Pyrolysis of cashew nutshells: Characterization of products and energy balance

Javier Ábrego, Daniel Plaza, Francisco Luño, María Atienza-Martínez, Gloria Gea

PII: S0360-5442(18)31064-8

DOI: 10.1016/j.energy.2018.06.011

Reference: EGY 13053

To appear in: *Energy*

Received Date: 16 April 2018

Revised Date: 31 May 2018

Accepted Date: 3 June 2018

Please cite this article as: Ábrego J, Plaza D, Luño F, Atienza-Martínez Marí, Gea G, Pyrolysis of cashew nutshells: Characterization of products and energy balance, *Energy* (2018), doi: 10.1016/j.energy.2018.06.011.

Pyrolysis of cashew nutshells: characterization of products and energy balance

Javier Ábrego[*], Daniel Plaza, Francisco Luño, María Atienza-Martínez, Gloria Gea

Thermochemical Processes Group (GPT), Aragón Institute for Engineering Research (I3A), Universidad de Zaragoza, Edificio I+D, C/ Mariano Esquillor s/n, 50018 Zaragoza, Spain

*Corresponding Author, abrego@unizar.es

ABSTRACT

Cashew cultivation leads to the generation of large amounts of nutshells. In order to determine whether pyrolysis could be a suitable method for the valorization of this agricultural residue, cashew nutshells (CNS) from Burkina Faso were pyrolyzed in the temperature range between 400 and 600 ºC in a laboratory-scale fixed bed reactor. The solid, liquid and gaseous fractions were quantified and characterized, with special focus on the solid product. Recovery of the cashew nutshell liquid (CNSL) was accomplished during pyrolysis separately from the pyrolysis liquid. Results suggest that, except for the aqueous fraction, all the products obtained from pyrolysis are suitable for fuel purposes, and that part of the CNSL can be recovered below 200 ºC during the heating process. A preliminary energy balance of the process shows that burning the gases can provide the energy necessary for the process at a pyrolysis temperature of 500 ºC.

Keywords: Cashew nutshell; Pyrolysis; Carbonization; Charcoal; CNSL.

1. Introduction

The cashew (*Anacardium occidentale*) is a bushy, evergreen tree cultivated in tropical zones all over the world. A pseudo-fruit (cashew apple) can be obtained from cashew cultivation and used in the food industry; however, the principal and most valuable product from the cashew is its edible nut. Cashew nuts are enclosed in a shell with an internal honeycomb structure which contains a phenolic liquid (cashew nutshell liquid, CNSL) that is a severe skin irritant, but also a valuable product for various industrial applications [1] that are attracting increasing interest.

Southeast Asian and West African countries are major cashew growers, accounting for 90% of the global production. Statistics for raw cashew nut production worldwide are considered to generally underestimate the actual production [2], but in any case these have consistently grown over time from 1.6 million tons in 2003 [2] to 2.13 in 2006-07 [3] and 3.30 in 2015 [4] due to increased demand for this product. The cashew industry thus generates increasingly significant amounts of shell residues which need appropriate valorization.

Burkina Faso accounts for approximately 2.3% of the world production (75,000 metric tons), with a planted surface area of 4 MHa according to the African Cashew Initiative [5]. Most of the production is destined for exportation and comes from smallholder farmers [6], where generally no special machinery or equipment is available for cashew nutshell processing or recovery of CNSL as a valuable product. Therefore, cashew nutshells are usually disposed of (or temporarily stored for burning) in the field margins [7], posing an important environmental problem if part of the CNSL is released and eventually accumulated or incorporated into soil or water courses, due to its toxicity [8,9]. Moreover, both empty nutshells and CNSL are potentially valuable feedstocks for a variety of applications [10], and their recovery or valorization would substantially increase the profitability of cashew cultivation and processing. Improvements in the cashew nut processing stages also lead to reduced greenhouse gas emissions [7].

CNSL is a valuable product with a variety of applications and a wholesale price estimated in the range of 500-1000 US$ton^{-1} [11]. It can be recovered with varying qualities and recovery yields prior to shelling by mechanical extraction, roasting (at temperatures around 180 ºC) or by means of a hot oil process [12]. Apart from the recovery of CNSL, these pretreatments make the nutshell more brittle and easier to break for nut extraction. Alternatively, steaming can be used as a preprocessing stage before extracting the nut, without CNSL recovery (thus keeping this product in the honeycomb shell structure). In all of these cases, the remaining nutshell residue still contains at least some CNSL (10-100%). As a consequence, acidic vapors are released during combustion [13]. This limits the direct use of this residue as a fuel for supplying energy in the cashew processing stages.

To overcome these issues and efficiently valorize empty nutshells, a pyrolysis process could be used. Batch pyrolysis of nutshells can sequentially achieve CNSL recovery (at temperatures around 200 ºC) and subsequent nutshell conversion into a high quality charcoal (at temperatures typical for pyrolysis processes, 400-600 ºC). In this higher temperature range, a pyrolysis liquid can also be obtained, as well as a combustible gas mixture that can be used to satisfy the energy needs of the process. A batch pyrolysis process could be an economically feasible option for small-scale cashew cultivation sites. Several potentially available kiln and retort designs can be found in the literature [14].

Relatively few studies regarding the pyrolysis of cashew nutshells can be found in the literature [15]. Das and Ganesh [16] reported product distributions from the vacuum pyrolysis of de-oiled CNS (CNSL removal at 150 ºC in an oven prior to pyrolysis) in the temperature range 400-600 ºC. The same authors further focused on the characterization of the liquid fuel products [17] by chromatography, NMR and FTIR, and on the separation of several liquid compounds of industrial interest [18]. Tsamba et al. [19] reported the pyrolysis kinetics of cashew nutshells in a thermogravimetric analyzer. An interesting study comparing pyrolysis of CNS with and without previous CNSL extraction was performed by Melzer et al. [20], with experiments both by TGA and in a tubular rapid pyrolysis reactor. Finally, Moreira et al. [15] recently evaluated the influence of the pyrolysis atmosphere (air or nitrogen) on the product yields and characteristics of pyrolysis.

Most of these studies regarding CNS pyrolysis, except that of Melzer et al. [20], assume a previous step for CNSL extraction. This is currently done in India, but not in West Africa, where there is no market for CNSL. Thus, both CNSL recovery and CNS valorization are major challenges for the development of the cashew sector in this region. In small-scale cashew cultivation sites, implementing a simple integral process that could achieve both objectives would be optimal, without the need for implementing additional processes such as mechanical extraction machines or roasting/oil cooking extraction systems that could require additional investment, increased energy inputs and/or release atmospheric pollutants.

Thus, the novelty in this work is the specific use of batch fixed bed pyrolysis as a single process to achieve integral valorization of the main organic residues of cashew processing, obtaining four product fractions (charcoal, non-condensable gases, CNSL and pyrolysis liquid) that have also been the subject of physicochemical characterization, with special focus on the solid product. In addition, a preliminary energy balance of the process has been performed, based on the product analyses and characterizations and considering the use of pyrolysis gases as the energy source for the process.

The two liquid fractions, CNSL and pyrolysis liquid, are obtained separately at different heating stages of the pyrolysis reactor. Due to the industrial importance of these liquid products (especially CNSL) and the large number of techniques required to undertake an extensive liquid characterization, a subsequent paper will be specifically devoted to the detailed liquid composition.

2. Materials and Methods

2.1. Feedstock

Cashew nutshells (CNS) were collected from a production site in Bobo-Dioulasso, Burkina Faso [21]. Empty nutshells were obtained after steaming and semi-manual nut extraction with no further treatments. Table 1 shows the proximate and ultimate analyses of the feedstock, as well as its heating value.

As can be seen in Table 1, the higher heating value (HHV) of CNS is relatively high if compared with most agricultural residues, and the C proportion is also higher. Both factors are probably related to the presence of CNSL within the internal honeycomb structure. Nutshells also have low moisture content.

Table 1. Characteristics of cashew nutshells (CNS).

Analysis		Instrument/Standard	Value
Proximate analysis (%, a.r.)	Moisture	ISO-589-1981	5.30 ± 0.30
	Volatiles	ISO-5623-1974	81.18 ± 1.35
	Ash	ISO-1171-1976	2.02 ± 0.04
	Fixed C	By difference	11.50
Elemental analysis (%, a.r.)	C	LECO CHN628	53.69 ± 2.11
	H		7.11 ± 0.01
	N		0.35 ± 0.03
	O	By difference[a]	36.83
Apparent density ($kg\cdot m^{-3}$)		[b]	365.2
Energy density ($MJ\cdot m^{-3}$)		-	8191 ± 321
HHV ($MJ\cdot kg^{-1}$, a.r.)		ISO-1928-2009	22.43

[a] Oxygen (% wt) = 100-Carbon (%)-Hydrogen (%)-Nitrogen (%)-ash content (%).

