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Cashew Nut Shell Oil — A Renewable and Reliable Petrochemical Feedstock

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Additional information is available at the end of the chapter

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Abstract

This study evaluates the occurrence of cashew plant, extraction processes and composition of cashew nut shell liquid (CNSL), modification and conversion processes, as well as environmental impact and controls of the liquid as petrochemical feedstock. The goal of this study is to bring the alternative usage of CNSL to the limelight and to mitigate the serious problems posed by the depleting petroleum reserves.

Cashew nut shell (CNS) was obtained fresh from the wild, pulverized and then extracted by pyrolysis and solvent extraction methods using *n*-hexane. The liquid obtained was characterized. Experimental results corroborated the fact that CNSL contains mainly phenolic compounds such as cardanol, cardol, anacardic acid and 6-methyl cardol. CNSL obtained by pyrolysis has a higher density with less moisture content, while solvent-extracted CNSL had higher contents of cardol and anacardic acid.

CNSL offers innumerable applications due to the phenolic nature of its constituents, with enshrined features for transformation into high-value specialty chemicals. Varied CNSL composition with varying extraction processes are a vantage opportunity with multiple application potentials as a valuable petrochemical feedstock.

Keywords: Cashew nut shell Liquid (CNSL), Petrochemical feedstock, Solvent extraction, Renewable resources, Characterization, Supercritical fluid

1. Introduction

Cashew Nut Shell Oil (CNSO) is a versatile component of the Cashew fruits' nut. The oil which is a dark reddish-brown in colour is resident in a soft honeycomb shell, that is the pericarp of the nut. It is a natural resin that could serve as a valuable raw material for multiple applications. Rapid growth in the world population and increasing standard of living has overstretched petroleum resources as petrochemical feedstock. This among other factors, has culminated in the fast depletion of global petroleum reserves. Therefore, to maintain the standard of living and continuity of industrial sector which is paramount to human survival this decade and beyond, there is a need to find alternative sources of fuel and petrochemical feedstock. Cashew nut shell, a by-product of the cashew industry, is an embodiment of a useful chemical serving as a raw material for the petrochemical industry.

Cashew (*Anacardium Occidentale* L.), a well-known species of the Anacardiceae family [1], is a tropical plant (shrub) found within the region between 23°N and 23°S of the equator. It is a drought resistant tree crop grown successfully in areas with annual rainfall of 50–350 cm. Its height is above 12 m and has a spread of about 25 m. It has an extensive root system which makes it adaptable to a wide range of moisture levels and soil types [2]. On the commercial scale, it is best grown on well-drained, sandy loam soils. Today, it is an economically valuable tree crop in Nigeria, with evergreen leaves, all year round.

The cashew tree consists of the cashew nut fruit (which is a curved edible seed, housed in a honeycomb-like shell), the apple, leaf and bark. The fruit consists of an outer shell, inner shell and the kernel. The thickness of the cashew nut shell is about 1/8 in. (0.32 cm). The soft honeycomb matrix, in between the outer and inner shell, contains a dark brown liquid, which is known as cashew nut shell liquid (CNSL) [3].

The Cashew plant is of great economic significance to Nigeria and other tropical countries due to its valuable products. These products are utilized in food, medicine, chemical and allied industries. In addition to providing shade, the cashew tree is an embellished ornamental plant that suitably controls soil erosion.

Usually, it takes about 3-4 years from planting time before fruiting. Thereafter, the tree can live up to 40 years and more. The cashew fruit (figures 1 and 2) is unusual in comparison with other tree nuts since the nut is outside the fruit. The cashew apple which is about 10 cm long is an edible false fruit, attached to the externally born nut by a stem. Its color ranges from yellow to red, fibrous in nature, very juicy, sweet, pungent and high in vitamins A and C. In its raw state, cashew nut shell (CNS), which is leathery in nature, contains the vesicant oily liquid (CNSL). The shell is separated from the kernel by the testa which is a thin skin surrounding the kernel.

1.1. Growth and development of cashew in Nigeria

The world production of cashew crop, according to the Food and Agriculture Organization (FAO), was around 2.7 million tons per annum. The major raw cashew producing countries with their production figures in 2005 (as per the United Nation's Food and Agriculture

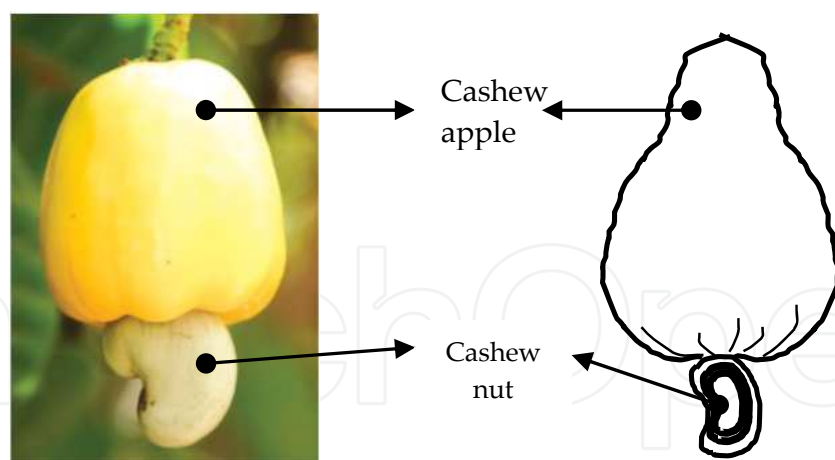


Figure 1. The Cashew fruit.

