AIMS Energy, 12(2): 387–407.
DOI: 10.3934/energy.2024018
Received: 27 September 2023
Revised: 13 November 2023
Accepted: 19 November 2023
Published: 04 March 2024

http://www.aimspress.com/journal/energy

Research article

Characterization and optimization of the heat treatment of cashew nutshells to produce a biofuel with a high-energy value

Boua Sidoine KADJO[1,2,*], Mohamed Koïta SAKO[1], Kouadio Alphonse DIANGO[1], Amélie DANLOS[2] and Christelle PERILHON[2]

[1] Laboratoire de Mécanique et Sciences des Matériaux, Institut National Polytechnique Félix Houphouët Boigny, 1093 Yamoussoukro, Côte d'Ivoire
[2] Arts et Métiers Institute of Technology, LIFSE, CNAM, HESAM University, 75013 Paris, France

* **Correspondence:** Email: bkadjo@ymail.com; Tel: +2250749486939; +330745748651.

Abstract: In the context of the fight against climate change and the development of renewable and new energies, the management of cashew nutshells is an issue. The physico-chemical and energetic properties of cashew nutshells show that they are good raw materials that can be used in thermochemical processes. Cashew nutshells were heated to temperatures of 300 °C, 350 °C and 400 °C for 40 to 120 minutes to extract the liquid from the cashew nutshells. Biochar yields by mass were 46.5–52.8 wt%, 46.2–35.9 wt% and 37.8–30.3 wt% at temperatures of 300 °C, 350 °C and 400 °C, respectively. Biochar with high higher heating value and low residual oil content was obtained at a heating temperature of 300 °C for a time of 120 min. The biochar obtained under these optimum conditions has a residual oil content of less than 1 wt% and a higher heating value of 32.1 $MJ \cdot kg^{-1}$. The other two products, bio-oil and smoke, have higher heating values of 36 $MJ \cdot kg^{-1}$ and 10.2 $MJ \cdot Nm^{-3}$, respectively. Temperature and heating time improve the energy density and quality of biochar with low residual oil content. Heat treatment is therefore a promising technique for the production of an environmentally friendly and sustainable high energy solid biofuel from cashew nutshells.

Keywords: cashew nutshells; biochar; CNSL; gas; heat treatment

1. Introduction

In recent years, Côte d'Ivoire has become one of the world's leading producers of cashew nuts, with production expected to reach 837,850 tonnes by 2021 [1]. Local processing of cashew nuts is increasingly being promoted by the authorities due to its high potential for value addition and job creation. However, this activity generates residues representing between 50 wt% and 72 wt% of the raw cashew nut mass [2,3]. The management of these residues, known as cashew nutshells, remains a challenge for processing units. About 30–35% by weight of them are a dark reddish-brown viscous liquid known as Cashew Nut Shell Liquid (CNSL) [4]. These residues are bulky and pose risks of fire and soil, water and air pollution if dumped directly into the environment. To compensate for energy shortages in processing units, some of the shells are often burned in boilers to provide the heat needed to soften the nuts and steam and dry the kernels [5]. In Côte d'Ivoire, units use about 15 wt% of the cashew nutshells generated in the transformation process in pyrolysis furnaces [3], which is not without ecological implications. CNSL contains a number of phenolic compounds. These molecules are harmful and produce toxic and carcinogenic fumes when the shells are burned directly [6]. In addition to these negative environmental and human health impacts, cashew nutshells and their liquid content (CNSL) can be used for a variety of purposes.

Besides their use for energy, cashew nutshells and CNSL can be used for agriculture and food security [7,8], water and environmental management and protection and sanitation [9–11], biotechnology and environmental engineering.

Cashew nutshells are potential feedstocks for the production of briquettes, biodiesel, heat and syngas. Raw and de-oiled cashew nutshells have higher heating values (HHV) between 16 and 22 $MJ \cdot kg^{-1}$ [3,12]. Studies have also been carried out on the production of briquettes by pyrolysis [13], torrefaction and carbonization [14,15] of cashew nutshells. These previous studies on pyrolysis, carbonization and roasting of cashew nutshells did not consider the residual oil content in the biochar. Heat treatment of these raw cashew nutshells resulted in a biochar with a higher heating value of between 24 and 31 $MJ \cdot kg^{-1}$ [16,17]. With a higher heating value of around 32 $MJ \cdot kg^{-1}$, CNSL is not suitable for use in pure form due to its viscosity and chemical composition, but can be used in blends with diesel [4,16]. The use of CNSL as a fuel of up to 60 vol% in a stationary diesel engine is possible [18]. Proper management of cashew nutshells could not only lead to significant income generation, but also provide environmental sustainability.

The recovery of industrial agricultural wastes in general, and cashew nutshells in particular, depends on their physical and biochemical properties. Figure 1 shows a model for the recovery of cashew nutshells in several ways. The shells can be used directly for energy purposes. However, this option is not recommended because of the harmful effects caused by the emission of black and toxic fumes. The cashew nutshell recovery model proposed in this study requires prior extraction of the CNSL. Three methods can be used: Mechanical, thermal and chemical. Extraction of the residual oil or CNSL results in a solid residue, the de-oiled cashew nutshells or biochar, depending on the method used. Solvent extraction and mechanical extraction methods produce de-oiled cashew nutshells. The thermal method produces biochar. Once the CNSL has been extracted, the de-oiled cashew nutshells or biochar can be converted directly into heat or synthesis gas using the combustion or gasification processes. The de-oiled cashew nutshell or biochar can also be converted into solid biofuels before being used in the combustion and gasification processes. The de-oiled cashew hull is brittle and largely free of anacardic acid and total phenolics, which can be limiting to anaerobic bacteria. It can therefore be used to produce biomethane through anaerobic digestion. However, co-digestion is recommended for better performance [15]. Deoiled cashew nutshells can also be subjected to heat treatment (carbonization, torrefaction or pyrolysis) or used directly to produce solid biofuels.

The conversion of de-oiled cashew nutshells or biochar into solid biofuels improves their energy properties. The solid biofuel produced is environmentally friendly, can withstand shocks during handling and transport and produces the heat needed for domestic cooking and industrial applications.

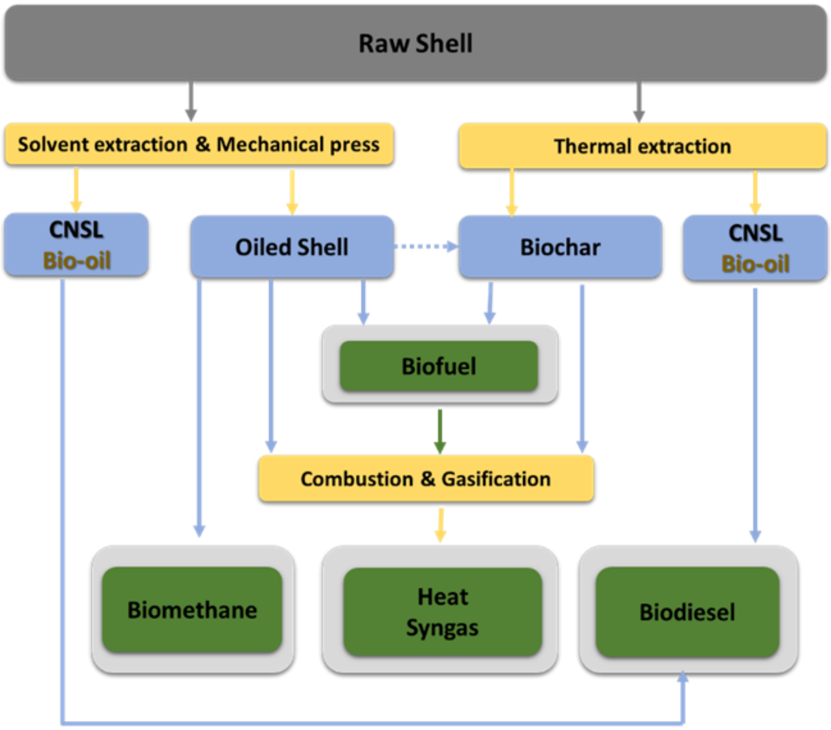

Figure 1. Scheme for recovering energy from cashew nutshells.

In addition to releasing CNSL, heat treatment facilitates the grinding and densification of cashew nutshells for the production of solid biofuels. The conversion of the shells into biochar improves the energy properties of the solid fuel. Our main objective is to determine the optimum conditions (temperature and residence time) at which the residual oil content in the biochar is minimized while maximising the mass yield and higher calorific value of the biochar. Raw cashew nutshells are heated to temperatures of 300 °C, 350 °C and 400 °C for varying lengths of time to produce a biochar. The biochar with the highest higher heating value could be used to produce solid biofuels. The biofuel could be used as an energy source for cooking in households or to produce heat and electricity in coal- or biomass-fired power plants.