[b] A known volume of material (25 mL) was weighed and the density was calculated.

2.2. Thermogravimetric experiments

Before the lab-scale pyrolysis experiments, the thermal degradation behavior of CNS was studied in a thermogravimetric analyzer (TGA) Netzsch STA 449 Jupiter®. Two types of raw material were used for TGA experiments: untreated and CNSL-extracted nutshells, respectively. In the second case, a Soxhlet extraction stage was performed using dichloromethane as solvent. Thus, the main differences in the TGA profiles of both samples can be attributed to the presence or absence of a fraction of CNSL. The samples (around 35 mg) were heated up to 900 °C at 10 °C min^{-1} under N_2 atmosphere (flow rate of 50 mL (STP)·min^{-1}). Two replicates were performed for each feedstock.

2.3. Lab-scale pyrolysis system

A bench-scale batch reactor was used to pyrolyze the untreated CNS. Approximately 800 g of cashew nutshells were placed in the reactor for each run. Eight K-type thermocouples were placed at different radial and axial positions to register the temperature profiles in the reactor. Experiments were performed at 400, 500 and 600 °C, with holding time of at least 30 min after reaching these target temperatures, and at a heating rate of 5 °C·min^{-1}. Most experiments were carried out under autogenous atmosphere, i.e. without using inert carrier gases such as N_2, and only in one case was N_2 (50 mL (STP) min^{-1}, final temperature 500 ºC) used as an internal standard to measure the gas flow rate exiting the reactor (hereinafter referred to as Pyr-N_2). Two separate condensable collection systems were included: first, a vertical outlet from the bottom of the reactor was connected to a flask to collect by gravity the CNSL released in the early stages of pyrolysis. Second, the vapors produced during the pyrolysis process exited the reactor through an outlet in the upper side and passed through the condensing zone. The condensable fraction (water and organic compounds) was collected in two ice-cooled condensers and one electrostatic precipitator. The composition of non-condensable gases (CO_2, CO, H_2, CH_4, C_2H_2, C_2H_4, C_2H_6 and H_2S) was analyzed by a micro-gas chromatograph (micro-GC) connected online. The experiments were conducted in duplicate. Figure 1 illustrates the laboratory scale setup, which is very similar to that used in previous works by our group [22] except for the absence in this case of a stirring device inside the reactor.

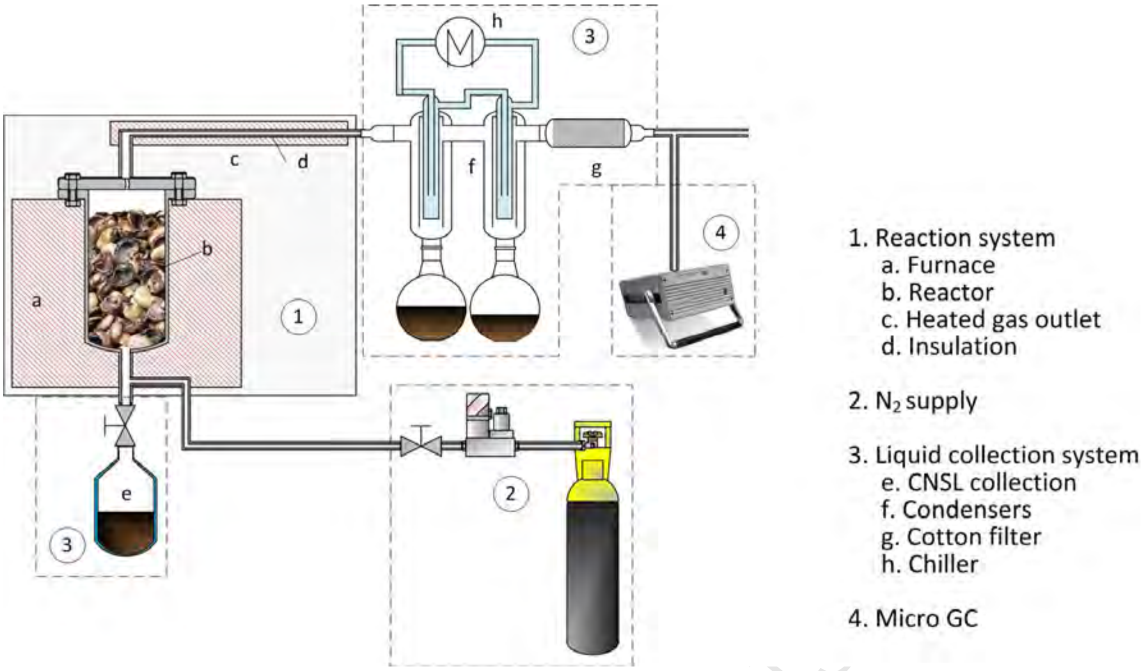

Figure 1.Diagram of the laboratory scale pyrolysis plant.

The mass yields of solid (char) and liquid (all liquid products including CNSL) were determined gravimetrically. The mass yield of gas was calculated by difference with the exception of the experiment performed using N_2 as internal standard for which the gas yield was determined taking into account the gas composition provided by the micro-GC and the known volumetric flow of nitrogen introduced.

The lower heating value of the gas (free of N_2) (LHV_{gas}) for the Pyr-N_2 experiment was calculated considering the gas composition and the lower heating value of each gas compound.

For all the runs, the ultimate and proximate analyses, the higher heating value, the apparent density and the pH and electrical conductivity of the char were measured following the International Biochar Initiative product testing guidelines [23,24].

The pyrolysis liquid obtained in all the experiments was separated into two phases (aqueous phase (AP) and organic phase (OP)) by decantation. Besides, the CNSL fraction was recovered separately. The water content (%) of AP, OP and CNSL was analyzed by the Karl-Fischer titration method. The density of the OP and CNSL was determined using a portable Mettler Toledo densimeter (model Densito 30 PX). Finally, the ultimate analysis and the higher heating value (HHV) of the OP and CNSL were also measured.

3. Results and discussion

3.1. TGA

Figure 2 shows the TGA and DTG curves for raw and extracted nutshells. CH_2Cl_2 extraction produced a loss of extractives corresponding to 31.2% of the original mass of cashew nutshells. The initial values of the TGA lines in Figure 2 reflect this mass difference caused by the extraction process. The DTG lines have been calculated accordingly to enable better comparison.

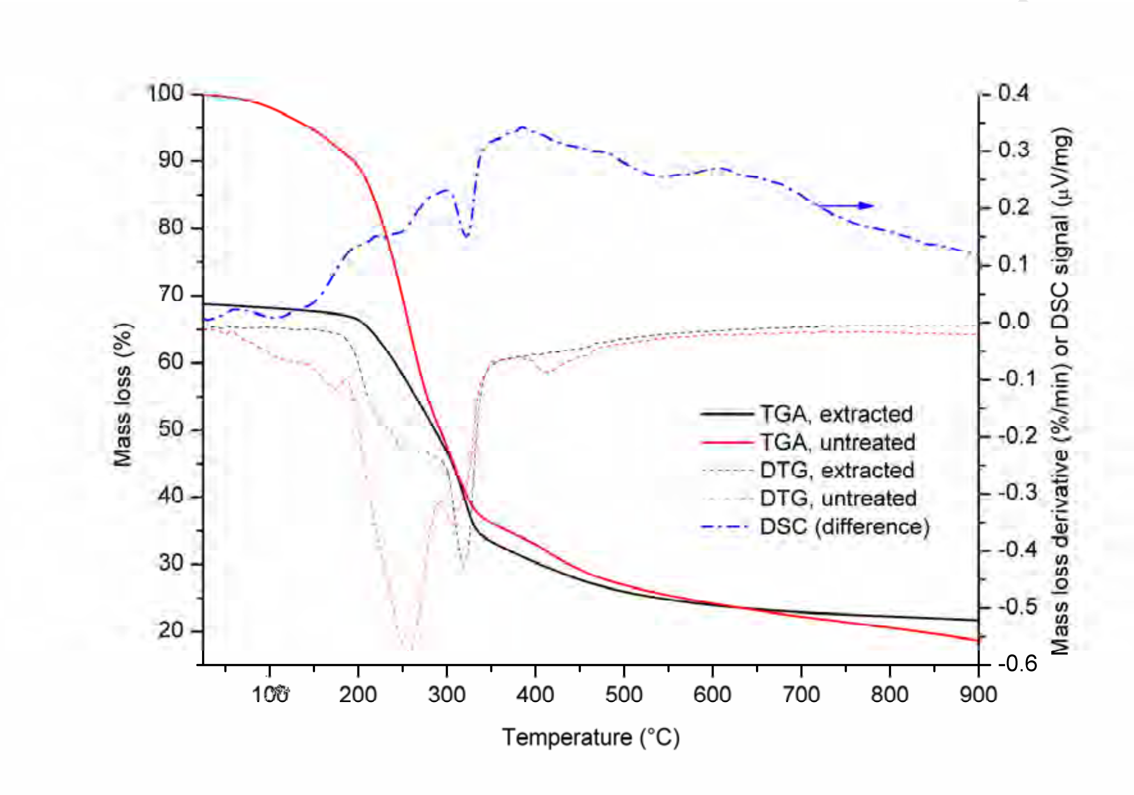

Figure 2. TGA-DSC for untreated and extracted CNS.

