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Physicochemical and calorific characterizations of balm from cashew nuts shells (*Anacardium occidentale L.*) from two processing factories in Ivory Coast

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ABSTRACT: In Ivory Coast, the cashew nut shells liquid (CNSL) from processing factories is a source of environmental pollution and concern for public health. The valorization of these balm is a promising solution to resolve this problem. Therefore, this study aims to evaluate their physicochemical and calorific characterizations. Shells were collected from two cashew processing factories. Physicochemical and calorific properties of balm extracted from shells by soxlhet were determined. The extraction yield of balm from cashew shells was between 31.98±0.11% and 35.95±0.10%. Hull sample, which had the lowest water content, had the highest extraction yield. Physical and chemical parameters of the extracted balm varied significantly ($P < 0.05$). Its water content, density, viscosity and refractive index oscillated from 1.63±0.03% to 1.93±0.02% respectively; from 0.95±0.00 to 0.98±0.01; from 426.00±6.56 to 465±5.00 mPa.s and from 1.46±0.01 to 1.51±0.05. pH and acid, peroxide, iodine and saponification indices varied from 2.43±0.06 to 2.62±0.04 respectively; from 1.67±0.16 to 2.12±0.14 mg KOH/g; 14.97±0.63 and 16.73±0.41 meq O2/kg; from 100.05±0.07 to 100.72±0.23 g/100g and from 169.08±2.24 to 181.95±6.72 mg KOH/g. Calorific parameters of CNSL also varied significantly ($P < 0.05$). Cetane index and calorific value were between 50.77±1.13 and 53.07±0.44 and between 40.25±0.26 and 40.75±0.09 Kj/Kg, respectively. These results highlight the potential for using the balm from the shells, from cashew nut processing factories, in various non-food industries.

KEYWORDS: cashew nuts, CNSL, extraction, physicochemical, calorific, Ivory Coast.

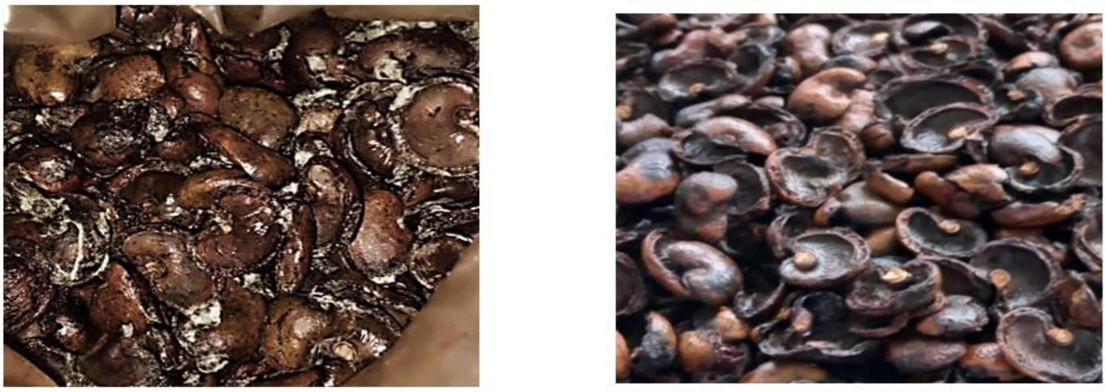
1 INTRODUCTION

Cashew (*Anacardium occidentale* L.), native of Brazilian coasts, was introduced to Africa by the Portuguese in 1960 with the aim of combating desertification and soil erosion [1]. In Ivory Coast, the introduction of cashew tree in 1961 aimed to counter erosion, deforestation, and to create hedges to protect agricultural operations [2]. Cashew cultivation has rapidly developed in the north of the country, becoming the main Ivorian export sector since the early 2000 [3]. Ivory Coast became the world's leading producer of cashew nuts in 2022, with a production of 1.028 million tonnes [4], [5]. In 2018, the processing rate reached 9%, and Ivory Coast became the third largest cashew processing country in the world in 2022, processing 22% of local production [5]. Despite this success, local cashew nut processing, started in 2008, faces challenges, notably the management of shell waste. Indeed, representing around 70% of the total weight of the nut, in 2022, around 3,270 tonnes of shells were produced each week [6]. Containing a balm called Cashew Nut Shell Liquid (CNSL), these shells represent risks to public health and the environment. Furthermore, in Ivory Coast, processing companies encounter difficulties in fully valorizing them. Hence the importance of this study which aims to contribute to the valorization of balm extracted from cashew nut shells coming from processing factories in Ivory Coast.