The research paper has the following structure. The first section presents the methodology used to characterize raw cashew nutshells and processed products. This is followed by the experimental procedure for biochar production. The characteristics of the raw cashew nutshells and heat-treated products are then presented and discussed.

2. Methodology

2.1. Sampling of cashew nutshells for the study

For this study, raw cashew nutshell samples were collected at the Cashew Nut Innovation and Technology Centre (CITA) in Yamoussoukro. The sample taken was preserved in a plastic bag to preserve its properties and then characterized at the chemical laboratory of the University of Man, Côte d'Ivoire, to determine its organic, inorganic and elemental composition and calorific value.

Knowing the main chemical and physical properties and the calorific value of the biomass makes it possible to choose the right type of management and recovery. In the context of energy recovery, the physico-chemical and energetic properties of cashew nutshells help to understand the behavior of the biofuel during its thermochemical conversion.

2.2. Proximate analysis

Moisture is defined as the ratio of the mass of water contained in the fuel to the mass of dry fuel. The moisture content is determined by the difference between the total mass of the initial sample and its anhydrous mass, in accordance with standard NF EN ISO 18134-1/2. Volatile matter (VM) is the relative dry matter lost during heat treatment of fuel dried at 850 °C for 10 minutes in a muffle furnace. The NF EN ISO 18123 standard is used to determine the amount of volatile matter. The fixed carbon (FC) is the difference in mass between the solid residue after the pyrolysis stage (fixed carbon + ash) and the ash obtained after combustion. It is determined in accordance with standard NF EN ISO 16948. Ash content is defined as the mass fraction remaining after complete combustion of the sample. The sample is placed in a muffle furnace at 550 °C under air until ashes without carbon residues are obtained and weighed. The ash content is determined according to standard NF EN ISO 18122.

2.2.1. Ultimate analysis

Ultimate analysis was used to determine the mass percentages, mostly of carbon (C) and oxygen (O), but also of compounds such as nitrogen (N), sulfur (S) and chlorine (Cl) in the raw cashew nutshells and biochars. C, H and N contents were determined according to standard NF EN ISO 16948. The S and Cl contents were determined according to NF EN ISO 16994. The O content was estimated according to standard NF EN ISO 16993.

2.2.2. Calorific value

The calorific value is the amount of energy (per unit of mass, $MJ \cdot kg^{-1}$ or volume or $MJ \cdot Nm^{-3}$) released by a fuel when completely burnt. The quality of a biofuel is assessed and its calorific value defined by the elemental chemical composition of the main elements (C, H, O and N). The higher heating value (HHV) of raw cashew nutshells was determined according to standard NF EN ISO 18125. The HHV of the bio-oil produced was measured using the standard calorimetric bomb C 7010 (IKA C7000, Germany). The HHV of the smoke was determined using the method described by [19].

2.2.3. Determination of the residual oil content and fibre composition

For the extraction of residual oil from biochar, the Soxhlet solvent method is used in this study. The sample of cashew nutshells or biochar is oven dried at 105 °C for 24 hours to release the liquid, CNSL, contained within. A 50 g sample is dispersed in 150 mL of hexane-ethanol solution (1:1). The mixture is stirred for 2 hours. The residue obtained by vacuum Büchner filtration was dried at 105 °C for 2 hours and then weighed to determine the residual oil content as a percentage by weight. Residual oil content corresponds to weight loss of sample.

Fiber composition was determined by Van Soest's method [20]. This method makes it easy to determine the content of hemicellulose, cellulose and lignin as a percentage by weight of the dry matter.

2.3. Biomass heat treatment

Heat treatment was carried out at low temperatures (300 °C, 350 °C and 400 °C) in an inert atmosphere for heating times between 40 and 120 min in a furnace at a rate of 1 °C/s (Figure 2). The oven loading device is designed to harvest the bio-oil efficiently without wastage. The device consists of a metal loading basket placed on top of a rectangular tank that serves as a receptacle for collecting the bio-oil (B, Picture a). At the end of the heating period, the biochar is collected in the basket (A, Picture a). The temperature conditions were defined on the basis of previous work and experimental trials. Indeed, in the studies carried out by [17,21–23], cashew nutshells were heated to temperatures above 400 °C. This favored the production of bio-oil to the detriment of biochar, as the higher the temperature, the more the biomass components degrade. The oven used allows the temperature and heating time to be adjusted. Once loaded, the oven is hermetically sealed before start-up to prevent any uncontrolled air supply that could burn the biochar, destroy the equipment or even cause a fire. Mass yields indicate the total mass ratio of products such as biochar, bio-oil and smoke to the raw feedstock.

The law of conservation of mass is used to estimate the mass of gas (m_{gas}), knowing the mass of raw cashew nutshells($m_{raw\ cashew\ nutshells}$), the mass of biochar ($m_{biochar}$) and the mass of bio-oil ($m_{bio-oil}$) (Eq 1). From the mass of each product, the mass yield (η_M) can be deduced (Eq 2).

$$m_{raw\ cashew\ nutshells} = m_{gas} + m_{biochar} + m_{bio-oil} \quad (1)$$

$$\eta_M = \frac{m_{product}}{m_{raw\ cashew\ nut\ shells}} * 100 \quad (2)$$

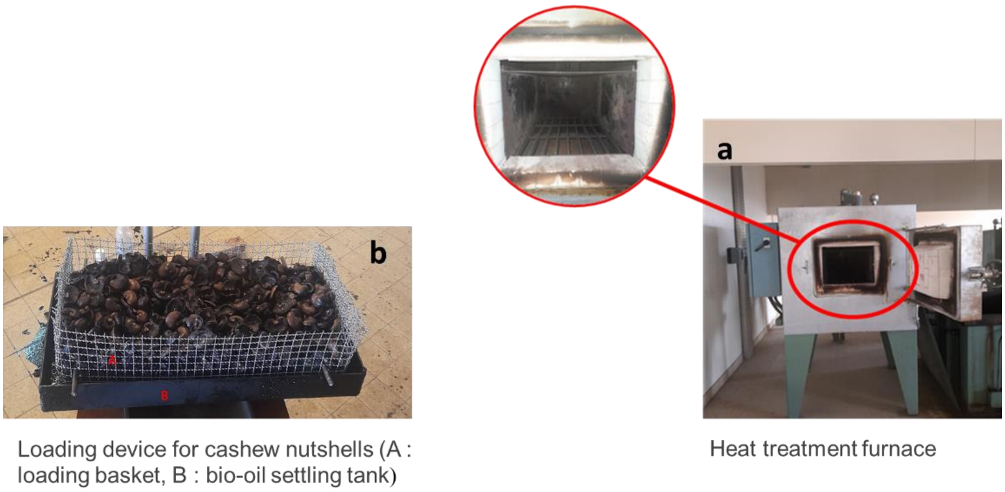

Figure 2. Heat treatment furnace (a) and loading device for cashew nutshells (b).

Tedlar sampling bags were used to collect the gases produced at ambient temperature and then analyzed off-line using a Micro GC varian CP 4900 coupled to a combustion analyser to measure the volumetric contents of CO_2, CO, CH_4, C_2H_4, C_2H_6, H_2 and H_2O.

3. Results and discussion

3.1. Raw cashew nutshell

3.1.1. Proximate and ultimate analysis

Table 1 shows the results of the proximate and ultimate analysis of cashew nutshells. The values for volatile matter, ash and fixed carbon are obtained on a dry matter basis.

Table 1. Results of proximate analysis and ultimate analysis of raw cashew nutshells.

	Proximate analysis (wt%)				Ultimate analysis (wt%)						Reference
	MC	VM	A	FC	C	H	O	N	S	Cl	
Cashew nutshells	3.9	81.4	2.1	16.5	61.85	5.96	28.52	0.94	0.11	0.52	this research
Sugarcane bagasse	13.12	59.68	1.8	26.0	43.04	5.59	45.89	0.49	0.25	-	[24]
Rice husk	14.18	51.96	15.15	18.39	39.32	5.78	31.59	0.43	0.02	-	[25]
Coconut shells	10.03	63.41	5.6	20.95	42.1	4.95	48.12	0.35	0.08	-	[24]

*M: Moisture content, VM: Volatile matter, A: Ash, FC: Fixed carbon

The values obtained from proximate analysis of cashew nutshells are close to those obtained by[3,17,21,26–28]. These studies showed that the volatile matter, fixed carbon, ash and moisture contents were 72–85 wt%, 8.7–18.2 wt%, 1.7–5 wt% and 5.3–9.50 wt% respectively. The differences between the values obtained in the present study and those reported in the literature could be explained by the variety of cashew nut, the region of cultivation and by the length of time and the technique used to preserve the cashew nutshells. The moisture and ash contents are below the normative limit FN EN ISO 17225-6 (≤12 wt% for moisture and ≤6 wt% for ash) for energy recovery. The moisture and fixed carbon contents of sugarcane bagasse, rice husks and coconut shells are higher than those of cashew nutshells. However, the volatile matter content of sugarcane bagasse, rice husks and coconut shells lower than that of cashew nutshells.