The TGA curve of the unextracted sample is analogous to those reported by Melzer et al. [20] and Moreira et al. [15]. As can be seen from comparing the TGA curves of the unextracted and extracted samples, partial evaporation or decomposition after release of CNSL causes major weight loss at temperatures below 300 ºC (the temperature at which the mass loss percentages of untreated and extracted samples are approximately equal). A major peak in the DTG curve for the unextracted sample evidences this fact. This evaporation overlaps with the onset of thermal decomposition of the CNS constituents (hemicellulose and cellulose). Moreover, due to the high boiling point of the liquid CNSL compounds (e.g. 225 ºC at 10 mmHg for cardanol), some partial evaporation still occurs at temperatures higher than 300 ºC. Therefore, it also partially overlaps with the main stage for lignin decomposition, that appears to proceed at around 322 ºC as reported by some authors working at similar temperatures [25–27]. The A small DTG peak around 175 ºC appears for unextracted CNS, previously attributed to the decarboxylation of anacardic acid to cardanol [20].

At temperatures higher than 350 ºC, the evolution of the DTG curves is similar, although lower decomposition rates (and therefore a higher final char yield) are found for the extracted sample. The main difference in this region is a small mass loss peak at around 420 ºC in the untreated samples that could correspond to the decomposition of polymeric materials that are formed as a result of thermally treating natural CNSL [10].

In Figure 2, a differential DSC signal is also presented. This curve has been calculated by subtracting the DSC curve of the extracted sample from that of the untreated sample, and accounts for the differences in heat evolution between the two samples. The increasing curve in the first half of the graph evidences the more endothermic character of raw CNS decomposition, as expected since additional sensible heat is needed for CNSL evaporation or decomposition. The negative peak in this curve at around 322 ºC may indicate lignin decomposition, more visible in the extracted samples. In the second half of the graph, decomposition of the untreated sample is still more endothermic (positive values) due to the increased solid mass loss at high temperatures. As a concluding remark, the TGA data suggest that solvent extraction of CNSL from nutshells could have a positive impact from the point of view of the energy requirements of pyrolysis.

3.2. Temperatures profiles in the fixed bed reactor

The evolution over time of the temperatures inside the fixed bed reactor gives additional insight into thermal events occurring during pyrolysis. This evolution is depicted in Figure S1 in the Supporting Information Section. During the reactor heating, two high temperature overshoots are found below 450 ºC. These thermal events have been observed for several biomasses heated along the lateral surface of cylindrical reactors, and are associated with exothermic degradation of hemicellulose and lignin, separated by a thermally neutral or endothermic stage of combined degradation of cellulose and lignin [28]. Furthermore, they could be correlated with the observed negative (exothermic) events in the differential DSC presented in Figure 2 at around 250 and 322 ºC respectively. Di Blasi et al. [29] also detected high temperature overshoots in the center of a packed bed during the pyrolysis of similar materials (hazelnut shells) and attributed this behavior to several factors: their chemical composition (rich in extractives, hemicellulose and lignin), the presence of inorganics that may exert a catalytic effect on char formation, and their textural structure that favors intraparticle secondary reactions.

In the lower part of the bed, temperatures are significantly lower in the first half of the experiment, possibly because of the gradual release of liquid CNSL that flows downwards through the reactor. Once these zones are free of CNSL (that is collected in the flask located below), they heat up rapidly and, as a result, the fixed bed temperatures are fairly uniform and close to the set point temperature above 400 ºC.

3.3. Product yields

The evolution of the lumped product yields (solid, liquid and gas) with temperature is shown in Figure 3.

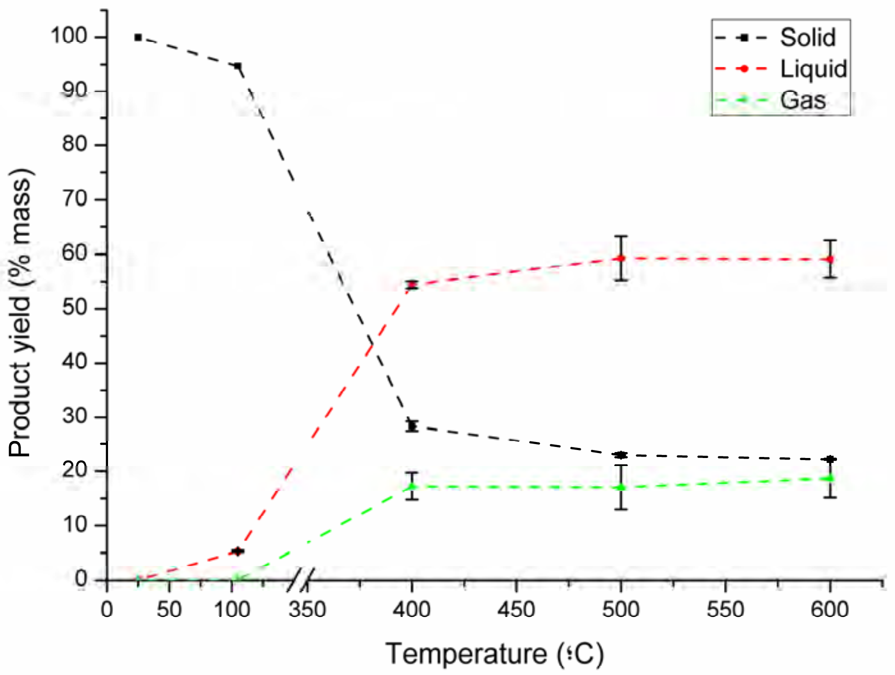

Figure 3. Product distribution from pyrolysis. Points at the left of the horizontal axis break are plotted as a reference and represent raw and dried CNS, respectively. The values are expressed as mean ± standard deviation.

The charcoal yield is below 30% in all the experimental range (400-600 ºC), and slightly decreases with an increase in temperature. The liquid yield is 54 ±2% at 400 ºC with further increases, if any, being statistically insignificant. The gas yield, calculated by difference, must therefore be in accordance with these observations (around 15%). In the only experiment where N_2 was used as internal standard, the balance closure was calculated at 97.9 %. This result suggests that gas yields calculated by difference in the rest of the experiments are reasonably accurate.

3.4. Solid fraction

Table 2 summarizes the solid product characteristics that were determined in this study. Chars present relatively constant low moisture contents (around 3%), decreasing contents of volatiles and oxygen and increasing contents of ashes, carbon and fixed C with increasing temperatures. These trends are in accordance with those extensively reported in the literature [30,31].

Table 2. Characteristics of chars produced in the temperature range of this study.