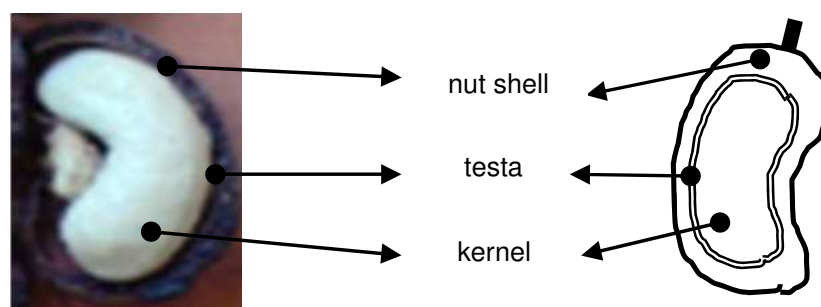


Figure 2. The cashew nut cross section

Organization) were Vietnam (960,800 tons), Nigeria (594,000 tons), India (460,000 tons), Brazil (147,629 tons) and Indonesia (122,000 tons). India ranks first in area utilized for cashew production, though its yields are relatively low. Collectively, Vietnam, India and Brazil account for more than 90% of all cashew kernel exports [4,5].

Cashew production in Nigeria dates back to the 15th century when it was introduced by Portuguese explorers [4,5]. The plant was then, purposefully planted for afforestation schemes in the now defunct Eastern Nigeria. Cashew became a popular commercial crop in 1953, when planted on a large scale principally for the nuts, afforestation and erosion prevention programmes in the escarpment areas of Dui, Mbala, Oghe, Oji, Isuochi and Kingie in Eastern Nigeria by the defunct Eastern Nigeria Development Corporation. In Western Nigeria, the first planting of cashew started in the 16th century at Agege in Lagos [4]. Commercial cultivation actually started in the 1950s at Iwo, Eruwa and upper Ogun in the defunct Western Nigeria by the then Western Nigeria Development Corporation.

Cashew was thereafter, introduced into the Middle Belt and Northern Nigeria from Eastern and Western Nigeria. These cashew nuts were mainly of the medium nut-size biotype, which according to ISO-6477 standards, fall within the W320 category. This cashew biotype therefore constitutes the main cashew species in Nigerian cashew plantations. This biotype, which was from the Asian continent, attracts low premium in the international market. However, Cocoa

Research Institute of Nigeria (CRIN) which was established in 1962, commenced research on the cultivation, uses and economy of cashew around 1972. The crop then rapidly spread to all agro-ecologies of Nigeria [6]. This brought about the cultivation for erosion control and the afforestation schemes of the Brazilian cashew biotype (jumbo nut-size), which is now being grown by cashew farmers [6]. This species mature within a year in contrast to the local wild varieties which take about 3 to 5 years to mature.

Today, cashew grows almost everywhere in Nigeria but its cultivation is concentrated primarily in the south and middle belt regions both in small holder farms and plantations [2]. Major cashew growing areas in Nigeria include Abia, Abuja, Anambra, Benue, Cross river, Enugu, Ebonyi, Ekiti, Kogi, Kwara, Kebbi, Nasarawa, Niger, Oyo, Osun, Ondo, Ogun, Sokoto, and Taraba states. High quality cashew nuts, suitable for export, are produced from the south west and south east regions of Nigeria. Figure 3 shows the spread of cashew production in Nigeria as published by National Cashew Association of Nigeria.

Establishment of the Premier Cashew Processing Factory in Oghe, Enugu State early in the 1980s marks the turning point in industrial processing of cashew in Nigeria. The primary objective of government then was to process the harvest from the government-owned 650 ha cashew plantation as well as to serve other small land holding farmers in and around the States of Kogi and Benue.

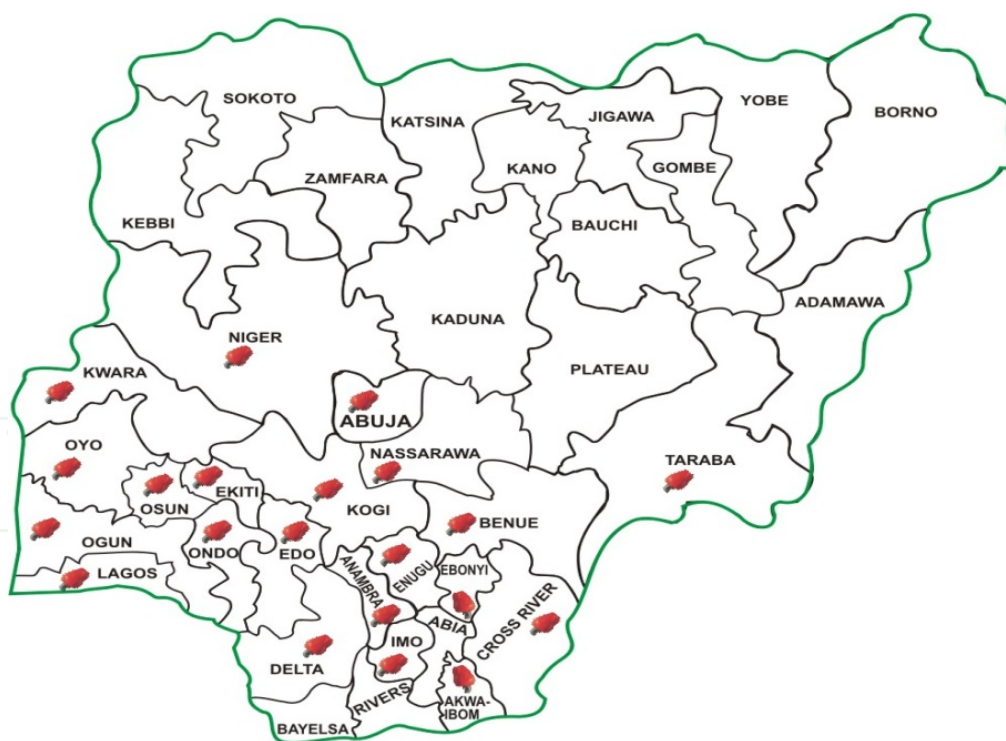


Figure 3. The spread of cashew cultivation in Nigeria

In 2002, Nigeria produced about 30,000 tons of cashew nut from the total holdings of 50,000 ha, which were mostly under small holdings. The average growth of cashew nut production

increased to 55,000 tons in 2004. In 2010, Nigeria ranked third among the top 10 world cashew nut-producing countries with a total production of 594,000 tons [7]. This stride improved to second worldwide in 2011 with a production of 835,000 metric tons, constituting 19.5% of the world's production according to FAOSTAT data 2013 [7]. The world production of cashew nuts is presented in Figure 4.