Ultimate analysis gave values close to those obtained by [3,17,21,26–28]. The carbon, hydrogen, oxygen and nitrogen contents of cashew nutshells obtained in these previous studies were 48–57 wt%, 5.7–14 wt%, 21–44 wt% and 0.2–0.7 wt%, respectively. Sulphur and chlorine contents were less than 1%. These levels are close to those found in wood in its natural state. The elemental chemical composition of wood varies very little from one species to another. On average, wood consists of approximately 30–50 wt% carbon, 42 wt% oxygen and 6 wt% hydrogen [29]. Elements such as nitrogen, sulfur and chlorine are often absent in natural wood. Where they are present, their content is generally less than 1 wt% [29]. The chlorine content of raw hulls is above the normative limit of NF EN ISO 17225-6 (≤0.1 wt%). A high chlorine content leads to the formation of hydrochloric acid in the boiler and gasifier. It can also lead to the formation of dioxins and furans, which are persistent pollutants in the environment. The low nitrogen content also makes shells a good raw material for the production of synthesis gas with a low ammonia content. However, this content is higher than that of sugarcane bagasse, rice husks and coconut shells. The oxygen content of sugarcane bagasse, rice husk and coconut shells are higher than that of cashew nutshells. On the other hand, the hydrogen and nitrogen contents of sugarcane bagasse, rice husk and coconut shells are lower than those of cashew nutshells.

3.1.2. Composition of fibers and residual oil

The fibre and residual oil composition of raw cashew nutshells is shown in Table 2. Cashew nutshells are very rich in residual oil.

Table 2. Composition of fibers and residual oil.

Composition of fibers (wt%)			Residual oil (wt%)
Hemicellulose	Cellulose	Lignin	31.00
31.40	46.00	22.60	

These high fibre contents justify the fact that raw cashew nutshells are difficult to grind. The values obtained are close to those obtained in previous studies. Lignocellulosic biomass contains 25–35 wt% cellulose, 23–32 wt% hemicellulose and 15–36 wt% lignin [21,26,27]. The cellulose content of cashew nutshells is much higher than reported by these authors. The fibre composition of cashew nut shells shows that they are good fuels for the production of syngas and heat. The decomposition of hemicellulose yields CO_2, while that of cellulose is abrupt and produces CO and a large amount of energy. As for H_2 and CH_4, they result from the degradation of lignin [30].

3.1.3. Calorific value of raw cashew nutshells

The higher heating value of raw cashew nutshells is 24.12 MJ·kg^{-1}. This calorific value is much higher than that of tropical wood, estimated to be around 17.50 MJ·kg^{-1} [29], and close to that of coal (25–35 MJ·kg^{-1}) [31,32]. The HHV obtained in this study is higher than those observed by [3,7,12,17,21,22], which ranged from 20 to 23.65 MJ·kg^{-1} in raw cashew nutshells. Cashew nutshells have a high calorific value. They are a good raw material and have enormous energy potential. The higher heating value of raw cashew nutshells is higher than that of several agro-industrial and agricultural residues, such as olive pomace (18–22 MJ·kg^{-1}) [24,33–35], sugarcane bagasse with 16–19 MJ·kg^{-1} [24,27,35] and cocoa shells with 15–18 MJ·kg^{-1} [36–39].

Cashew nutshells have enormous energy potential due to their high calorific value and physicochemical properties. However, the energy recovery of cashew shells in combustion and gasification processes for electricity and heat production requires treatment due to the high residual oil content of 31 wt%. This content should not exceed 6.5 wt% to enable the formation of quality pellets [40]. Consequently, de-oiled and heat-treated hulls would be more suitable for gasification and combustion as they have a higher calorific value than raw cashew nutshells [3,12], in addition to the low CNSL content.

3.2. Heat treatment product yield

The thermochemical treatment of cashew nut shells carried out at temperatures of 300 °C, 350 °C and 400 °C at times ranging from 40 to 120 minutes made it possible to obtain three products: Biochar, bio-oil and smoke (Figure 3).

Figure 3. Products of the heat treatment process (biochar, bio-oil and smoke).

3.2.1. Biochar production

Biochar yields ranged from 46.5 to 52.8 wt%, 46.2 to 35.9 wt% and 37.8 to 30.3 wt% at temperatures of 300 °C, 350 °C and 400 °C for heating times between 40 and 120 min, respectively (Figure 4).

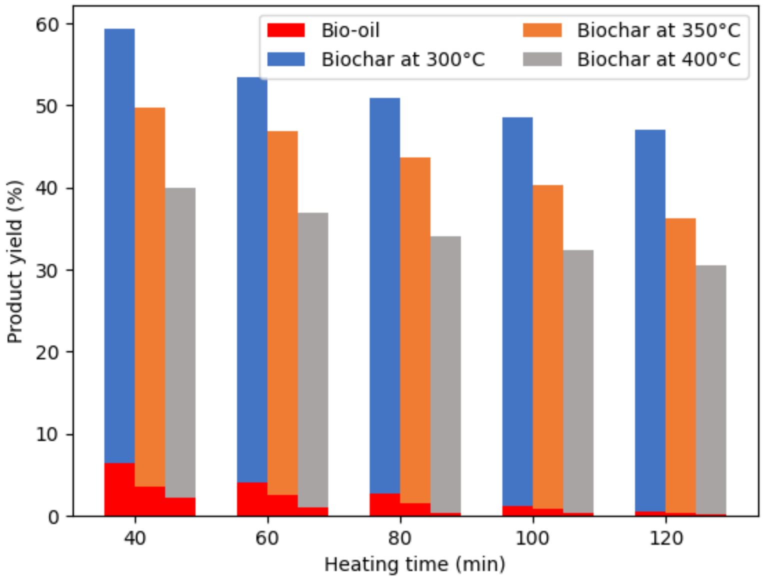

Figure 4. Evolution of the production of biochar and the residual oil content.

The mass yield of biochar decreases with increasing temperature and heating time. The decrease in mass yield is due to moisture loss and decomposition of organic matter with the formation of volatile products such as CO, CO_2, CH_4 and many other compounds as a result of the decomposition of hemicellulose and cellulose and certain short chain lignin compounds [41]. The residual oil content of biochar decreases with increasing temperature and heating time. At 300 °C, it is less than 1 wt% after 120 minutes of heating. At temperatures of 350 °C and 400 °C, the minimum times to achieve a residual oil content in biochar of less than 1 wt% are 80 min and 100 min (shorter times), respectively. However, the mass yields of biochar at these times and temperatures are lower than the mass yield when the biomass is heated to 300 °C for 120 minutes. This is because heating the biomass to lower temperatures maximises the biochar yield [17,22] .

3.2.1.1. Evolution of calorific value

Increasing the temperature and time improves the calorific value of the biochar, except that the calorific value of the biochar decreases from 100 minutes at temperatures of 350 °C and 400 °C. The maximum calorific value is obtained at a temperature of 300 °C for a time of 120 minutes. Higher heating values range from 25.2 to 32.1 MJ·kg^{-1} (Figure 5). These values are close to those obtained for agricultural waste biochar, which ranged from 27 to 32 MJ·kg^{-1} [41].