Analysis		Pyrolysis temperature (ºC)		
		400	500	600
Proximate analysis (%, a.r.)	Moisture	3.64 ± 0.04	2.80 ± 0.03	3.30 ± 0.60
	Volatiles	28.3 ± 0.5	14.0 ± 1.0	9.6 ± 0.4
	Ash	7.24 ± 0.05	9.6 ± 0.3	11 ± 1
	Fixed C	60.8	74	77
Ultimate analysis (%, a.r.)	C	71.64 ± 0.27	75.83 ± 2.24	77.42 ± 3.99
	H	4.31 ± 0.04	2.94 ± 0.06	2.14 ± 0.01
	N	1.48 ± 0.08	1.56 ± 0.14	1.32 ± 0.05
	O	15.33 ± 0.29	10.07 ± 2.26	8.12 ± 4.11
Fixed carbon yield, y_{FC} (%)		17.6 ± 0.7	17.3 ± 0.4	17.4 ± 0.4
Apparent density ($kg\cdot m^{-3}$)		159.6 ± 7.3	155.3 ± 8.6	166.5 ± 6.4
Energy density ($MJ\cdot m^{-3}$)		4760 ± 218	4601 ± 260	4777 ± 220
HHV ($MJ\cdot kg^{-1}$, a.r.)		29.8 ± 0.1	29.6 ± 0.3	28.7 ± 0.7
pH		8.85 ± 0.02	9.17 ± 0.06	9.40 ± 0.04
Electrical conductivity ($\mu S\cdot cm^{-1}$)		355 ± 4	539 ± 91	1475 ± 12

The fixed carbon yield (y_{FC}), defined as a function of the char yield (y_{Char}), the fixed C content of chars (*%FC*) and the ash content of the biomass (*%feed ash*), is a good indicator of the carbonization efficiency [30,32]:

$$y_{FC} = y_{\,Char} \cdot \frac{\%FC}{100-\%feed\ ash} \qquad (1)$$

The values of y_{FC} remain approximately constant in the temperature range of this study, at around 17.5%. The same applies to the apparent density and energy density of chars. However, both values are considerably lower than those of the parent biomass. The decrease in apparent density can be mainly attributed to the release of CNSL, and also partially to the development of porosity in the carbon matrix [31]. Indeed, the release of CNSL (which has a very high HHV, as will be discussed in Section 3.5) also contributes to the lower values of energy density of the chars. The HHVs of chars are near 30 MJ·kg^{-1}, but unlike other biomasses [31] show a slight decrease with increasing pyrolysis temperatures. This behavior is typical of biomasses with high ash contents [33].

Both the O/C and H/C molar ratios for CNS and chars were calculated on a dry matter basis and are represented in Figure 4 in a Van Krevelen diagram. As expected, the O/C and the H/C molar ratios of chars obtained are significantly lower compared to CNS. The evolution of these values illustrates the change in composition from CNS (similar to lignocellulosic biomass) to char (similar to coal) as the pyrolysis advances.

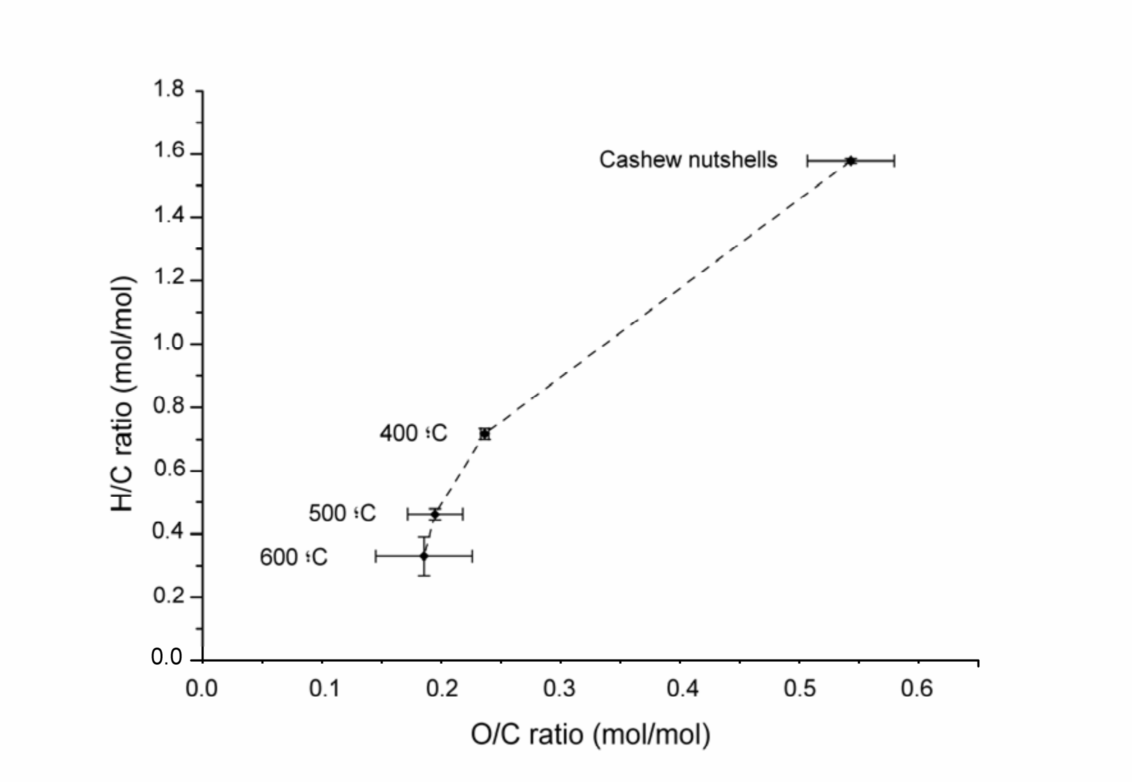

Figure 4. Van Krevelen diagram for CNS and chars.

Beyond the use of chars as a fuel, electrical conductivity and pH are additional parameters which are relevant if chars are intended for use as soil amendment (biochar) [23]. The pH values are between 8.85-

9.40 and increase with temperature, as reported elsewhere [31]. Finally, the electrical conductivity increases with increasing temperature. This is in accordance with the observed decrease in electrical resistivity (the inverse of conductivity) of chars with temperature, although in this case the variation is modest and does not span several orders of magnitude [30,31].

In the context of smallholder farmers in Burkina Faso, the use of CNS chars as a fuel may be optimal since charcoal for domestic cooking is extensively used in the country, especially in urban areas [34]. Nevertheless, recent results also show promise for the application of biochars from agricultural residues in tropical soils in Burkina Faso [35], so this end use cannot be ruled out. In general, the characteristics of the produced chars make them suitable for cooking purposes, according to Foley [36], although they have relatively high ash contents.

3.5. Liquid fractions

Two main liquid products can be distinguished after pyrolysis: a significant fraction of CNSL was recovered in the specific collection system for this purpose (shown in Figure 1), whereas a pyrolysis liquid was condensed in the upper reactor outlet. This liquid could be further separated into two fractions after simple decantation: an aqueous phase (AP), with water contents ranging between 85 and 89%, and an organic phase (OP).

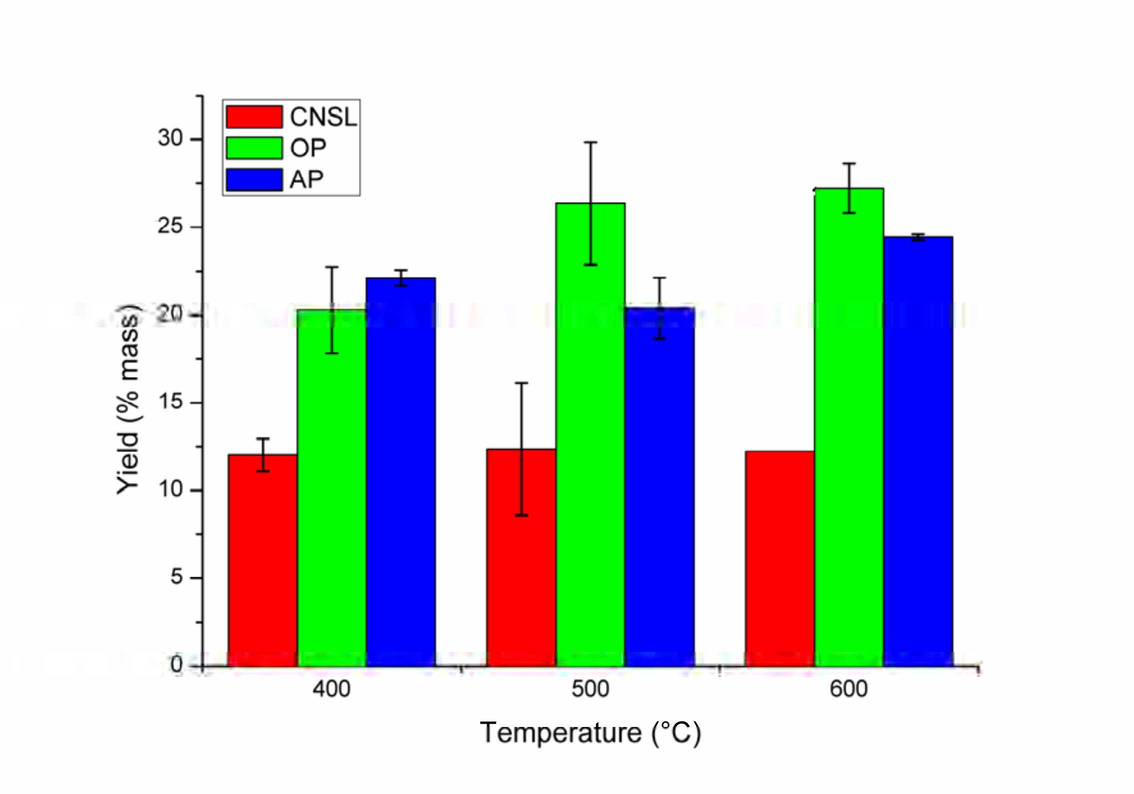

Figure 5. Yields of the pyrolysis liquid fractions as a function of temperature.