2 MATERIAL AND METHODS

2.1 BIOLOGICAL MATERIAL

Biological material was the shell of cooked cashew nuts. These samples were collected from two cashew kernel production factories, coded UCAJOU 1 and UCAJOU 2, located in Yamoussoukro. Furthermore, a control, uncooked shells, was made from shells manually separated from cashew kernels collected from producers in Korhogo. Thus, this last sample did not undergo the steam heating of cashew nuts commonly practiced in factories to facilitate shelling.



A B

***Fig. 1.** Uncooked cashew shells (A) and steamed cashew shells (B)*

2.2 CHEMICAL AND REAGENTS

Chemicals used in the experiment were hexane, HCl, KOH, Na_2CO_3, sodium argon thiosulfate, Nitrogen, $KMnO_4$, Wijs reagent, ethanol and iodine. All of these products were analytical grade and products of VWR International, Leuven, Belgium. Chemicals were obtained from Equipment Laboratories Chimie, Abidjan, Ivory Coast.

2.3 PREPARATION OF CASHEW SHELL SAMPLES

Samples taken from the factories (UCAJOU 1 and UCAJOU 2) and the one collected from producers in Korhogo (control) were each worth approximately 5 kg of cashew shells. These three samples were packaged separately and sent to the laboratory. Upon receipt, the shells were washed then dried in an oven at 40°C for 24 hours. After drying, they were ground using a food processor (Silver Crest, Lanfand Moor Technology, Hebei, China) until a fine paste was obtained. Pastes obtained were packaged in hermetically sealed smashed bags in a cabinet at laboratory temperature (22°C) and protected from light.

2.4 DETERMINATION OF CNSL EXTRACTION PARAMETERS

Water content of the pasta was determined using a moisture analyzer (MB90 halogen Ohaus, Parsippany (New Jersey), United States) following the method used by [7]. Extraction yield was obtained gravimetrically after extraction of cashew shell balsam (CNSL) using Soxhlet according to the method described by [8]. After extraction, the CNSL obtained were packaged in bottles fitted with lids and stored under conditions similar to those applied to pastes.

2.5 DETERMINATION OF PHYSICAL PROPERTIES OF CNSL

Density was obtained by dividing the density of cashew balsam by that of distilled water under the same conditions according to the method described by [9] using a pycnometer. Viscosity was determined using a viscosimetric tube according to the [10] standard based on the principle of gravity. Refractive index was determined at a temperature of 20 °C using a digital refractometer according to the [11].

2.6 Determination Of Chemical Properties Of CNSL

pH was measured using a pH meter (PH/TEMP, Juanjuan, Guangdong, China) according to the method described by [12]. Acid and saponification index were determined by acid-base assay according to the [11]. Determinations of peroxide and iodine index were carried out by the methods described by [13].

2.7 Determination Of The Calorific Parameters Of The CNSL

Cetane index (Ic), which measures the capacity of CNSL for self-ignition in a diesel engine, was determined by calculation according to the Klofenstein formula [14]. Lower calorific value (LCV), quantitative measure of the energy capacity of the CNSL, was calculated using the formula of Batel et al. (1980).

$Ic = 43.3 + (5458/Is) - (0.225 \times Ii)$; $LCV = 47645 - 4,187\ Ii - 38,31\ Is$ (kJ/kg)

Is: saponification index
Ii: iodine index

2.8 Statistical Analyzis

All tests were carried out in triplicate. All values are expressed as the mean ± standard error. Analysis of variance (ANOVA) was applied to compare means. When a significant difference was observed, ANOVA was followed by Turkey's HSD (Honest Significant Difference) test to classify the means. These statistical tests were carried out using STATISTICA 7.0 software and the error threshold was set at P = 0.05 or 5%.