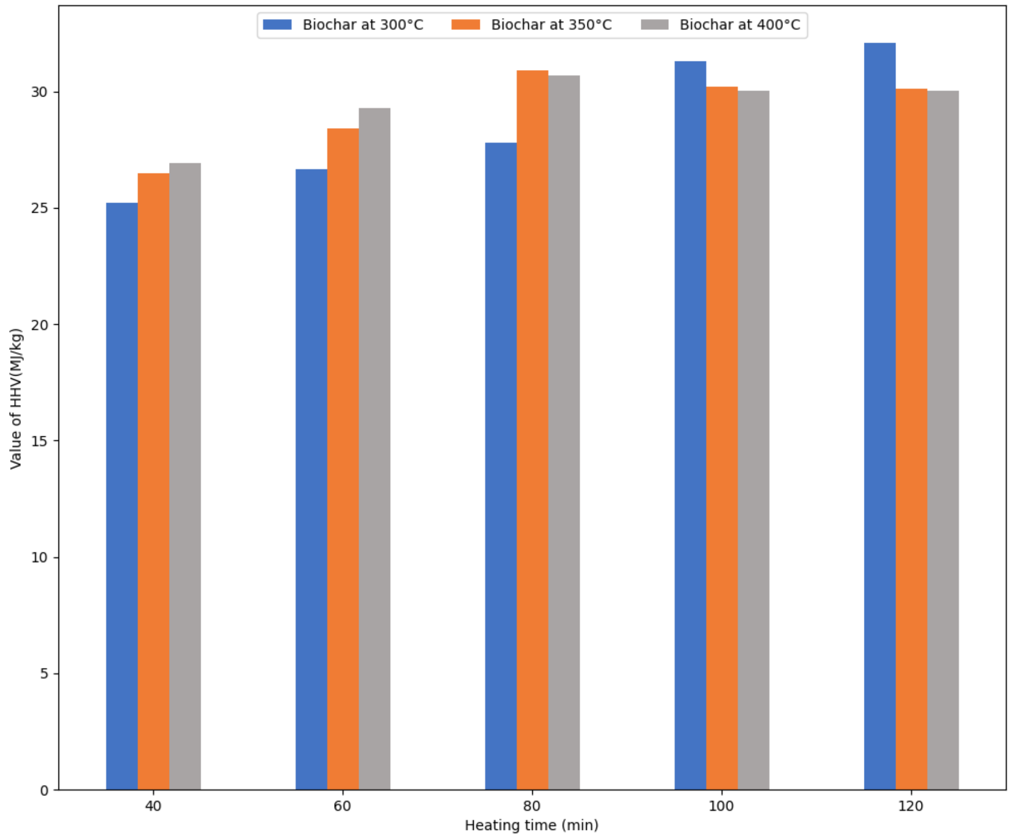

Figure 5. Evolution of the higher heating value of biochar.

3.2.1.2. Evolution of moisture

Moisture content decreases with increasing temperature and heating time. It decreases from 3.2 wt% to 1.6 wt% (Figure 6). This decrease in moisture content is due to the destruction of hydrogen bonds, which improves the hydrophobic properties of the biochar [42].

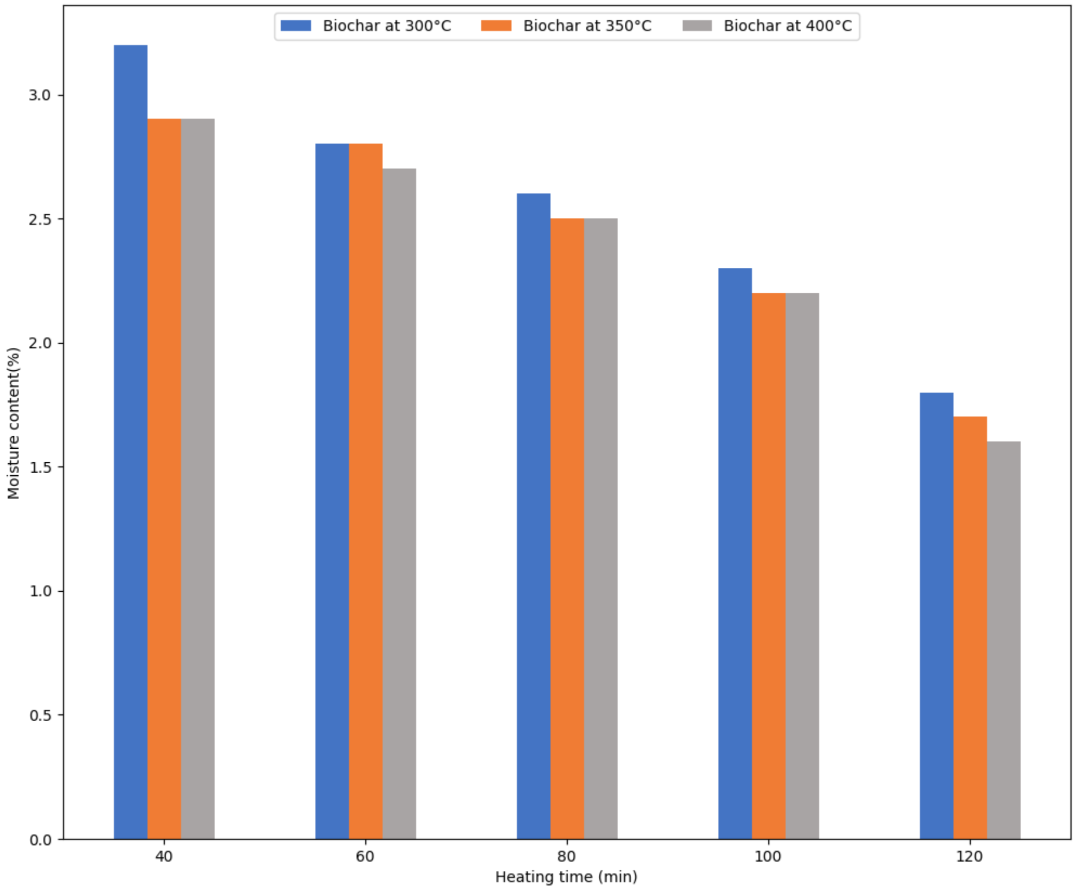

Figure 6. Evolution of biochar moisture content.

3.2.1.3. Evolution of volatile matter content

Compared to raw cashew nutshells, the volatile matter content decreases with increasing temperature and heating time (Figure 7). It decreases from 81.46 wt% in the raw biomass to 65.51 wt% in the biochar obtained at 300 °C for 40 minutes. It then decreases to 35.4 wt% at a temperature of 400 °C and a heating time of 120 minutes. In addition, a greater mass of volatile matter is lost with increasing temperature and heating time. This is due to degassing and thermal cracking reactions associated with the increase in heating temperature [17,43].

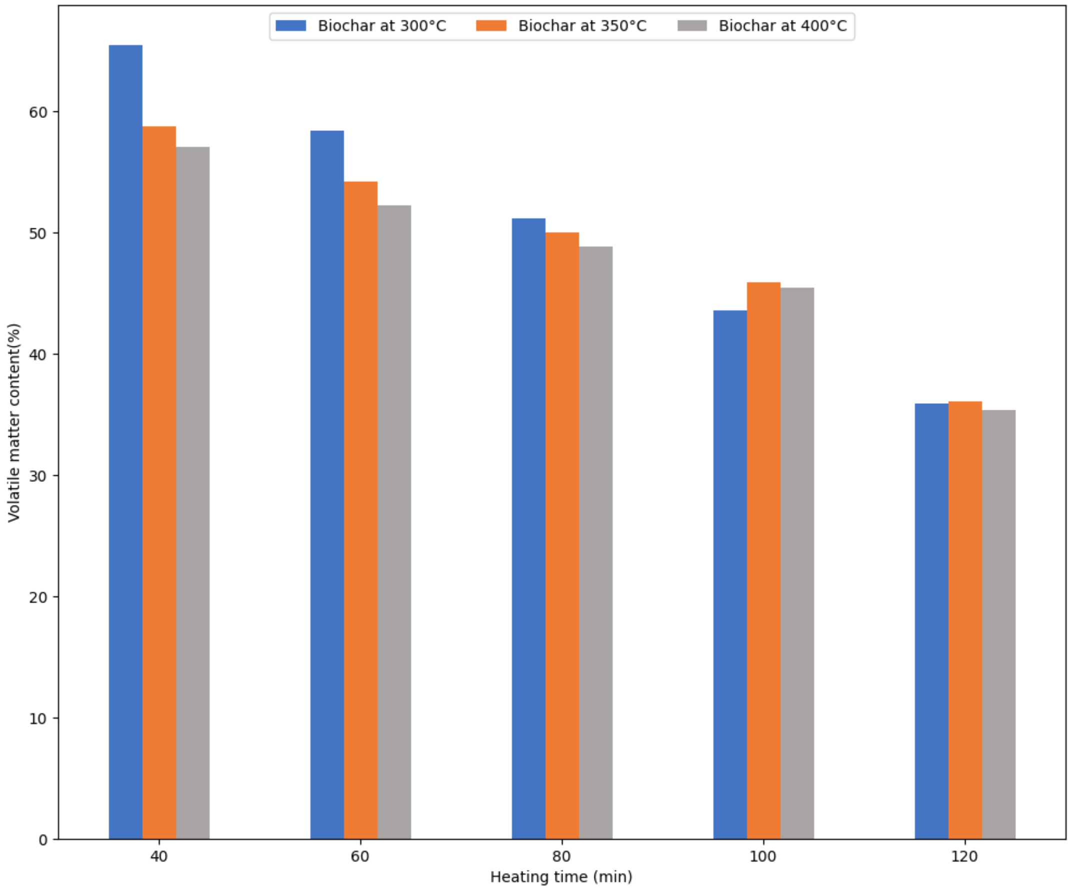

Figure 7. Evolution of biochar volatile matter.