Figure 5 shows the mass yields of each one of these liquid products. As seen in the Figure, the amount of CNSL recovered is independent of temperature, whereas the OP and AP experience a statistically significant increase from 400 to 500 ºC, and from 500 to 600 ºC, respectively. The yield of CNSL (around 12%) is far from the value of 31.2% obtained by CH_2Cl_2 extraction, as shown in the earlier TGA analysis. Thus, the efficiency of pyrolysis for CNSL recovery is less than half that of solvent extraction (the rest of this liquid fraction either ends up in the bio-oil fraction or is decomposed into lighter compounds). However, the CNSL yield is comparable to those reported in the literature under low-temperature pyrolysis conditions [16], and pyrolysis has the additional benefit of obtaining char and a potentially valuable organic phase (in which some of the unextracted CNSL might be present).

Table 3 summarizes the main characteristics of the CNSL and OP fractions. The low water content of the organic phases (below 2.2%), the low oxygen content and the high HHV (close to values of petroleum fuels, 41-43 $MJ\cdot kg^{-1}$ [37]) make this liquid fraction highly suitable for its use as a fuel, with prior separation of the aqueous phase. Applying higher pyrolysis temperatures produces an OP with higher HHVs, lower oxygen contents and slightly lower water content. CNSL has almost no water, and its heating value is similar to that of the OP and is constant regardless of the pyrolysis temperature. The latter would be expected due to the fact that CNSL is recovered in the initial stages of each experiment (below

200 ºC) and further heating does not affect this recovery. Its ultimate analysis also shows similar composition to the OP. The incorporation of a fraction of CNSL into the OP can partly explain this fact.

Table 3. Characteristics of CNSL and OP produced in the temperature range of this study.

Analysis		Recovered CNSL			Organic phase (OP)		
		Pyrolysis temperature (ºC)			Pyrolysis temperature (ºC)		
		400	500	600	400	500	600
Water content (%)		0.3 ± 0.2	0.4 ± 0.1	0.3 ± 0.1	2.2 ± 0.4	1.8 ± 0.3	1.6 ± 0.02
Ultimate analysis (%, a.r.)	C	80.8 ± 0.3	81.3 ± 0.5	81.4 ± 0.5	77.6 ± 0.2	79.3 ± 0.9	79.0 ± 0.5
	H	10.1 ± 0.04	10.1 ± 0.1	10.3 ± 0.1	10.0 ± 0.1	10.2 ± 0.3	10.9 ± 0.6
	N	0.24 ± 0.01	0.24 ± 0.14	0.24 ± 0.04	0.8 ± 0.1	0.8 ± 0.1	0.7 ± 0.1
	O	8.9 ± 0.3	8.3 ± 0.5	8.1 ± 0.5	11.6 ± 0.2	9.7 ± 1.0	9.4 ± 0.8
Density ($kg \cdot m^{-3}$)		907 ± 2	909 ± 16	912 ± 12	931 ± 17	936 ± 11	927 ± 24
HHV ($MJ \cdot kg^{-1}$, a.r.)		39.9 ± 0.1	39.7 ± 0.3	39.9 ± 0.1	37.8 ± 0.03	38.3 ± 0.3	39.6 ± 0.9

Comparing data from Table 3 with compositional data available from the literature [10], it can be concluded that the CNSL obtained as a byproduct of pyrolysis has a similar composition to that of the technical CNSL usually obtained in the cashew industry, with a slightly higher oxygen content that might be caused by higher proportions of anacardic acid or cardol. A graphical comparison of these compositions in a Van Krevelen diagram can be found in the Supporting Information Section.

3.6. Gas fraction

The gas product obtained from pyrolysis is composed of CO_2, CO, H_2 and light hydrocarbons (CH_4, C_2H_4 and C_2H_6). Only trace amounts of H_2S were detected. The mass yield to each gas species was able to be calculated at 500 ºC with data from the Pyr-N_2 experiment. These values are presented in Table 4, together with the average HHV of the gases. CO_2 is the main component (representing around 68% of the total gas mass) followed by CH_4 and CO (15 and 12%, respectively).

Table 4. Mass yields of each gas component (% of original CNS mass) and average higher heating value. Experiment at 500ºC.

Individual gas yields						HHV_{avg}
CO_2	CO	H_2	CH_4	C_2H_4	C_2H_6	
11.65	2.08	0.09	2.57	0.13	0.55	11.9 $MJ \cdot kg^{-1}$ gas

Additionally, the evolution of the gas flow rate at the same final temperature of 500 ºC can be found in Figure S3 in the Supporting Information Section. The maximum peak of gas generation is found at an average temperature of around 400 ºC. Very similar gas evolution profiles have been reported for other types of biomass [38].

To provide additional insight into the evolution of each gas species during pyrolysis, gas compositions against average temperature and reaction time are plotted in Figure 6 for the experiments carried out at 600 ºC, which can be considered representative of the entire experimental range studied in this work (experiments at lower temperatures show almost identical curves).

CO_2 is the major compound up to 500 ºC, and its formation can be attributed to hemicellulose and cellulose decomposition, together with the decarboxylation of the remaining fraction of cardanoic acid (not recovered as CNSL) to cardanol. At around 450 ºC, its volume percentage decreases dramatically, and significant amounts of CH_4, H_2 and light hydrocarbons begin to evolve. These products are important in cellulose and lignin decomposition [25]. At the end of the temperature range, CH_4 and H_2 become the dominant gases with very low amounts of the rest of the compounds. CO briefly peaks at 200 ºC, which might be caused by the onset of hemicellulose degradation, as observed by Yang et al. [25]. After this peak disappears, this component experiences a steady increase that may be caused by the subsequent decomposition of cellulose and lignin. The evolution of gas products is similar to that reported by Moreira et al. [15], the main difference being the continued increase of the CH_4 evolution beyond 500 ºC.

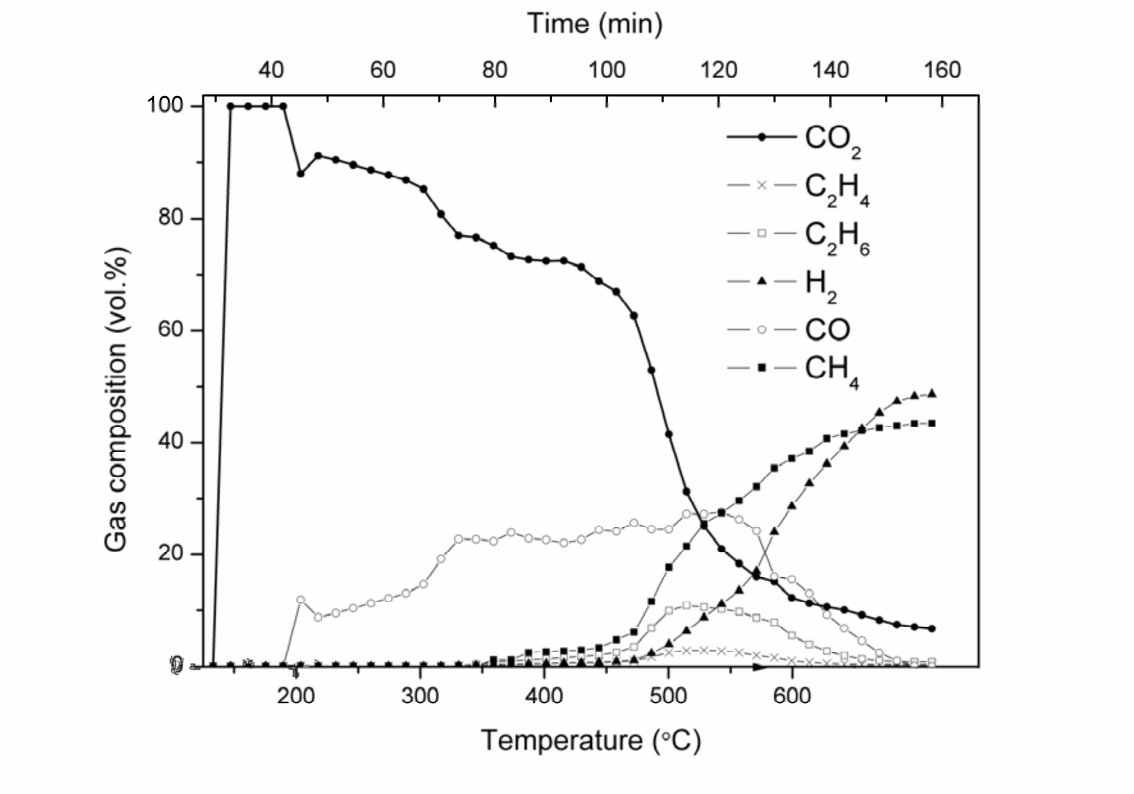

Figure 6. Evolution of gas composition as a function of time and pyrolysis temperature.