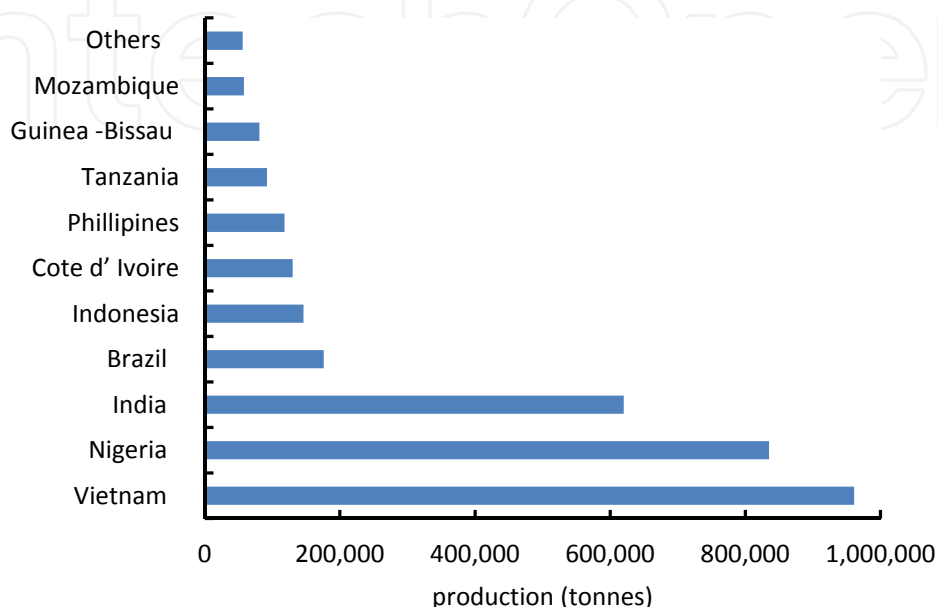


Figure 4. Main producer countries of cashew nuts

Recently, a cashew export programme was initiated in Lagos, Nigeria by the Nigerian Export Promotion Council (NEPC), the National Cashew Association of Nigeria (NCAN) and USAID/ Nigeria Expanded Trade and Transport (NEXTT). The move is to expand further the production of cashew nut for export purposes. The National Cashew Association of Nigeria (NCAN) is the umbrella body for the Nigerian cashew industry. It is actively involved in developing a strategy and action plan to improve the quality of raw nuts, to increase the coordination in the sector and to improve the business climate for processing.

India is a leading exporting country of cashew nuts. Its production volume stems from the skilled labour force and technology deployed at the processing stage. The popularity of cashew nuts arose from its applicability as natural vitamin pills [(balita.ph/.../cashew-nuts-gain-popularity-as-natures-vitamin-pill/)]. Cashew kernels on the other hand, have high protein content (about 19.5%), which accounted for its use in place of soybean meal in broiler chickens [8], whereas the nuts serve a major source of alkenyl phenolic compounds [9].

1.2. Processing

Basic physical operations before extraction are required on the samples of cashew nuts to ensure a high degree of purity and the quality of the product. These operations constitute the

basic pretreatment on samples and include washing, drying, shelling and size reduction. Sometimes, washing may involve the use of detergents to remove likely contaminants.

Drying is purposely to make the nuts moisture-free. Both sun- and oven-drying have been found effective. Size reduction creates a better contacting surface area for the shell and solvent to enhance removal of the CNSL.

Traditionally, the kernel is removed for the CNS manually. However, to improve the deshelling process, several methods have been adopted [1,8,10], which include, among others, soaking the nuts in water to improve the moisture content thereby reducing the scorching and cracking tendencies during roasting. Roasting the nuts makes the shell brittle and loosens the kernel from the shell easily. Also, CNSL is released during the roasting [10]. Figure 5 shows the nut-processing stages.

1.3. Extraction of CNSL

Several methods are available in the literature for the extraction of CNSL. Oil extraction efficiency varies with the method adopted. Raw CNS has been reported to contain over 20% oil. The oil bath process leaves about 10% of the oil as a by-product in the spent shell. However, using an expeller extraction process, further quantities of oil may be recovered from the spent CNS.

The extraction processes can be classified into two basic types: those that involve heating and those that are done in cold or room temperature. The heating process (roasting) can be achieved by open recipients or drums [11]. In a thermomechanic (hot oil) process, the cashews can be heated by the actual CNSL [12]. In the cold process, the CNSL can be obtained by extrusion in solvents or by pressing. The cashew's liquid so obtained is denoted as natural CNSL and that extracted by the hot method is called technical CNSL [13].

Various hot methods reported in the literature for the extraction of CNSL from cashew nut shells (CNS) include, open pan roasting, drum roasting and hot oil roasting, while cold extrusion, solvent extraction, etc. are cold methods. References [14] and [15] reported CNSL extraction through pyrolysis. The extraction of CNSL using supercritical carbon dioxide has also been reported by [16,17]. Solute extracted using supercritical carbon dioxide in the extraction process is generally significantly different from those obtained by other conventional alternative processes.