3.2.1.4. Evolution of ash content

With increasing temperature and heating time, the percentage of ash increases (Figure 8). The ash content of biochar varies between 2.23 wt% and 4.9 wt%. At a temperature of 400 °C for 120 minutes, the highest ash content (4.9%) is obtained. The loss of volatile matter under the influence of temperature is probably responsible for this increase in ash content. However, in terms of ash content (≤6 wt%), the maximum ash value obtained complies with the requirements of standard NF EN ISO 17225-6. In fact, a high ash content is a disadvantage. It leads to the emission of dust and pollutants during combustion.

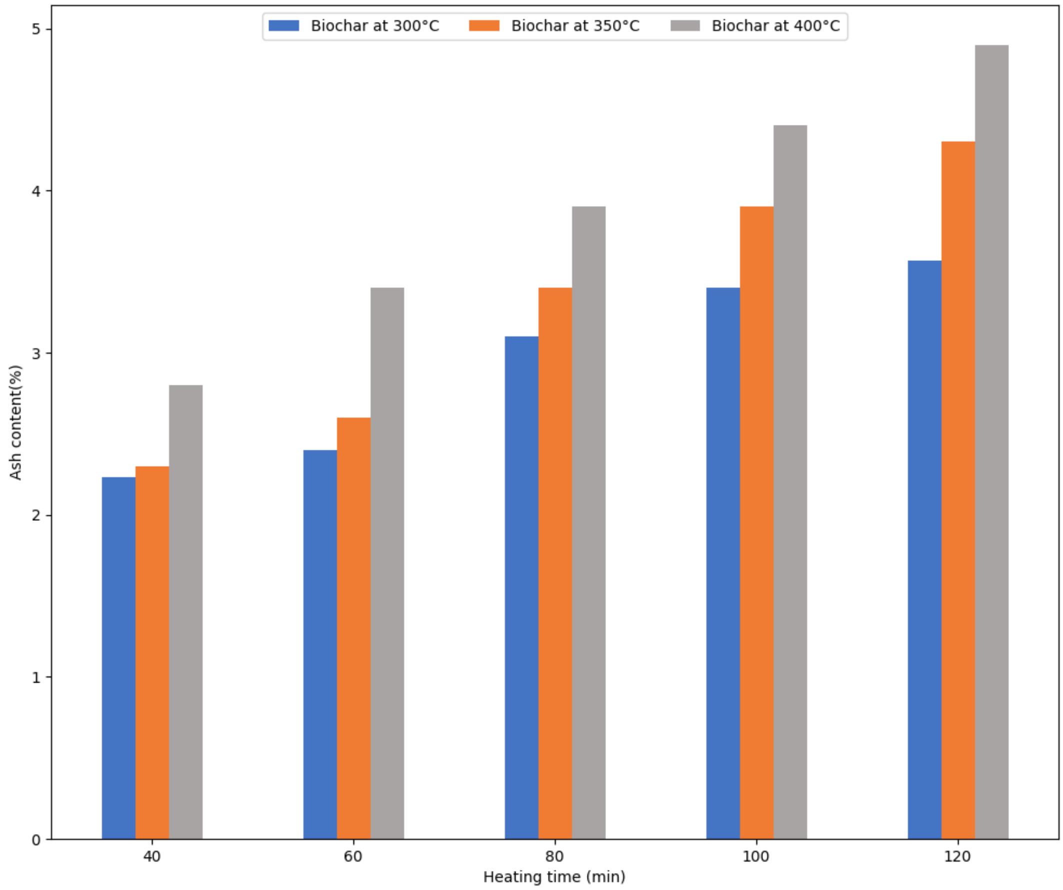

Figure 8. Evolution of biochar ash.

3.2.1.5. Evolution of fixed carbon content

The fixed carbon content rose from 32.26 wt% to 60.53 wt% as the temperature and heating time increased (Figure 9). This increase in fixed carbon is linked to the decrease in volatile matter.

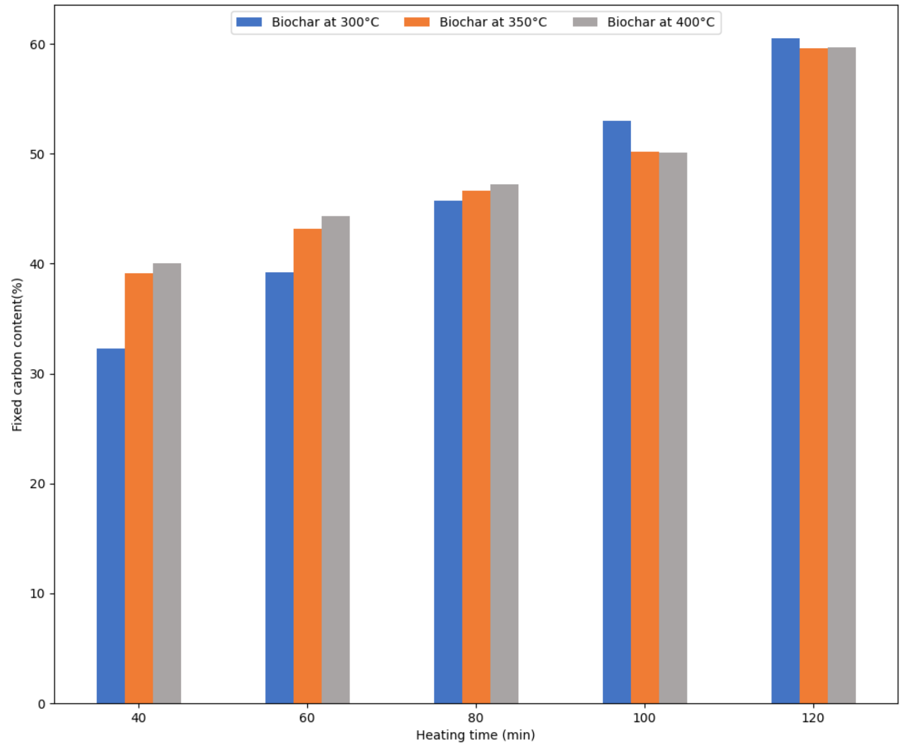

Figure 9. Evolution of fixed carbon in biochar.

3.3. Bio-oil production

In contrast to biochar, the proportions of bio-oil increase with temperature and heating time. The mass yields of bio-oil increase from 21.7 to 27.6 wt%, from 24.4 to 29.1 wt% and from 24.3 to 30.2 wt% at temperatures of 300 °C, 350 °C and 400 °C respectively. The highest bio-oil content (30.2 wt%) was obtained at 400 °C for a heating time of 60 minutes (Figure 10).

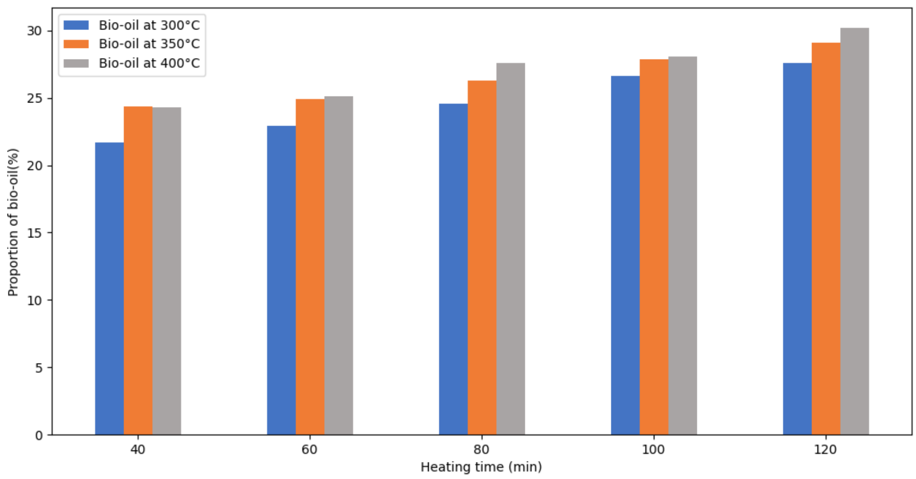

Figure 10. Evolution of bio-oil production.

However, the bio-oil yield by mass remains lower than those obtained at 400 ℃ by [21,22] during the pyrolysis of cashew nutshells. Some studies have shown high bio-oil production at high temperatures (400–900 ℃) [17,21,22]. In fact, bio-oil yield increases with increasing temperature due to increased degradation of biomass components.

With a higher heating value of 35.8 $MJ \cdot kg^{-1}$ and a moisture content of 1.1%, the bio-oil yield is 27.6 wt%. The HHV of crude oil, natural gas (NG) and liquefied petroleum gas (LPG) are 38.78 $MJ \cdot L^{-1}$, 38.95 $MJ \cdot m^{-3}$ and 50.08 $MJ \cdot kg^{-1}$, respectively [19]. The HHV of the bio-oil obtained from the cashew nutshells is lower than that of the pyrolysis oil obtained from jatropha seeds at 500 ℃ (38 $MJ \cdot kg^{-1}$) [44]. When the bio-oil is cooled, an organic phase is formed by decantation. This observation has been reported in [16,17,22]. The organic phase also has a low water content (2.2 wt%) and a composition and calorific value that are similar to those of CNSL [22].