3.7. Atomic balance

The elemental analyses of most of the pyrolysis products (char, CNSL, OP), and the gas composition for the experiment made at 500 ºC using N_2, allow us to estimate the distribution of the main CNS elements (C, H, O) in the products obtained at that temperature. Since no ultimate analysis was performed for the AP fraction, the amount of each element in this phase was estimated considering its water content (86.0 %) and assuming that acetic acid is the only organic compound it contains. Acetic acid has been extensively mentioned in the literature as a major component of the aqueous fraction of pyrolysis liquids [39,40]. Using this approach, reasonable balance closures were found for the three elements (ranging between 89.8 and 109.0%). The results are shown in Figure 7. As can be seen, the high oxygen content of the starting CNS is concentrated after pyrolysis in the AP and the gas phases. Both fractions contain more than 82% of this element. In accordance with this observation, these phases show the lowest carbon content (around 14%).

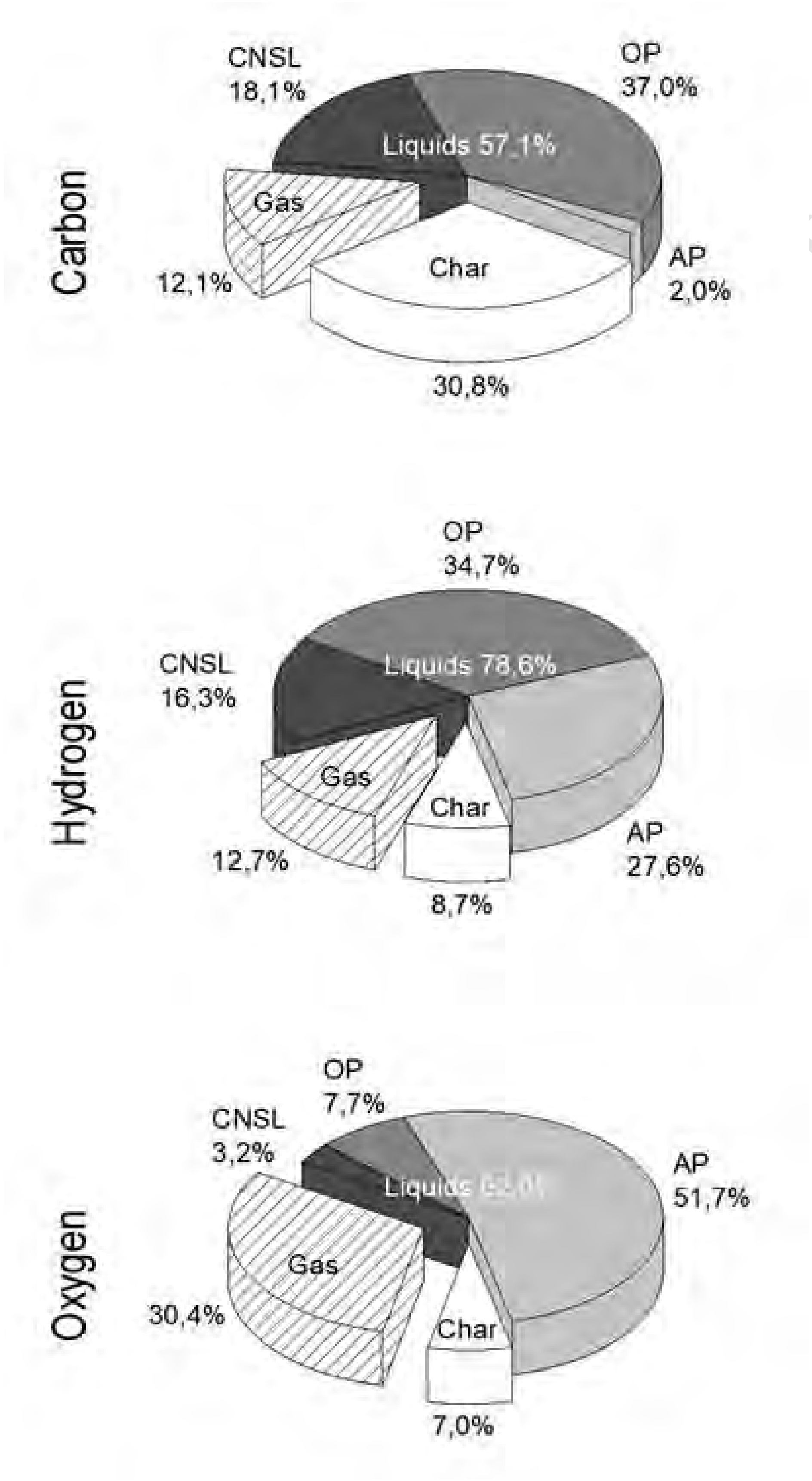

Figure 7. Distribution of the main elements (C, H, O) in the pyrolysis products at 500 ºC.

3.8. Energy balance and heat for pyrolysis

Two approaches were taken for performing an energy balance, using data from the experiments made at the intermediate temperature of 500 ºC. First, an energy balance considering the products (char, AP, OP, CNSL and gases) and reactant (CNS) at the standard temperature of 25 ºC was made by subtracting the standard enthalpies of formation of each one of them, which were calculated from their HHVs and the enthalpies of the corresponding combustion products, as detailed elsewhere [41,42]. The resulting value, Q_{py}^0, represents the standard heat for pyrolysis, i.e., without considering the sensible and latent heat of all the obtained products. Second, we estimated the energy flows associated with the sensible heat carried by the products (and latent heat of the condensable vapors), and thus obtained the heat for pyrolysis Q_{py}. This constitutes a more practical approach, since full recovery of this heat is unachievable. However, in order to do this, some assumptions and simplifications were needed:

- In batch pyrolysis reactors, gases and condensable fractions are continuously released within wide temperature ranges. Thus, average temperatures were taken: 250 ºC for the release of AP and OP, 400 ºC for gases, and 180 ºC for the release of CNSL. These temperatures coincide with the median temperature of the main mass loss stage in TGA (mainly attributable to liquid formation), with the maximum gas flow rate depicted in Figure S3, and with the reported value of CNSL released from the nutshells, respectively.
- The main difficulty of this approach is estimating the enthalpy of the condensable vapors from pyrolysis. Assumptions on this point were made as follows: (a) AP, as mentioned in the atomic balance calculations, was considered to be formed only by water and acetic acid. (b) CNSL, due to its high boiling point (225 ºC at 10 mmHg [43]), was assumed to be entirely released in liquid phase at the mentioned temperature of 180 ºC. The composition of CNSL was simplified as cardanol, and due to the lack of available data its specific heat capacity was estimated ($2.09\ kJ \cdot kg^{-1} \cdot K^{-1}$) using the Benson module from HSC Chemistry software [44]. (c) Estimation of the enthalpy of formation (vapor phase) and sensible heat of OP was made using the procedure described by Yang et al. for bio-oil [45], which requires knowledge of the H/C and O/C atomic ratios of this fraction (which were calculated from data shown in Table 3). In the work of Yang et al., the estimation was performed for all the organic compounds of bio-oil, and relatively high errors were found for carboxylic acids. Therefore, considering acetic acid

separately from AP in our case seems reasonable. Water vapor was also considered separately in the referenced work.

- The energy balance could only be made for experiments made at 500ºC, since the mass yield of gases was determined for this temperature only.

Taking into account all these factors, Q_{py}^{0} was estimated as 0.47 MJ/ kg CNS, which represents an energy requirement of 2.1% of the HHV of the raw material. Q_{py} was estimated as 2.02 MJ/kg CNS (9.0% of HHV CNS). This value is slightly above the range reported by Yang et al. [45] or Daugaard and Brown [46] for various biomasses (0.8-1.6 MJ/kg dry at 500 ºC) and is partly attributable to the use of as-received biomass in this work (with 5.3% moisture). Sensible and latent heat of the product streams made up 5.9% of the HHV of the raw CNS.