Extraction methods affect the selectivity towards various compounds in CNS [18]. High concentrations of mono-unsaturated cardanol were extracted with Supercritical water (SCW) and soxhlet extraction methods (See Table 1).

Extraction fluid, substrate and operating conditions affect the extract composition (Table 2). CNSL directly obtained from CNS by SC extraction contains traces of acids whereas the same obtained from CNSL through heat exchanger mainly contains cardanol along with acids and alkanes. The oil composition of CNSL obtained through pyrolysis of CNS includes phenols and substituted phenols along with cardanol. For resin production, the CNSL obtained through pyrolysis route is the most suitable feed for extraction by SC method [3].

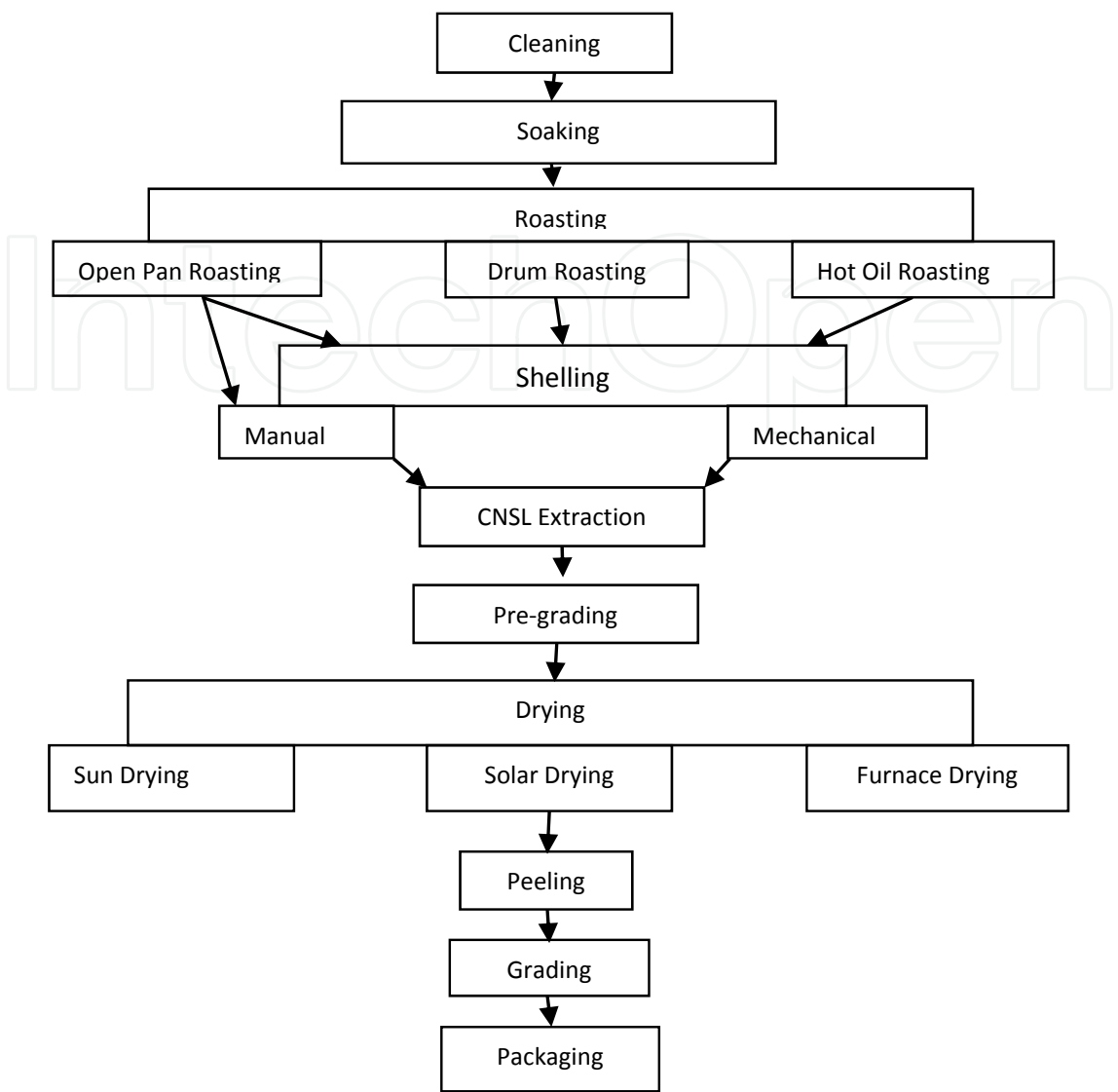


Figure 5. Flow diagram of cashew nut shell processing

Constituents	Soxhlet extraction		SCW extraction	SC-CO ₂ extraction	Two-step extraction	
	Hexane	Methanol			Hexane-SCW	Methanol-SCW
Monounsaturated cardanol	26.64	27.19	68.93	1.09	48.84	49.22
Saturated cardanol	1.22	1.45	2.4	1.52	1.04	1.84
Unknown hydrocarbon	–	–	3.42	–	1.57	1.42
Unknown hydrocarbon	–	–	3.29	–	1.51	1.37
Octacosene	–	–	4.91	–	2.25	2.04
Stigmasterol	–	–	3.44	–	1.57	1.43

Constituents	Soxhlet extraction		SCW extraction	SC-CO ₂ extraction	Two-step extraction	
	Hexane	Methanol			Hexane-SCW	Methanol-SCW
Monounsaturated anacardic acid	27.90	19.06	9.47	52.24	18.64	11.4
β-Sitosterol	1.38	1.86	1.63	1.63	0.75	1.76
Monounsaturated cardol	1.05	–	–	–	0.57	–
Saturated cardol	20.31	34.88	1.85	29.58	9.76	12.64
Di-unsaturated cardol	7.62	10.39	–	6.72	4.13	6.07
Unknown hydrocarbon	5.7	–	–	–	–	3.33
Triacontene	3.33	3.41	–	4.31	1.85	5.45
Others	4.85	1.76	0.66	2.91	7.52	2.03

Source: [18]

Table 1. Compound distribution of CNSL obtained by various extraction methods.