Solvents and mechanical pressing can also be used to obtain CNSL. In this case, it is referred to as natural CNSL. The composition, quantity and quality of CNSL vary depending on the extraction method. Natural CNSL contains anacardic acid (60–70 vol%), cardanol (3–15 vol%), cardol (10–24 vol%), 2-methylcardols (2–5 vol%) and other minor components [4,45,46]. Technical CNSL is a blend of 60–70 vol% cardanol, 10–20 vol% cardol and 2–5 vol% 2-methylcardol and 5–10 vol% polymeric materials [45,46]. The low moisture content makes CNSL suitable for direct combustion. The CNSL obtained can be used as biofuel [47,48]. However, with a calorific value of around 36 $MJ \cdot kg^{-1}$ and due to its high viscosity, it is not suitable for use as a pure biofuel, but can be used in a blend with diesel. Coulibaly et al., 2022 [18] have shown that it is possible to use up to 60 vol% CNSL as a biofuel in a stationary diesel engine. Experimental work has also shown that an engine fuelled with blends of pure methyl ester derived from CNSL and alcohol performs well, with a significant reduction in emissions of pollutant gases such as nitrogen oxides compared to diesel [48]. In addition to energy use, CNSL can be used to produce pharmaceuticals, cosmetics, food, resins, coatings, laminates, adhesives, biopesticides and biofertilisers [8,45,49–52].

3.4. Smoke production

As in the case of bio-oil, the mass yields of the exhaust gases increased with temperature and heating time. These proportions were 25.5 to 28.1 vol%, 29.4 to 35 vol% and 37.9 to 39.5 vol% at temperatures of 300 ℃, 350 ℃ and 400 ℃ respectively (Figure 11). The highest smoke content (39.5%) was obtained at 400 ℃ for a heating time of 120 min. With increasing temperature, volatiles, oxygen and water in the raw biomass are eliminated in the form of gaseous components (CO_2, H_2O and CO) and liquid compounds (e.g., acids, phenols, furans and ketones) during hemicellulose, cellulose and lignin degradation reactions [53,54]. The degradation of cellulose, hemicellulose and lignin takes place at temperatures of 275–355 ℃, 180–300 ℃ and 250–500 ℃ respectively [30]. Gas mass yields are higher in the 300–500 ℃ temperature range (17.5–23.1 vol%) than those obtained by [21]. According to [41], the amount of emissions produced during thermal decomposition depends on the composition of the feedstock, the heating rate, the temperature and the residence time.

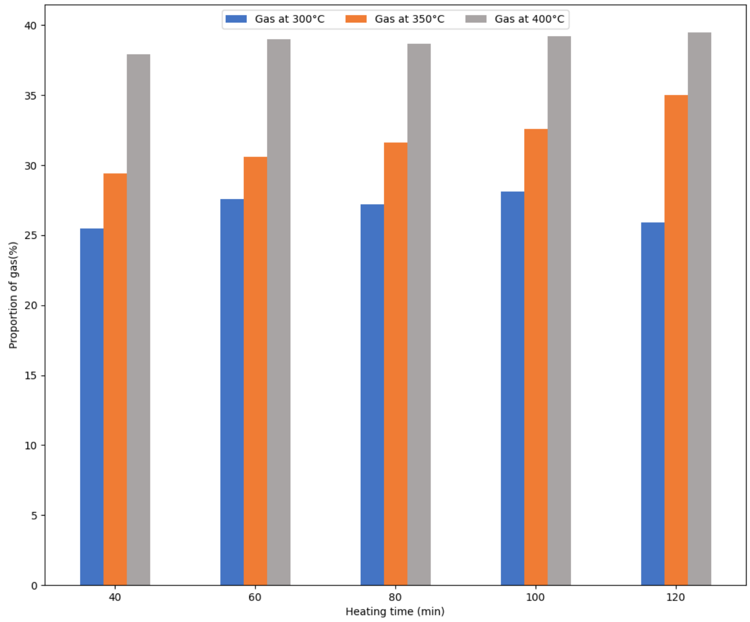

Figure 11. Evolution of gas production.

On average, 25.9 vol% gaseous products are obtained when treated according to optimum conditions. The emitted flue gas is composed of CO (38.2 vol%), CO_2 (51.8 vol%), H_2 (1.5 vol%), CH_4 (5.9 vol%), C_2H_4 (0.37 vol%), C_2H_6 (0.83 vol%) and H_2O (1.4 vol%). The mass yield of gaseous products is close to the range observed by [21]. The predominance of CO_2 and CO at temperatures below 400 ℃ was also observed by [16]. The HHV of the gas is 10.2 MJ/Nm^3, close to the values determined by [3,35] (8–18 MJ/Nm^3). Due to its high energy value, the gas produced during the heat treatment of cashew nutshells can be used in the process by incorporating a recovery and upgrading system to significantly reduce economic and environmental problems.

A processing temperature of 300 ℃ and a residence time of 120 minutes appear to be the most appropriate for the production of biochar from cashew nutshells, given the mass yield, high calorific value of the biochar and low residual oil content in the biochar. A high mass yield of biochar generally correlates with high residual oil, moisture and volatile content in the biochar. The heat treatment of cashew nutshells produced a biochar with a higher heating value of 32.10 MJ·kg^{-1}.

3.5 Properties of the biochar produced under the optimal conditions of the heat treatment

Cashew nutshells are processed according to the optimal temperature and time conditions determined for biochar production. The results of the products obtained are presented and discussed in the following sections.

The average mass yield of biochar was 46.5 wt%, which is higher than the values reported in the literature. In fact, the maximum mass yield of cashew nutshells biochar was 41.0 wt% at 350 ℃ [13], 17.00 wt% at 450 ℃ [3], 25.02 wt% at 400 ℃ [55] and 30 wt% at 400 ℃ [22].

The main elements of biochar such as carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S) and chlorine (Cl) are given in Table 3. These values are improved compared to the raw cashew nutshells in terms of carbon, sulphur, nitrogen and chlorine. The chlorine content (<0.02 wt%) has been reduced, thus respecting the normative limit NF EN ISO 17225-6 (≤0.1 wt%), unlike that obtained in the raw cashew nutshells. Hydrogen and oxygen contents also decreased due to decarboxylation, decarbonization and dehydration reactions [41].

Table 3. Ultimate analysis of biochar.

	Ultmiate analysis (wt%)						References
	C	H	O	N	S	Cl	
Biochar	75.2	4.66	16.5	0.95	0.05	<0.02	This research
Biochar	69.50	5.19	24.35	0.962			[27]
Deoiled cashew nutshells	45.8	6.3	46.8	0.7	0.4		[21]

The heat treatment also effectively reduced the moisture and volatile content and increased the fixed carbon content and calorific value compared to raw cashew nutshells and cake. Table 4 shows the results of the proximate analysis and higher heating value of the biochar.

Table 4. Proximate analysis and higher heating value of biochar.

	Proximate analysis (wt%)				HHV($MJ \cdot kg^{-1}$)	References
	Moisture	Volatile matter	Ash	Fixed carbon		
Biochar	1.80	35.90	3.57	60.53	32.1	This research
Biochar	3.55	48.85	7.24	43.92	27.69	[27]
Deoiled cashew nutshells	5.77	83.69	1.17	8.4	16.13	[21]

Biomass components, such as water and ash, reduce the energy content [56]. Reducing or eliminating these components increases the energy content of the biomass. The reduction in oxygen and increase in fixed carbon are also the main reasons for the increase in HHV of biochar [57]. The higher heating value increased from 24.12 $MJ \cdot kg^{-1}$ in the raw cashew nutshells to 32.10 $MJ \cdot kg^{-1}$ in the biochar. This value is higher than those observed by [3,7,12,17] in cashew nutshell biochar, which ranged from 24 to 31 $MJ \cdot kg^{-1}$. The calorific value of biochar is also higher than that of raw deoiled cashew nutshell cake (16.13–20.11 $MJ \cdot kg^{-1}$) [21,51].

Therefore, except for the low residual oil content and small particle size, the physicochemical properties of deoiled cashew nutshells are virtually identical to those of raw cashew nutshells. The increased energy density and improved quality of biochar with low residual oil content is the main benefit of the heat treatment.

4. Challenge and future perspective

For biofuel applications, the criteria evaluated were chosen to consider only the physico-chemical and energy properties of biochar. Given the challenges and future prospects in the field of converting waste into high value-added products, biochar, like bio-oil and smoke, needs to be explored and used in other areas.