3 Results

3.1 CNSL Extraction Parameters

Table 1 presents two CNSL extraction parameters. For each parameter, the values were significantly ($p < 0.05$) different due to at least one sample. Moisture content of the hulls of UCAJOU 1 (5.19 ± 1.40%) was higher than that of the hulls of UCAJOU 2 (3.73 ± 0.31%). On the other hand, the UCAJOU 1 sample demonstrated a CNSL extraction yield (31.98 ± 0.11%) lower than that of the UCAJOU 2 sample (35.95 ± 0.10%). Furthermore, the hulls of the control showed a water content (3.24 ± 0.29%) quite close to that of the hulls of UCAJOU 2; while its CNSL extraction yield (34.50 ± 0.49%) was a value between those obtained by the UCAJOU 1 and UCAJOU 2 samples.

Table 1. CNSL extraction parameters

Samples	Hulls moisture (%)	Extraction yield (%)
Control	3.24 ± 0.29^{b}	34.50 ± 0.49^{b}
UCAJOU 1	5.19 ± 1.40^{a}	31.98 ± 0.11^{c}
UCAJOU 2	3.73 ± 0.31^{b}	35.95 ± 0.10^{a}

3.2 Physical Parameters Of The CNSL

Physical characteristics of the CNSL are recorded in Table 2. Refractive index of the CNSL (1.46 – 1.51) did not significantly ($p > 0.05$) vary. However, significant differences ($p < 0.05$) were observed between samples for water content, density and viscosity of CNSL. The water content, density and viscosity of the CNSL of UCAJOU 1 (1.93 ± 0.02%; 0.98 ± 0.01 and 465.00 ± 5.00 mPa.s, respectively) were greater than those of the CNSL of UCAJOU 2 (1.82 ± 0.02%; 0.95 ± 0.00 and 441.33 ± 7.09 mPa.s, respectively). In addition, the CNSL of the control showed a lower water content (1.63 ± 0.03%) than the CNSL of UCAJOU 2; while its density and viscosity (0.95 ± 0.01 and 426.00 ± 6.56 mPa.s, respectively) were quite close to those of the CNSL of UCAJOU 2.

Table 2. Physical parameters of CNSL

Samples	Moisture (%)	Density	Viscosity (mPa.s)	Refraction index
Control	1.63±0.03[c]	0.95±0.01[b]	426.00±6.56[b]	1.46±0.01[a]
UCAJOU 1	1.93±0.02[a]	0.98±0.01[a]	465.00±5.00[a]	1.51±0.05[a]
UCAJOU 2	1.82±0.02[b]	0.95±0.00[b]	441.33±7.09[b]	1.51±0.04[a]

3.3 Chemical Parameters Of CNSL

Table 3 summarizes the chemical parameters of CNSL. For each parameter sought, the samples demonstrated significantly ($p < 0.05$) different values. CNSL of UCAJOU 1 had a pH and iodine and peroxide index (2.43 ± 0.06; 100.26 ± 0.12 g I2/100g and 14.97 ± 0.63 meq O2/ kg, respectively) lower than those of the CNSL of UCAJOU 2 (2.54 ± 0.03; 100.72 ± 0.23 g I2/100g and 16.11 ± 0.11 meq O2/kg, respectively); while its acid and saponification index (2.12 ± 0.14 mg KOH and 181.95 ± 6.72 mg KOH, respectively) were not significantly different from those of the CNSL of UCAJOU 2 (1, 93 ± 0.03 mg KOH and 176.80 ± 1.49 mg KOH, respectively). In addition, the CNSL of the control showed pH and, acid, saponification and peroxide index (2.62 ± 0.04; 1.67 ± 0.16 mg KOH; 169.08 ± 2.24 mg KOH and 16.73 ± 0.41 meq O2/kg, respectively) quite close to those of the CNSL of UCAJOU 2; while its iodine index (100.05 ± 0.07 g I2/100g) was similar to that of the CNSL of UCAJOU 1.