Operating Parameter (P bar/T°C)	SC-CNSL from CNS	SC-CNSL from CNS Obtained through Heat Exchanger Unit	SC-CNSL from Pyrolysis CNSL
200/60	Hexadecanoic acid (0.71) Oleic acid (0.62) Cardanol-C13 (0.69) Cardanol-C15 (84.20) Methyl Cardanol (2.83)	Pentadecane (0.67)	
		Hexadecane (0.67)	
		Heptadecane (0.77)	
		2,6,10,14 tetra methyl	3-ethyl phenol (7.64)
		pentadecane (0.65)	2-methyl benzaldehyde (20.51)
		8 methyl heptadecane (0.70)	3-butyl phenol (1.39)
		Hexadecanoic acid (0.61)	Cardanol diene (48.61)
		Elicosane (0.47)	
		Cardanol (62.31)	
		Cardanol diene (31.24)	
225/60	Hexadecanoic acid (0.56) Oleic acid (0.684) Cardanol-C13 (0.65) Cardanol-C15 (86.26) Methyl Cardanol (3.11)		3-ethyl phenol (3.31)
			Azulene (1.89)
			Ethyloxybenzene (11.21)
			Acenaphthylene (7.12)
			3-butyl phenol (2.28)
			Cardanol diene (66.82)
250/60	Hexadecanoic acid (0.58) Cardanol-C13 (7.42) Cardanol-C15 (64.89)	Pentadecane (0.04)	4-ethyl phenol (5.01)
		Heptadecane (0.08)	Propyl benzene (11.96)
		tetradecanal (1.99)	Acenaphthylene (2.83)

Operating Parameter (P bar/T°C)	SC-CNSL from CNS	SC-CNSL from CNS Obtained through Heat Exchanger Unit	SC-CNSL from Pyrolysis CNSL
300/60	Methyl Cardanol (3.03) Diethyl Phthalate (12.34)	cardanol 13 (1.62)	
		Hexadecanoic acid (1.27)	3-pentyl phenol (3.18)
		Cardanol (81.54)	3-butyl phenol (1.35)
	Hexadecanoic acid (0.80) Oleic acid (0.67) Cardanol-C13 (2.32)	2 methyl Cardanol diene (2.97)	Cardanol (64.91)
		Hexadecanoic acid (1.01)	
		Oleic acid (0.98)	2-ethyl phenol (4.89)
	Cardanol-C15 (61.34)	Cardanol diene (81.94)	2-methyl benzaldehyde (8.73)
	Cardanol c17 (2.06)	2 methyl Cardanol diene (2.97)	Cardanol (80.50)
	Diethyl Phthalate (13.35)		

Source: [3]

Table 2. Chemical characterization of CNSL extracted by SCFE

Purification or refining of CNSL involves vacuum distillation of raw CNSL. However, supercritical fluid extraction SFE of CNSL can offer selective separation of the components present in CNSL by varying the operating parameters [19].

2. Experimental materials and methods

2.1. Sample collection and pretreatment

Cashew was obtained from local markets in Ile-Ife, Osun State and a commercial farm in Owu-Ijebu in Ogun state. The shell was detached from the apple, washed and sun-dried prior to deshelling the nut. The cashew nut shell was further oven-dried and milled using a ball mill at the Petrochemical laboratory of the Department of Chemical Engineering, Obafemi Awolowo University, Ile-Ife. The milled CNS was sieved to obtain a particle size range of 5 mm. The ground sample was stored at 4°C in a refrigerator for further experimentation.

2.2. Extraction of the CNS oil

The pyrolysis of the cashew nut shells was carried out in the pyrolysis reactor designed and fabricated at the Chemical Engineering Department of Obafemi Awolowo University, Ile-Ife. About 150 g of the ground and dried CNS sample was placed in the reactor and heated. The reactor is connected to a condensing unit which has several condensers in series, in order to effectively recover the exhaust gases. The experimental rig is as shown in figure 6.