The first limitation concerns the use of biochar as a solid biofuel for the production of heat and electricity. A more detailed study of the conversion of biochar into solid biofuels in the form of briquettes is needed to better utilize it as an alternative energy source to charcoal and fossil coals in homes and coal-fired power stations, and this will be the subject of forthcoming publications. Other uses for biochar are also conceivable, such as the production of activated carbon, biomaterials, soil amendments etc.

The second limitation relates to the assessment of bio-oils and smoke. Further experiments are recommended to characterize the bio-oil and smoke from the thermal treatment in more detail, to enable physico-chemical and energetic characterization and to point to other routes of recovery, including chemicals with higher total values. Large scale biochar production will produce large quantities of bio-oil and smoke, and improved properties of these products could be achieved through optimization and further adaptation and blending. The bio-oil and smoke produced could be used directly for decentralized power and heat generation in industrial processes for the production of solid biofuels from biochar.

5. Conclusion

The physico-chemical properties of cashew nutshells show that they are good raw materials to be used in thermo-chemical processes for the recovery of energy. However, due to the high CNSL content, their direct use in these thermal processes has a negative impact on the environment and human health. Moeover, the chlorine content of raw cashew nutshells exceeds the limit set by the Standard NF EN ISO 17225-6 (≤0.1 wt%). The heat treatment of the cashew nutshells has allowed the identification of the optimal temperature and heating time conditions, which are 300 °C and 120 minutes respectively, with a biochar yield of 46.5% by mass. The biochar obtained has a higher heating value of 32.10 $MJ \cdot kg^{-1}$ with a residual oil content in the biochar of less than 1%. The higher calorific value of the biochar is 1.3 times higher than that of the raw cashew nutshell. The chlorine content of the biochar (<0.02 wt%) is within the normative limit of Standard NF EN ISO 17225-6 (≤0.1 wt%), unlike that of the raw cashew nutshells. The heat treatment significantly reduced the mass yield, but improved the energy yield as well as the physico-chemical properties of the cashew nutshell. Heat treatment also effectively reduced the moisture and volatile matter content and increased the fixed carbon content and calorific value compared to raw cashew nutshells and cake. The bio-oil and smoke produced have higher heating values of 36.00 $MJ \cdot kg^{-1}$ and 10.20 $MJ \cdot Nm^{-3}$, respectively. Due to their high energy values, the bio-oil and smoke produced during the heat treatment of cashew nutshells can be used in the process by integrating an energy recovery and utilization system or as other high added value energy products, thereby significantly reducing economic and environmental problems.

Use of AI tools declaration

The authors state that they did not utilize Artificial Intelligence (AI) tools in crafting this article.

Conflict of interest

The authors assert that there are no competing interests in relation to the publication of this manuscript.

References

1. FAO (2023) Crops and livestock products 2023. Available from: https://www.fao.org/faostat/en/#data/QCL.
2. Away4Africa, ACA (2018) Environmental Study of Waste Management in Cashew Processing in eight African countries Benin, Burkina Faso, Côte d'Ivoire, Ghana, Guinea-Bissau, Kenya, Mozambique, Tanzania. Final report, funding from the AfTra Project (African Development Bank) For African Cashew Alliance. Available from: https://www.away4africa.nl/wp-content/uploads/2019/06/2018-A4A_Report_ACA-study-cashew-by-products_Final.pdf
3. Kouamé KM, Fofana A, Abouo NV, et al. (2020) Sustainable thermochemical valorization of cashew nut waste in West Africa: Experimental study and evaluation of the energy potential in Côte d'Ivoire. *Int J Renew Energy Res* 10: 1404–1414. https://doi.org/10.20508/ijrer.v10i3.11106.g8016
4. Mubofu EB, Mgaya JE (2018) Chemical valorization of cashew nut shell waste. *Top Curr Chem* 376: 8. https://doi.org/10.1007/s41061-017-0177-9
5. Godjo T, Tagutchou JP, Naquin P, et al. (2015) Valorisation des coques d'anacarde par pyrolyse au Bénin. *Déchets Sci Tech* 70: 11–18. https://doi.org/10.4267/dechets-sciences-techniques.3282
6. Sawadogo M, Tanoh ST, Sidibé S, et al. (2018) Cleaner production in Burkina Faso: Case study of fuel briquettes made from cashew industry waste. *J Cleaner Prod* 195: 1047–1056. https://doi.org/10.1016/j.jclepro.2018.05.261
7. Panwar NL, Pawar A, Salvi BL (2019) Comprehensive review on production and utilization of biochar. *Appl Sci* 1: 19. https://doi.org/10.1007/s42452-019-0172-6
8. Pandiyan VC, Shylaja G, Srinivasan RG, et al. (2020) Studies on use of Cashew Nut Shell Liquid (CNSL) in biopesticide and biofertilizer. *Nat Env Poll Tech* 19: 103–111. https://neptjournal.com/upload-images/(9)B-3614.pdf
9. Nyirenda J, Zombe K, Kalaba G, et al. (2021) Exhaustive valorization of cashew nut shell waste as a potential bioresource material. *Sci Rep* 11: 14. https://doi.org/10.1038/s41598-021-91571-y
10. Papadaki MI, Mendoza-Castillo DI, Reynel-Avila HE, et al. (2021) Nut Shells as Adsorbents of Pollutants: Research and perspectives. *Front Chem Eng* 3: 15. https://doi.org/10.3389/fceng.2021.640983
11. Jijo J, Roshna R, Santhiya S (2022) Cashew nut shell ash as a supplementary additive in lime stabilized expansive soil composites. *Mater Today Proc* 62: 644–649. https://doi.org/10.1016/j.matpr.2022.03.627
12. Ba MS, Ndiaye LG, Youm I (2019) Thermochemical characterization of Casamance biomass residues for production of combustibles briquettes. *Open J Phys Chem* 9: 170–181. https://doi.org/10.4236/ojpc.2019.93009
13. Ifa L, Yani S, Nurjannah N, et al. (2020) Techno-economic analysis of bio-briquette from cashew nut shell waste. *Heliyon* 6: 9. https://doi.org/10.1016/j.heliyon.2020.e05009
14. Ajith Kumar TT, Mech N, Ramesh ST, et al. (2022) Evaluation of composite briquettes from dry leaves in energy applications for agrarian communities in India. *J Clean Prod* 350: 131312. https://doi.org/10.1016/j.jclepro.2022.131312
15. Nikiema M, Somda MK, Sawadogo JB, et al. (2020) Valorization of agricultural waste: theoretical estimation and experimental biomethane yield from cashew nut hulls. *J Sustain Bioeng Syst* 10: 113–130. https://doi.org/10.4236/jsbs.2020.104009

16. Moreira R, Dos Reis Orsini R, Vaz JM, et al. (2017) Production of biochar, bio-oil and synthesis gas from cashew nut shell by slow pyrolysis. *Waste Biomass Valorization* 8: 217–224. https://doi.org/10.1007/s12649-016-9569-2
17. Nam NH, Anh KD, Truc LGT, et al. (2020) Pyrolysis of cashew nut shell: A parametric study. *Vietnam J Chem* 5: 506–511. https://doi.org/10.1002/vjch.202000015
18. Coulibaly A, Sako MK, Soro D, et al. (2022) Valuation of cashew nut shell for the production of biofuel. *Energy Rep* 8: 691–707. http://dx.doi.org/10.1016/j.egyr.2022.07.090
19. Sakulkit P, Palamanit A, Dejchanchaiwong R, et al. (2020) Characteristics of pyrolysis products from pyrolysis and co-pyrolysis of rubber wood and oil palm trunk biomass for biofuel and value-added applications. *J Environ Chem Eng* 8: 15. https://doi.org/10.1016/j.jece.2020.104561
20. Van Soest PJ, Robertson JB, Lewis BA (1991) Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition. *J Dairy Sci* 74: 3583–3597. https://doi.org/10.3168/jds.S0022-0302(91)78551-2
21. Kaur R, Kumar VT, Krishna BB, et al. (2023) Characterization of slow pyrolysis products from three different cashew wastes. *Bioresour Technol* 376: 128859. https://doi.org/10.1016/j.biortech.2023.128859
22. Ábrego J, Plaza D, Luño F, et al. (2018) Pyrolysis of cashew nutshells: Characterization of products and energy balance. *Energy* 158: 72–80. https://doi.org/10.1016/j.energy.2018.06.011
23. Mehetre SA, Sengar SH, Panwar NL, et al. (2016) Performance evaluation of improved carbonized cashew nut shell based cookstove. *Waste Biomass Valorization* 7: 1221–1225. https://doi.org/10.1007/s12649-016-9497-1
24. Anand A, Gautam S, Chand Ram LC (2023) A characteristic-based decision tree approach for sustainable energy applications of biomass residues from two major classes. *Fuel* 339: 127483. https://doi.org/10.1016/j.fuel.2023.127483
25. Homchat K, Ramphueiphad S (2022). The continuous carbonisation of rice husk on the gasifier for high yield charcoal production. *Results Eng* 15: 6. https://doi.org/10.1016/j.rineng.2022.100495
26. Raza M, Abu-Jdayil B (2023) Synergic interactions, kinetic and thermodynamic analyses of date palm seeds and cashew shell waste co-pyrolysis using Coats–Redfern meth-od. *Case Stud Therm Eng* 47: 14. https://doi.org/10.1016/j.csite.2023.103118
27. Nunes LJR, Matias JCO, Loureiro LMEF, et al. (2021) Evaluation of the potential of agricultural waste recovery: energy densification as a factor for residual biomass logistics optimization. *Appl Sci* 11: 23. https://dx.doi.org/10.3390/app11010020
28. Muthu Dineshkumar R, Meera Sheriffa Begum KMKM, Ramanathan A (2020) Comprehensive characterization of cashew nutshell for biomass gasification. *Mater Today Proc* 46: 9814–9819. https://doi.org/10.1016/j.matpr.2020.10.932
29. Rodriguez-Jimenez S, Duarte-Aranda S, Canche-Escamilla G (2019) Chemical composition and thermal properties of tropical wood from the Yucatán dry forests. *Bioresources* 14: 2651–2666. https://doi.org/10.15376/biores.14.2.2651-2666
30. Preradovic M, Papuga S, Kolundžija A (2023) Torrefaction: Process review. *Period Polytech Chem Eng* 67: 49–61. https://doi.org/10.3311/PPch.20636
31. Chen WH, Peng J, Bi XT (2015) A state-of-the-art review of biomass torrefaction, densification and applications. *Renew Sust Energ Rev* 44: 847–866. https://doi.org/10.1016/j.rser.2014.12.039

