed the predominance of CO<sub>2</sub> formation and above 400 °C the CO<sub>2</sub> production decrease strongly with the increase of the temperature. The amount of CO reached its maximum at 300 °C, and with the



**Fig. 5** Chromatograms of gas products at different temperatures in nitrogen (a) and air (b) flow rate of 250 mL min<sup>-1</sup>

increase of the temperature it was observed a slight decrease in its production. The CH<sub>4</sub> formation showed an increase of production in the temperature range of 200–500 °C; a decrease was observed above this temperature. The amount of H<sub>2</sub> begins to increase more sharply from 400 °C and its production becomes predominant at 500 °C resulting in a synthesis gas (syngas—a mixture of H<sub>2</sub> and CO) and varying amounts of CO<sub>2</sub> and CH<sub>4</sub>. Similar results were described by Ryu et al. [33] on the slow pyrolysis of wood, cardboard and textile waste. They also observed two-phase evolution of pyrolysis gas composition; the predominance of CO<sub>2</sub> and CO formation at temperatures below 400 °C and the preferential formation of H<sub>2</sub> from this temperature. Yang et al. [34] studied the pyrolysis of hemicellulose, cellulose and lignin using TGA-FTIR and Micro-GC and observed that hemicellulose degraded at low temperature (200–400 °C) leading to a high CO<sub>2</sub> yield. Cellulose decomposed at 300–450 °C leading to high CO yield and above 400 °C the cracking and deformation of lignin released H<sub>2</sub> and CH<sub>4</sub>. By analyzing the temperatures of the thermal degradation of hemicellulose, cellulose and lignin present in CNS (Fig. 2a) and the resulting gas products of its slow pyrolysis (Fig. 5a) it can be seen that the results are in accordance with the results described by Yang et al. [34].

In the experiments performed in air flow (Fig. 5b), the profile of CO<sub>2</sub> and CH<sub>4</sub> was similar to that observed in nitrogen flow. However, the profile of CO and H<sub>2</sub> were different. Under nitrogen flow, a slight decrease in CO production was observed above 300 °C, and a final H<sub>2</sub>:CO molar ratio of about 3:1 was observed at 700 °C. Under air flow, the CO production increased at 300 °C and remained practically constant until 600 °C, having further increase at 700 °C. With respect to H<sub>2</sub>, its production increased until 600 °C and decreased at 700 °C resulting in a H<sub>2</sub>:CO molar ratio of about 1:1 at this temperature. Synthesis gas with a stoichiometric ratio H<sub>2</sub>:CO of 2:1 or ranging from 1:1 to 2:1 is generally used in major synthesis gas based chemicals production [35].

## Conclusions

CNS slow pyrolysis under nitrogen flow yields 30 wt% of solid (biochar), 40 wt% of liquid (aqueous phase + bio-oil) and 30 wt% of gas products. Under air flow an increase of gas products (46 wt%) were observed with a decrease in the production of biochar and, mainly bio-oil. The biochars obtained under nitrogen and air flows have high contents of carbon (70–75 wt%) and HHV values in the range of 25–28 MJ kg<sup>-1</sup>, which is greater than that of raw CNS (20.7 MJ kg<sup>-1</sup>), presenting suitable properties for use as energy source. Biochars also contain significant quantities of

K (8 wt%) and minor amounts of Mg, Ca, Cu, Zn and Fe showing potential as fertilizer. The bio-oils showed HHV values of about 32 MJ kg<sup>-1</sup> and are not suitable for use in pure form, but can be used in mixtures with Diesel (42.5 MJ kg<sup>-1</sup>). The bio-oils produced under nitrogen flow contain greater quantities of oxygenated carbon compounds like aldehydes, ketones, and alcohols than the ones produced under air flow. The analysis of the gas phase revealed the predominance of CO<sub>2</sub> and CO at temperatures lower than 400 °C and, above this temperature, there was a preferential formation of H<sub>2</sub> resulting in a syngas with different H<sub>2</sub>:CO ratios under nitrogen and air flows. The gas products could be burned to produce the heat needed for the pyrolysis process and/or to produce organic chemicals.

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