Table 3. Chemical parameters of CNSL

Samples	pH	Acid index (mg KOH/g)	Saponification index (mg KOH/g)	Iodine index (g I_2/100g)	Peroxide index (meq O_2/kg)
Control	2.62±0.04[a]	1.67±0.16[b]	169.08±2.24[b]	100.05±0.07[b]	16.73±0.41[a]
UCAJOU 1	2.43±0.06[b]	2.12±0.14[a]	181.95±6.72[a]	100.26±0.12[b]	14.97±0.63[b]
UCAJOU 2	2.54±0.03[a]	1.93±0.03[ab]	176.80±1.49[ab]	100.72±0.23[a]	16.11±0.11[a]

3.4 Calorific Parameters Of CNSL

Calorific parameters of the CNSL are presented in Table 4. For these two parameters, significant differences ($p < 0.05$) were observed due to the control sample. Indeed, the CNSLs of UCAJOU 1 and UCAJOU 2 demonstrated lower cetane index (50.77 ± 1.13 versus 51.51 ± 0.21) and calorific values (40.25 ± 0.26 KJ/Kg against 40.45 ± 0.06 KJ/Kg) which are not significantly different. However, the cetane index and the lower calorific value of the CNSL of the control (53.07 ± 0.44 and 40.75 ± 0.09 KJ/Kg, respectively) were significantly higher than those of the CNSL of UCAJOU 1, although they were not significantly different from those of the CNSL of UCAJOU 2.

Table 4. Calorific parameters of CNSL

Samples	Cetane index	Lower Calorific Value (KJ/Kg)
Control	53.07±0.44[a]	40.75±0.09[a]
UCAJOU 1	50.77±1.13[b]	40.25±0.26[b]
UCAJOU 2	51.51±0.21[ab]	40.45±0.06[ab]

4 Discussion

CNSL extraction revealed that, UCAJOU 1 samples had higher water content (5.19% ± 1.40) with lower extraction yield compared to UCAJOU 2 samples. These results are consistent with a study by [16], who reported lower extraction yields for Safou (Dracyodes edulis) samples with higher water content. High water content can negatively affect extraction yield, as water can interfere with the CNSL extraction process. These differences can be attributed to variations in the growing, harvesting, and processing conditions of cashew nuts, as well as the quality of the shells used in CNSL extraction.

Physical parameters of CNSL, the samples differed in terms of water content, density, viscosity, and refractive index. These physical characteristics can influence the properties and performance of CNSL in various applications. Moisture content of CNSL is an important parameter because high moisture content can affect the stability and quality of CNSL. Moisture content of our samples varied between 1.63% and 1.93%. These values are lower than the values 5.7 ± 0.2% and 6.7% reported respectively by [17], [18].

Density of CNSL is an important parameter to determine its potential for use in different industrial applications. Density obtained in the case of our study varied between 0.95 and 0.98; this value is approximately equal to that of the CNSL (0.984 and 0.941) obtained in the literature [18], [19]. When we compare our results (density) to those of the Ivorian diesel specification which vary between 0.820 and 0.880, we notice that the density of the CNSL is high. This therefore implies that CNSL is denser than diesel. This property of oils has detrimental effects on diesel engines, because it leads to a higher inertia than that of diesel for the same injection pressure. Thus, the high density of vegetable oils leads to an increase in the length of fuel jets, driving them to the bottom of the combustion chamber [20]. On the other hand, a high density may indicate greater molecular compactness of the CNSL; which can be beneficial for certain applications, such as coatings and adhesives.

Viscosity of CNSL is a key parameter for its use in various applications, including coatings, adhesives and lubricants. Viscosity varied between 426 and 465 mPa.s. These values are close to those found in the literature, namely 410 and 440 mPa.s respectively for CNSL extracted by pressure and by solvent [21]. We also note that the viscosity value of CNSL is very high compared to that given by the Ivorian specification for diesel (1.6-5.9 mPa.s) [22]. However, a high viscosity does not promote spraying or atomization during fuel injection and also causes obstruction of the engine's supply organs [20]. However, for certain applications a higher viscosity may indicate a better ability to form films or adhere to different surfaces [23].