With Q_{py} and the HHVs of the product fractions, the energy balance of the pyrolysis process can be summarized in a Sankey diagram, as shown in Figure 8. The balance closure is reasonably good at 105%. Interestingly, the energy content of the pyrolysis gases is 9.4% of the HHV of CNS, enough to supply the energy requirements for pyrolysis at 500 ºC. This is in accordance with the lower limit of 450 ºC reported by Crombie and Masek for self-sustainable pyrolysis processes of wood chips and wheat straw [47].

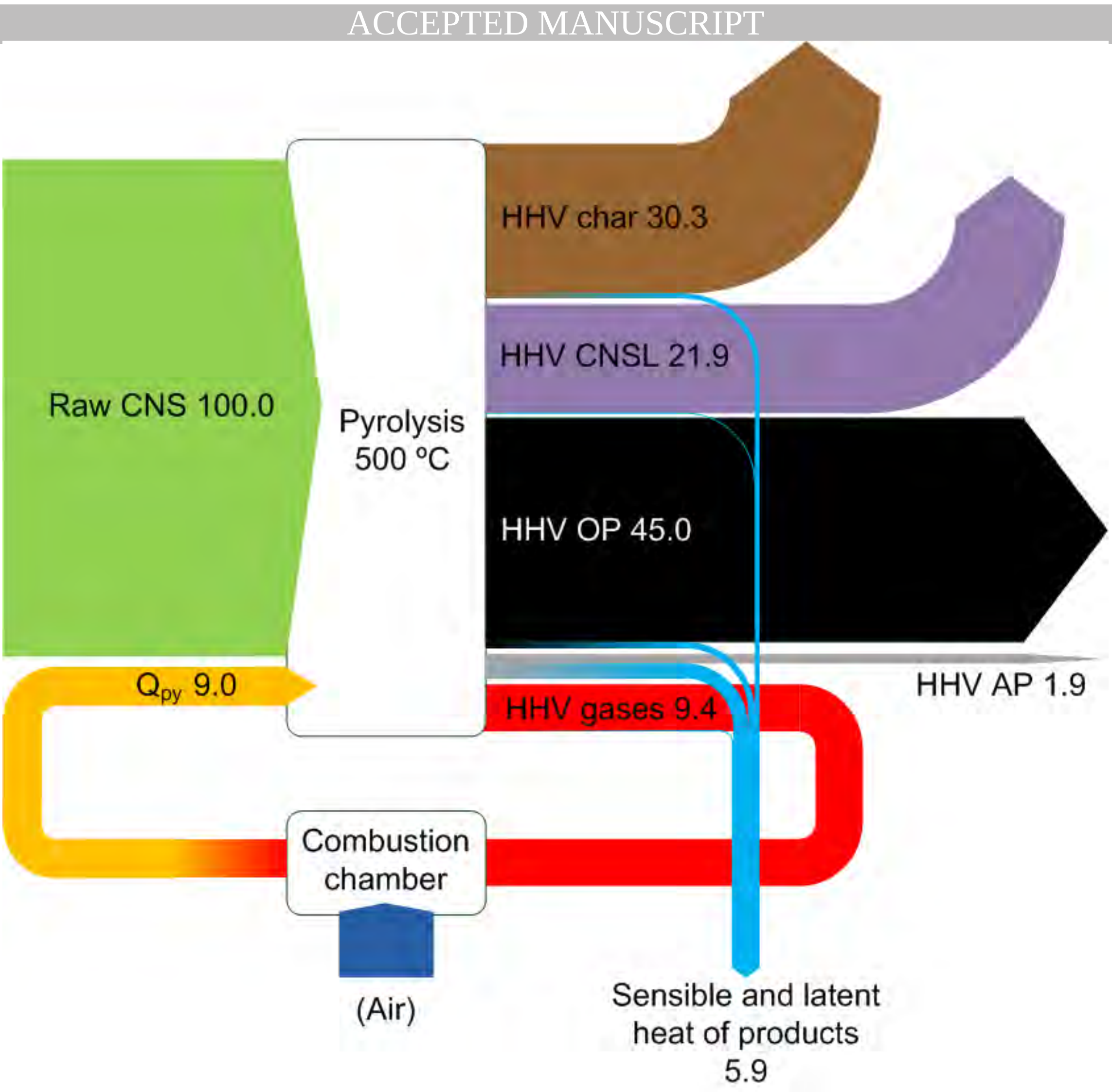

Figure 8. Sankey diagram for pyrolysis of CNS at 500 ºC (energy units based on % HHV of CNS).

4. Conclusions

Pyrolysis represents a promising valorization pathway for the large amounts of cashew nutshells that are nowadays underutilized in many production sites. Lab scale experiments performed in the range 400-600 ºC demonstrate the feasibility of obtaining solid and liquid fractions usable as fuels while also allowing the recovery of a fraction of the CNSL contained in the nutshells, which can be used as a fuel or for other industrial uses. 500 ºC seems to be the optimal temperature in this range, since no significant changes in the product distribution are observed at higher temperatures. The combined heating values of the readily available energy products (char and organic liquid phase) represent around 75% of the HHV of the raw material. Char could be alternatively used as soil amendment where soil characteristics make it advisable; however, further studies are needed to confirm the feasibility of this option. A preliminary energy balance shows that combustion of the pyrolysis gases (9.0 % of the starting HHV) is enough to energetically sustain the pyrolysis process. A subsequent paper will focus on a detailed analysis of the liquid products (CNSL and pyrolysis liquid) obtained as a result of the proposed process.

Acknowledgments

The authors are indebted to the Universidad de Zaragoza (Cátedra de Cooperación para el Desarrollo, Project Call 2016) for providing funding support for this work, and to Julia Artigas (Fullwell Mill Co. Ltd) for her guidance in Bobo-Dioulasso and for providing the CNS for the study.

References

[1] Anilkumar P, editor. Cashew Nut Shell Liquid - A goldfield for functional materials. Cham: Springer International Publishing; 2017. doi:10.1007/978-3-319-47455-7.

[2] Clay JW. World agriculture and the environment : a commodity-by-commodity guide to impacts and practices. 1st ed. Washington, DC: Island Press; 2004.

[3] Foretell Business Solutions Private Limited. Cashew Handbook 2008. A global perspective 2008:261. http://cashewinfo.com/pdf/CashewHandbook_2008.pdf (accessed May 30, 2018).

[4] Rabany C, Rullier N, Ricau P. The African Cashew Sector in 2015 - General trends and country profiles. Analysis of cashew production, processing and trade in Africa 2015. http://www.rongead.org/IMG/pdf/african_cashew_market_review_rongead_ica_2015.pdf (accessed May 30, 2018).

[5] Kankoudry Bila N, Djibo O, Constant P, Sanon B. Analysis of the Cashew Value Chain in Burkina Faso 2010. http://www.africancashewinitiative.org/imglib/downloads/ACI_BurkinaFaso_gb_high resolution.pdf (accessed May 30, 2018).

[6] Fitzpatrick J. Cashew Nut Processing Equipment Study – Summary African Cashew initiative 2011. http://www.africancashewalliance.com/sites/default/files/documents/equipment_study_ab_pdf_final_13_9_2011.pdf (accessed May 30, 2018).

[7] Agyemang M, Zhu Q, Tian Y. Analysis of opportunities for greenhouse emission reduction in the global supply chains of cashew industry in West Africa. J Clean Prod 2016;115:149–61. doi:10.1016/j.jclepro.2015.12.059.

[8] Matias R, Rosa AC, Kleber A, Oliveira M, Cristina K, Pereira L, et al. Cashew nut shell liquid and formulation: toxicity during the germination of lettuce, tomato seeds and coffee senna and seedling formation. Acta Sci Agron Mar n.d.;39:487–95. doi:10.4025/actasciagron.v39i4.32603.

[9] Harlita NH, Niken Satuti NH, Sagi M, Astuti P. Acute Toxicity of Cashew Nut Shell Extract (Anacardium occidentale L.) In Albino Rat (Rattus norvegicus Berkenhout 1769). Pakistan J Biol Sci 2016;19:89–94. doi:10.3923/pjbs.2016.89.94.

[10] Lomonaco D, Mele G, Mazzetto SE. Cashew Nutshell Liquid (CNSL): From an Agro-industrial Waste to a Sustainable Alternative to Petrochemical Resources. In: Anilkumar P, editor. Cashew Nut Shell Liq. - A Goldf. Funct. Mater., Cham: Springer International Publishing; 2017, p. 19–38. doi:10.1007/978-3-319-47455-7_2.