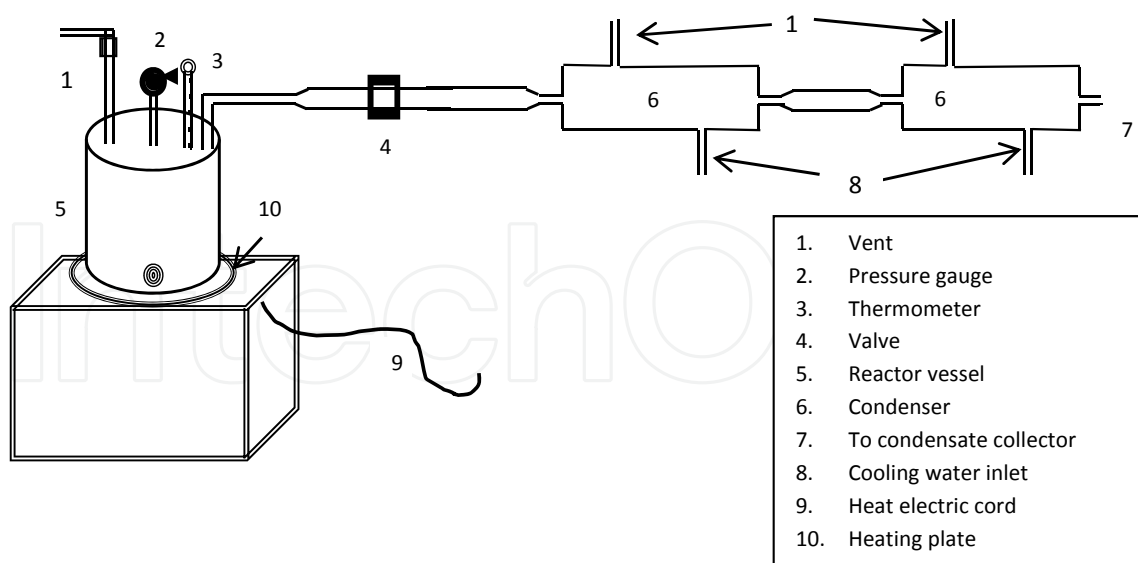


Figure 6. The experimental rig set-up.

The temperature of the reactor tank and that of the exhaust gas stream were measured and recorded at regular intervals. The volatiles which condensed at the condensing Unit were collected in several glass bottles. The heating was stopped when no significant changes in temperature and gas condensates was observed. The reactor was then allowed to cool for about 6 h; the ash and char were separated, weighed and recorded. The mass of pyrolysis oil produced was determined by mass balance calculation of the whole recovery system, before and after the experiment. For the purpose of comparison, 10 g of the CNS sample was extracted by soxhlet extraction using *n*-hexane as a solvent.

2.3. Characterization of the extracted CNSL samples

Moisture content was determined by standard Dean and Stark apparatus as outlined by the Association of Official Analytical Chemists [20]. Viscosity was determined using a capillary viscometer in water bath maintained at 40°C. A pH meter model PYE 290 was calibrated and used to determine the pH of the samples. Specific Gravity was measured using a pycnometer at 25°C. Iodine value was obtained by the method of [21].

An oxygen bomb calorimeter (model 6400) was used to determine the calorific value of the CNSL samples under adiabatic condition. The heat of the system was regulated by using an electrolyte. The calorific values of CNS and its spent cake were measured by placing them in a capsule, which was then put in the calorimeter crucible. The calorific value is given by equation 1.

$$\text{calorific value (kcal/kg)} = \frac{(W + w) (T_1 - T_2)}{X} \quad (1)$$

where

W = weight of water in calorimeter (kg),

w = water equivalent of apparatus,

T_1 = initial temperature of water ($^{\circ}\text{C}$),

T_2 = final temperature of water ($^{\circ}\text{C}$),

X = weight of fuel sample taken (kg)

3. Results and discussion

Table 3 shows the physicochemical characteristics of CNSL obtained including the decarboxylated CNSL. The quantity and characteristics of the CNSL extract varies with the extraction method.

Parameter	CNSL (pyrolysis)	CNSL (hexane extracted)	CNSL (decarboxylated)
Colour	Dark brown	Dark brown	Dark brown
Moisture content	4.1	6.4	3.2
Refractive index	1.693	1.688	1.698
Specific gravity	0.943	0.926	0.928
Viscosity (centipoise)	57	40	38
Ash (%)	1.22	1.53	1.50
Saponification value (mgKOH/g)	58.5	47.2	56.3
Iodine value (mg/100g)	212	236	227
Acid value (mgKOH/g)	12.4	15.6	12.9
Free fatty acid (mgKOH/g)	6.5	7.9	8.2
pH	4.8	4.5	5.2
Calorific value (kJ/g)	47.62		

Table 3. Physico-chemical characteristics of CNSL obtained including the decarboxylated CNSL.

CNSL obtained by pyrolysis although a little less in quantity than the soxhlet extraction, is denser (943 kg/m^3) with less moisture content (4.1%) and higher saponification value (58.5%). Solvent-extracted CNSL presented higher contents of cardol and anacardic acid and a lower percentage of cardanol than thermally extracted CNSL (Table 4). The higher content of cardanol, viscosity and impurity were the significant differences in CNSL obtained through pyrolysis. This gave credence to the report of Rodrigues *et al.* [22].

Components	CNSL (pyrolysis)	CNSL (hexane extracted)	CNSL (decarboxylated)
Cardol (%)	27	30	31
Cardanol (%)	54	20	65
Anacardic acid (%)	5	43	2
Others (%)	14	7	2

Table 4. Composition of the extracted CNSL

Decarboxylation of raw CNSL involves loss of a carbon dioxide molecule from anacardic acid. The anacardic acid in the oil was converted to cardanol. This is reflected in the composition variation of the components reported in table 4. It is also significant that the pyrolysis of the CNS results in loss of the carboxylic acid content of the cashew nut shell to the process. The decarboxylated anacardic acid is termed CNSL biodiesel. The biodiesel obtained from CNSL does not require further processing like Trans esterification.

CNSL biodiesel is considered as offering many advantages, including sustainability, decrease of HC, CO, NOx gas emissions and many harmful pollutants [23]. Reference [24] explains the pyrolysis procedure of CNSL. The decarboxylation of CNSL is responsible for the trend in the pH obtained for the extracts.

Most of the characteristics evaluated gave similar results as those already reported in the literature. In the present findings, the highest occurrence of cardanol was in the decarboxylated CNSL while anacardic acid and cardol occur most in the hexane-extracted and pyrolysis CNSL, respectively. This gave credence to the report of [25].

Heating CNSL decomposed the anacardic acid into cardanol and CO₂. Decarboxylation of CNSL to convert anacardic acid into cardanol could be done by heating, with an optimum heating temperature of 140°C for 1 h.