Refractive index of the CNSL was similar for all samples, with values around 1.51. It is an important optical parameter, especially for optical applications and reflective coatings. Previous studies have shown that the refractive index of CNSL can be changed by adding additives or mixing it with other polymers to achieve specific optical properties [24]

Concerning chemical parameters, pH, acid, saponification, iodine and peroxide index provide information on the chemical composition and quality of the CNSL. pH values were similar, with slight variations (between 2.43 ± 0.06 and 2.62 ± 0.04). These pH values indicate the presence of anacardic acid necessary for the synthesis of other compounds. These results are very far from the values 4.06; 4.49; 4.6 and 5.0 obtained respectively in the work of [19], [25], [26]. High acidity of CNSL would promote corrosion of metal parts during its direct use in engines.

Concerning acid index, CNSL of UCAJOU 1 presented the highest value (2.12 ± 0.14 mg KOH/g), which is higher than the value 1.94 mg KOH/g reported by Victor -Oji et al. (2019). On the other hand, the CNSL of the control demonstrated the lowest value (1.67 ± 0.16 mg KOH/g), which is slightly higher than that (1.63 mg KOH/g) reported by [25]. Acidity of the extracted CNSL would be due to the presence of carboxylic acid.

Saponification index of the CNSL of UCAJOU 1 (181.95 ± 6.72 mg KOH/g) was the highest, followed by those of UCAJOU 2 (176.80 ± 1.49 mg KOH/g) and control (169.08 ± 2.24 mg KOH/g). These values are low compared to those of CNSL reported in the scientific literature [6]. This low saponification index obtained in this study suggests that the extracted CNSL contains high molecular weight fatty acids and is therefore not suitable for soap making.

Iodine index was similar for all samples, with values around 100g iodine/100g. These values are practically identical to that found in the literature which is 100.25 g of iodine/100g [6], and imply the presence of unsaturated carbon chain in the extract. Therefore, CNSL can be classified as a drying oil and could find application in paints, varnishes and surface coatings. These chemical characteristics can be modified by various CNSL refining and purification processes.

Regarding calorific parameters of CNSL, cetane index and lower calorific value are important indicators of the performance of CNSL as a fuel. Samples showed similar cetane index values, with slight variations (between 50.77 ± 1.13 and 53.07 ± 0.44). These values are greater than 46.00, the minimum value required by the Ivorian diesel specification. This shows that CNSL has a good ability for autoignition. A higher cetane number indicates better combustion quality and reduced polluting emissions [27].

Lower heating value is a measure of the amount of energy released when CNSL burns. Lower calorific value was also similar for all samples, with values around 40.5 Kj/Kg. This value is similar to that found by [28] which is 40.3 KJ/kg. CNSL is therefore a fuel capable of producing energy. It can therefore replace diesel after having undergone certain transformations. It is important to note that the calorific value can vary depending on the chemical composition of CNSL, particularly the content of phenolic compounds and fatty acids [29].

5 CONCLUSION

At the end of this study, it appears that the water content of cashew nut shells negatively influences the extraction yield of CNSL. Use of CNSL as a fuel in engines is limited by its high acidity (pH < 3) and its density (0.95 - 0.98) and viscosity (426 - 465 mPa.s) values higher than those of the Ivorian diesel specification. In addition, the extracted CNSL is not suitable for soap making due to its low saponification values (169.08 - 181.95 mg KOH/g). However, CNSL extracted from the shells has good preservability due to its low water content (1.6 - 1.93%). In addition, the determinations of physicochemical parameters (density, viscosity and, refractive and iodine indices) and calorific parameters (cetane index and lower calorific value) highlighted the possibility of using CNSL extracted from walnuts cashew in various industrial applications such as coatings, adhesives, lubricants and fuels. This study provides a solid basis for a better understanding of the key parameters of CNSL. It opens the way to new opportunities for innovation and application of CNSL in various fields, thus contributing to sustainable development and the efficient use of this precious plant resource.

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