32. Mamvura TA, Danha G (2020) Biomass torrefaction as an emerging technology to aid in energy production. *Heliyon* 6: 17. https://doi.org/10.1016/j.heliyon.2020.e03531
33. Ducom G, Gautier M, Pietraccini M, et al. (2020) Comparative analyses of three olive mill solid residues from different countries and processes for energy recovery by gasification. *Renew Energ* 145: 180–189. https://doi.org/10.1016/j.renene.2019.05.116
34. Castilla-Caballero D, Barraza-Burgos J, Gunasekaran S, et al. (2020) Experimental data on the production and characterization of biochars derived from coconut-shell wastes obtained from the Colombian Pacific Coast at low temperature pyrolysis. *Data in Brief* 28: 11. https://doi.org/10.1016/j.dib.2019.104855
35. Diedhiou A, Ndiaye LG, Bensakhria A, et al. (2019) Thermochemical conversion of cashew nut shells, palm nut shells and peanut shells char with CO_2 and/or steam to aliment a clay brick firing unit. *Renew Energ* 142: 581–590. https://doi.org/10.1016/j.renene.2019.04.129
36. Lu F, Rodriguez-Garcia J, Van Damme I, et al. (2018) Valorisation strategies for cocoa pod husk and its fractions. *Curr Opin Green Sustain Chem* 14: 80–88. https://doi.org/10.1016/j.cogsc.2018.07.007
37. Vásquez ZS, de Carvalho Neto DP, Pereira GVM, et al. (2019) Biotechnological approaches for cocoa waste management: A review. *Waste Manage* 90: 72–83. https://doi.org/10.1016/j.wasman.2019.04.030
38. Adjin-Tetteh M, Asiedu N, Dodoo-Arhin D, et al. (2018) Thermochemical conversion and characterization of cocoa pod husks a potential agricultural waste from Ghana. *Ind Crops Prod* 119: 304–312. https://doi.org/10.1016/j.indcrop.2018.02.060
39. Zinla D, Gbaha P, Koffi PME, et al. (2021) Characterization of rice, coffee and cocoa crops residues as fuel of thermal power plant in Côte d'Ivoire. *Fuel* 283: 9. https://doi.org/10.1016/j.fuel.2020.119250
40. Kaliyan N, Morey RV (2009) Factors affecting strength and durability of densified biomass products. *Biomass Bioenergy* 33: 337–359. https://doi.org/10.1016/j.biombioe.2008.08.005
41. Kosakowski W, Bryszewska MA, Dziugan P (2022) Biochars from post-production biomass and waste from wood management: Analysis of carbonization products. *Materials* 13: 13. https://doi.org/10.3390/ma13214971
42. Srisang S, Phetpan K, Ruttanadech N, et al. (2022) Charcoal briquette production from waste in the coffee production process using hydrothermal and torrefaction techniques: A comparative study with carbonization technique. *J Cleaner Prod* 372: 133744. https://doi.org/10.1016/j.jclepro.2022.133744
43. Lubwama M, Yiga VA (2018) Characteristics of briquettes developed from rice and coffee husks for domestic cooking applications in Uganda. *Renew Energ* 118: 43–55. https://doi.org/10.1016/j.renene.2017.11.003
44. Hawash SI, Farah JY, El-Diwani G (2017) Pyrolysis of agriculture wastes for bio-oil and char production. *J Anal Appl Pyrolysis* 124: 369–372. https://doi.org/10.1016/j.jaap.2016.12.021
45. Sharma P, Gaur KV, Sirohi R (2020) Valorization of cashew nut processing residues for industrial applications. *Ind Crops Prod* 152: 11. https://doi.org/10.1016/j.indcrop.2020.112550
46. Adekanbi ML, Olugasa TT (2022) Utilizing cashew nut shell liquid for the sustainable production of biodiesel: A comprehensive review. *Clean Chem Eng* 4: 17. https://doi.org/10.1016/j.clce.2022.100085

47. Scaldaferri CA, Pasa VMD (2019) Green diesel production from upgrading of cashew nut shell liquid. *Renew Sustain Energy Rev* 111: 303–313. https://doi.org/10.1016/j.rser.2019.04.057
48. Devarajan Y, Munuswamy DB, Nagappan BK (2017) Emissions analysis on diesel engine fuelled with cashew nut shell biodiesel and pentanol blends. *Environ Sci Pollut Res* 24: 13136–13141. https://doi.org/10.1007/s11356-017-8915-7
49. Bamgbola AA, Adeyemi OO, Olubomehin OO, et al. (2020) Isolation and characterization of cellulose from cashew (Anacardium occidentale L.) nut shells. *Curr Opin Green Sustain Chem* 3: 8. https://doi.org/10.1016/j.crgsc.2020.100032
50. Selvamuthukumar M, Harish babu B, Sujith bobba, et al. (2021) Investigation on the lubricating behavior of cashew nut shell liquid oil as a renewable and reliable petrochemical product. *Mater Today Proc* 44: 3583–3588. https://doi.org/10.1016/j.matpr.2020.09.458
51. Ganesan S, Vedagiri P (2022) Production of sustainable biomass briquettes from de-oiled cashewnut Shell. *Mater Today Proc* 68: 2484–2492. https://doi.org/10.1016/j.matpr.2022.09.179
52. Cruz Reina LJ, López GD, Durán-Aranguren DD, et al. (2023) Compressed fluids and Soxhlet extraction for the valorization of compounds from Colombian cashew (Anacardium occidentale) nut shells aimed at a cosmetic application. *J Supercrit Fluids* 192: 105808. https://doi.org/10.1016/j.supflu.2022.105808.
53. Abdulyekeen KA, Umar AA, Patah MFA, et al. (2021) Torrefaction of biomass: Production of enhanced solid biofuel from municipal solid waste and other types of biomass. *Renew Sust Energ Rev* 150: 21. https://doi.org/10.1016/j.rser.2021.111436
54. Thengane SK, Kung KS, Gomez-Barea A, et al. (2022) Advances in biomass torrefaction: Parameters, models, reactors, applications, deployment, and market. *Prog Energy Combust Sci* 93: 101040. https://doi.org/10.1016/j.pecs.2022.101040
55. Ahmadou A, Brun N, Alfredo N, et al. (2019) Effect of pyrolysis temperature on ochratoxin A adsorption mechanisms and kinetics by cashew nut shell biochars. *J Food Sci Technol* 4: 877–888. https://doi.org/10.25177/JFST.4.7.RA.565
56. Tumuluru JS, Yancey NA, Kane JJ (2021) Pilot-scale grinding and briquetting studies on variable moisture content municipal solid waste bales-Impact on physical properties, chemical composition, and calorific value. *Waste Manage* 125: 316–327. https://doi.org/10.1016/j.wasman.2021.02.013
57. Nobre C, Alves O, Longo A, et al. (2019) Torrefaction and carbonization of refuse derived fuel: Char characterization and evaluation of gaseous and liquid emissions. *Bioresour Technol* 285: 9. https://doi.org/10.1016/j.biortech.2019.121325