4. CNSL as petrochemical feedstock

As a substituted phenol which can take part in a variety of reactions, naturally occurring cashew nut shell liquid (CNSL), a renewable product, offers advantages over synthetics. Its innumerable application stems from the phenolic nature of its constituents, with enshrined features for transformation into high value specialty chemicals [26].

The industrial applications of CNSL-based products are numerous and include fungicide, pesticide, insecticide, brake linings, paints and primers, foundry chemicals, lacquers, cements, specialty coatings and resin. The application of CNSL component in bacteriostatic antibiotics is recently gaining attention. Their effect on plant growth, acid activity, wood preservative and pressure treatment activity are being explored. From the literature [27 - 29], much of the biological activity of CNSL has been attributed to anacardic acid: a major constituent of CNS.

Conversely, technical CNSL, as obtained by roasting or oil bath method contained mainly cardols and cardanols [27].

CNSL reduces the extent of the electrochemical processes taking place on carbon steel surface undergoing corrosion. The inhibition tendency is excellent for both static and dynamic conditions. CNSL and its derivatives have antioxidative characteristics [28 - 30]. This antioxidative tendency is related to the electron-donating nature and steric effect of the substituents. The electron-donating effect usually enhances the electron density at the phenolic oxygen of the cashew nut oil, resulting in the trapping of the radicals which normally propagates oxidation reaction. CNSL is a mixture of hindered phenols with long alkyl substitution at the *meta* position. The unsaturation on the long side chain substituents is an important factor enhancing higher anti-oxidant activity of CNSL. CNSL films are thermally stable. This stability increases in the presence of thiophosphate ester additives.

Olefin metathesis (OM) reaction on cardanol is an important class of reactions that allows for the synthesis of new olefins that are sometimes impossible to prepare via other methods [31]. Cardanol- a renewable, low cost, main constituent (about 85%) of CNSL possesses characteristic long alkyl chains in *meta* position of its phenol ring [12] that promotes this OM reaction, and also influences several chemical transformations leading to novel functionalities [31].

Cardanol based polyhydriins improve the photo-catalytic activity of bare TiO₂. The porphyrins are brown-red sticky solids, very soluble in CHCl₃ or CH₂Cl₂ [32]. This substituted cardanol-based porphyrin and their metallic complexes have been used extensively in photo degradation of toxic, bio-refractory 4-nitro phenol in water, which is dangerous for the ecosystem and for human health [32]. CNSL is also useful in fuel blends and fuel mixtures [33] and for producing diesel oil [34]. Cracking of CNSL with a molecular sieve at 500° C for 2 h generates brown coloured liquid product. This is diesel fuel.

Cashew Nut Shell Liquid (CNSL) was used as an alternative fuel for diesel engine. The viscosity of CNSL is 30 - 35 times higher than diesel; hence different blends of CNSL would have different properties and application. Also, modification of the oil and its application condition such as, injection pressure, injection timing and preheating the oil also optimizes the performance of the engine. There were indications that preheating of CNSL25 blends at 200 kg/cm² injection pressure and 28° injection timing gives encouraging results suitable for commercial purposes [35]. CNSL as a bioadditive in engines increases the durability of the equipment. Hence, the application of CNSL as a bioadditive will reduce the dependency on petroleum products besides preserving the environment by lowering pollutant residues from fuel combustion products. Some of the properties of diesel, biofuel and ethanol are presented against CNSL in Table 5.

CNSL has higher density than diesel. It can be reduced by degumming and trans esterification. Cetane for CNSL is expected to be poor due to the presence of aromatic compounds. The usual C:H:O ratio for vegetable oils is 78:12:10 whereas for CNSL it is 80:12:8; hence, it justifies the higher calorific value of CNSL (47 MJ/kg), whereas for diesel it is 42 MJ/kg. Also, ash content is well within the limits for CNSL. The water content of CNSL is quite high. The sulphur content does not exceed 0.006% for any vegetable oil. Thus it is anticipated that CNSL has no sulphur

content. The flash point for CNSL is 164°C; this is higher than the flash point for diesel and represents the higher starting ignition temperatures and compression of CNSL [35].

Properties	Diesel*	Ethanol*	CNSL
Density (kg/m ³)	0.84	0.789	0.9326
Kinematic viscosity (cost)	2-5	1.19	17.2
Calorific value (kJ/kg)	42000	30000	47600
Flash point (°C)	62	16	193
Auto-ignition temperature (°C)	210	362	206

*Source: [28]

Table 5. Fuel properties

The physicochemical properties of cashew nut shell liquid (CNSL) make it potentially useful for improved adhesion between bitumen and aggregates. Thus, the asphalt resulting from bitumen modified with CNSL has better stripping resistance and satisfactory mechanical properties compared with conventional asphalts. The CNSL, as an additive, prevents stripping in the asphalts, thereby contributing to its moisture damage resistance [36].

CNSL has also been used in production of asbestos with free friction composition for brake linings [37]. In combination with cardanol, it is used extensively in automotive break-lining applications [38]. CNSL/cardol-based surface coatings possess excellent gloss and surface finish with a high level of toughness and elasticity.

Valuable chemicals result from the pyrolysis of CNSL at high temperatures (450°C to 750°C) and at short residence times [39]. The products of pyrolysis include tar, phenols, hydrocarbons and gases with high petrochemical values.

On the other hand, cardanol which is highly resistant to softening action of mineral oil, acids, alkalis, microbes, termites and insects is widely used in the coating and resin industry. Reference [40] reported that technical CNSL may also contain phytosterol, such as stigma sterol and β -sitosterol, which have cholesterol-lowering properties.