[11] Fellows P, Axtell B, editors. Opportunities in Food Processing: A handbook for setting up and running a small-scale business producing high-value foods. Wageningen: ACP-EU Technical Centre for Agricultural and Rural Cooperation (CTA); 2014.

[12] Dendena B, Corsi S. Cashew, from seed to market: a review. Agron Sustain Dev 2014;34:753–72. doi:10.1007/s13593-014-0240-7.

[13] Mohod AG, Khandetod YP, Powar AG. Processed cashew shell waste as fuel supplement for heat generation. Energy Sustain Dev 2008;12:73–6. doi:10.1016/S0973-0826(09)60009-0.

[14] Garcia-Nunez JAA, Pelaez-Samaniego MRR, Garcia-Perez ME, Fonts I, Abrego J, Westerhof RJMJM, et al. Historical Developments of Pyrolysis Reactors: A Review. Energy & Fuels 2017;31:5751–75. doi:10.1021/acs.energyfuels.7b00641.

[15] Moreira R, dos Reis Orsini R, Vaz JM, Penteado JC, Spinacé E V. Production of Biochar, Bio-Oil and Synthesis Gas from Cashew Nut Shell by Slow Pyrolysis. Waste and Biomass Valorization 2017;8:217–24. doi:10.1007/s12649-016-9569-2.

[16] Das P, Ganesh A. Bio-oil from pyrolysis of cashew nut shell—a near fuel. Biomass and Bioenergy 2003;25:113–7. doi:10.1016/S0961-9534(02)00182-4.

[17] Das P, Sreelatha T, Ganesh A. Bio oil from pyrolysis of cashew nut shell-characterisation and related properties. Biomass and Bioenergy 2004;27:265–75. doi:10.1016/j.biombioe.2003.12.001.

[18] Patel RN, Bandyopadhyay S, Ganesh A. Extraction of cardanol and phenol from bio-oils obtained through vacuum pyrolysis of biomass using supercritical fluid extraction. Energy 2011;36:1535–42. doi:10.1016/J.ENERGY.2011.01.009.

[19] Tsamba AJ, Yang W, Blasiak W. Pyrolysis characteristics and global kinetics of coconut and cashew nut shells. Fuel Process Technol 2006;87:523–30. doi:10.1016/j.fuproc.2005.12.002.

[20] Melzer M, Blin J, Bensakhria A, Valette J, Broust F. Pyrolysis of extractive rich agroindustrial residues. J Anal Appl Pyrolysis 2013;104:448–60. doi:10.1016/j.jaap.2013.05.027.

[21] Anatrans S.A.R.L. n.d. http://www.tradedevelopment.nl/factories/anatrans-burkina-faso/ (accessed May 30, 2018).

[22] Ruiz-Gómez N, Quispe V, Ábrego J, Atienza-Martínez M, Murillo MB, Gea G. Co-pyrolysis of sewage sludge and manure. Waste Manag 2017;59. doi:10.1016/j.wasman.2016.11.013.

[23] IBI. “Biochar standards”. Standardized product definition and product testing guidelines for biochar that is used in soil - product definition and specification standards 2015. http://www.biochar-international.org/sites/default/files/IBI_Biochar_Standards_V2.1_Final.pdf (accessed May 30, 2018).

[24] Rajkovich S, Enders A, Hanley K, Hyland C, Zimmerman AR, Lehmann J. Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. Biol Fertil Soils 2012;48:271–84. doi:10.1007/s00374-011-0624-7.

[25] Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 2007;86:1781–8. doi:10.1016/j.fuel.2006.12.013.

[26] Watkins D, Nuruddin M, Hosur M, Tcherbi-Narteh A, Jeelani S. Extraction and characterization of lignin from different biomass resources. J Mater Res Technol 2015;4:26–32. doi:10.1016/J.JMRT.2014.10.009.

[27] Brebu M, Vasile C. THERMAL DEGRADATION OF LIGNIN – A REVIEW. Cellul Chem Technol Cellul Chem Technol 2010;44:353–63.

[28] Di Blasi C, Branca C, Galgano A. On the Experimental Evidence of Exothermicity in Wood and Biomass Pyrolysis. Energy Technol 2017;5:19–29. doi:10.1002/ente.201600091.

[29] Di Blasi C, Branca C, Sarnataro FE, Gallo A. Thermal runaway in the pyrolysis of some lignocellulosic biomasses. Energy and Fuels 2014;28:2684–96. doi:10.1021/ef500296g.

[30] Antal Jr MJ, Grønli M. The Art, Science, and Technology of Charcoal Production. Ind Eng Chem Res 2003;42:1619–40. doi:10.1021/ie0207919.

[31] Weber K, Quicker P. Properties of biochar 2017. doi:10.1016/j.fuel.2017.12.054.

[32] Antal Jr MJ, Allen SG, Dai X, Shimizu B, Tam MS, Grønli M. Attainment of the Theoretical Yield of Carbon from Biomass. Ind Eng Chem Res 2000;39:4024–31. doi:10.1021/ie000511u.

[33] Ábrego J, Sánchez JL, Arauzo J, Fonts I, Gil-Lalaguna N, Atienza-Martínez M. Technical and energetic assessment of a three-stage thermochemical treatment for sewage sludge. Energy & Fuels 2013;27:1026–34. doi:10.1021/ef3018095.

[34] Yamamoto S, Sié A, Sauerborn R. Cooking fuels and the push for cleaner alternatives: a case study from Burkina Faso. Glob Health Action 2009;2. doi:10.3402/gha.v2i0.2088.

[35] Burgeon V. Biochar effects on soil physicochemical properties and on maize yields (Zea mays L.) in tropical soils of Burkina Faso (Master Thesis). Université de Liège, 2017.

[36] Foley G. Charcoal Making in Developing Countries - (Earthscan energy information programme; technical report no. 5). London, UK: Earthscan; 1986.

[37] Lu Q, Li W-ZZ, Zhu XF. Overview of fuel properties of biomass fast pyrolysis oils. Energy Convers Manag 2009;50:1376–83. doi:10.1016/j.enconman.2009.01.001.

[38] Fagernäs L, Kuoppala E, Tiilikkala K, Oasmaa A. Chemical Composition of Birch Wood Slow Pyrolysis Products. Energy & Fuels 2012;26:1275–83. doi:10.1021/ef2018836.

[39] Stankovikj F, McDonald AG, Helms GL, Olarte M V., Garcia-Perez M. Characterization of the Water-Soluble Fraction of Woody Biomass Pyrolysis Oils. Energy & Fuels 2017;31. doi:10.1021/acs.energyfuels.6b02950.

[40] Lievens C, Mourant D, He M, Gunawan R, Li X, Li C-Z, et al. An FT-IR spectroscopic study of carbonyl functionalities in bio-oils. Fuel 2011;90:3417–23. doi:10.1016/j.fuel.2011.06.001.

[41] Atienza-Martínez M, Ábrego J, Mastral JF, Ceamanos J, Gea G. Energy and exergy analyses of sewage sludge thermochemical treatment. Energy 2018;144. doi:10.1016/j.energy.2017.12.007.

[42] Harvey MT. Process of destructively distilling cashew nut shell liquid. US2098824 A, 1937.

[43] Outotec Research. HSC chemistry 9.0, Chemical reaction and equilibrium software with thermochemical database and simulation module 2016. https://www.outotec.com/products/digital-solutions/hsc-chemistry/ (accessed May 30, 2018).

[44] Yang H, Kudo S, Kuo H-P, Norinaga K, Mori A, Mašek O, et al. Estimation of Enthalpy of Bio-Oil Vapor and Heat Required for Pyrolysis of Biomass. Energy & Fuels 2013;27:2675–86. doi:10.1021/ef400199z.

[45] Daugaard DE, Brown RC. Enthalpy for Pyrolysis for Several Types of Biomass. Energy & Fuels 2003;17:934–9. doi:10.1021/ef020260x.

[46] Crombie K, Mašek O. Investigating the potential for a self-sustaining slow pyrolysis system under varying operating conditions. Bioresour Technol 2014;162:148–56. doi:10.1016/j.biortech.2014.03.134.

HIGHLIGHTS

- Simultaneous attainment of pyrolysis products and CNSL from cashew nutshells.
- Detailed characterization of pyrolysis products from cashew nutshells (CNS).
- Burning product gases can provide the energy needed for pyrolysis.
- Pyrolysis needs an energy input of around 9% of HHV of cashew nutshells.
- Feasibility of small-scale batch valorization of CNS in cultivation sites.