Cardanol polysulfide (CPS) has been used as a vulcanizing agent for natural rubber as reported by [41]. Coordination bond linkage in cardanol-aldehyde condensation polymers improved its physicomechanical properties. This positively influences the anticorrosive properties and stability of the polymeric compound at high temperature [42]. The blend of cardanol-based novolac-type phenolic resins, with commercial epoxy or isocynate monomers produces thermoset polymers [43]. Also, in [44], the conversion of CNSL-based cardols (6-alkenylresorcinols) into lasiodiplodin, a naturally occurring 12-membered orsellinic acid type macrolide, exhibits plant growth-regulating and antileukemic properties.

Immature CNSL (iCNSL) has excellent protective activities in strains of *S. cerevisiae* against oxidative damage induced by hydrogen peroxide and inhibits acetyl cholinesterase activity [45]. The high in vitro antibacterial activity of cashew nut shell liquid (CNSL) has been

attributed to its anacardic acid content [46]. Both anacardic acid and cardol were reported to have antitumor [47-49], antimicrobial [48], urease inhibitory [50] and lipoxygenase activities [51]. Gram positive bacteria, which cause tooth decay, acne, tuberculosis, *Streptococcus pneumonia*, *Francisella tularensis*, and leprosy are killed by anacardic chemicals [52].

Anacardic acid has also been found to reduce the expression of survivin and X-linked inhibitor of apoptosis protein, anti apoptotic proteins associated with cellular survival and radio resistance, and radio-sensitized pituitary adenoma cells [53]. Also, these acids have been used effectively against tooth abscesses due to their lethality to bacteria.

The monophenolics of CNSL have been found to form stable quaternary nitrogen compounds which are soluble in water, odourless and act as surface-active agents [54]. These properties including their high bacterial activity, have made them significantly useful as germicides, disinfectants and sanitizing agents in food and dairy industries. Also, sodium salts of anacardic acid, for example disodium anarcadates, are anionic surfactant and could be used as bactericidal surfactant while sodium anarcadate is useful for the control of vector mosquitoes which are responsible for causing dengue fever [55].

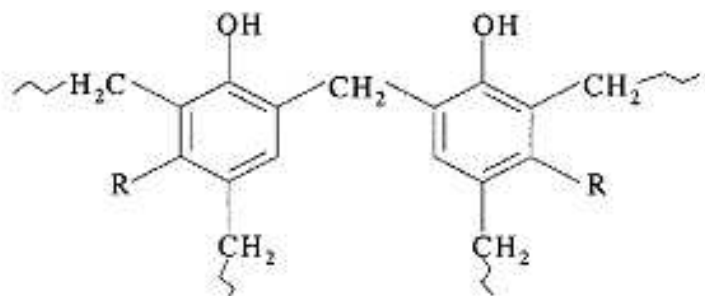
Energy studies established that cashew nut by-products CNSL, its isolates and spent CN Shell compare quite favourably with conventional fuels in terms of energy content. CNSL, cardanol and cardol, which are liquid by-products, were superior to conventional liquid and solid fuels while spent CN shell was more superior to a number of liquid fuels, e.g. ethanol and methanol, as well as fire wood in terms of energy content. This material is advocated for use by cashew nut processors and other industries as fuel to reduce environmental pollution. This material is not only a cleaner fuel but also has low ash and is renewable [56].

Substitution of phenol with CNSL in both resol and novolacs decreased the tensile strength, but improved the impact strength of wood flour-based laminate of these resins. Thermal properties of phenol-cardanol-based resin depletes with increasing cardanol content in the resin [57, 58].

The synthesis of polymers from renewable resources has attracted considerable attention worldwide due to its potential attribute as a substitute for petrochemical feedstock. CNSL may act as a potential raw material for the manufacture of polymers in the 21st century [58] due to its components and depletion in petroleum production which increasingly faces exhaustion. Long-chain, *m*-substituted phenol in CNSL is highly reactive. Thus a wide variety of resins are synthesized from CNSL, such as polyesters, phenolic resins, epoxy resins, polyurethanes, acrylics, vinyls and alkyds to mention a few [59].

CNSL contains four major components: 3-pentadecenyl phenol (cardanol), 5-pentadecenyl resorcinol (cardol), 6-pentadecenyl salicylic acid (anacardic acid) and 2-methyl 5-pentadecenyl resorcinol (2-methyl cardol), which can be good replacement for synthetic resins, owing to the current climate of diminishing petroleum reserves. Cardanol, which is a phenol derivative, has a meta substitute of a C15 unsaturated hydrocarbon chain with one to three double bonds [31, 32, 60, 61]. Being a major component of CNSL, its abundant production promised renewable feedstock for the petrochemical industry with a total production of CNS approaching 2.6 million tons annually [1].

Resoles and novolacs resins are the major products of reaction of CNSL with formaldehyde. While novolac results from acid-catalyzed reactions, resoles are a product of base-catalyzed reactions.



CNSL can be polymerized by different methods. This includes addition polymerization through the side-chain double-bonds using cationic initiators such as diethylsulphate, condensation polymerization through the phenolic rings with aldehydic compound, e.g. formaldehyde, oxidative polymerization, polymerization after chemical modification to produce specialty properties, etc. The most common method is condensation reaction with formaldehyde. The CNSL-based polymers offer advantages such as improved flexibility and reduced brittleness, solubility in organic solvents, improved process ability, compatibility with other polymers, high performance and resistance to microbes, insects and termites.

CNSL were successfully applied as a thermosetting wood adhesive for wood panels to reduce formaldehyde emission. These renewable phenolic compounds give excellent adhesive performance, good moisture resistance and tend to give a lower formaldehyde emission than UF resin [62, 63].

4.1. Environmental impact

CNSL may be a weak promoter of carcinogenesis but no mutagenic or carcinogenic activity has been reported [64]. Epidemiological studies suggested that CNSL may contribute to oral sub-mucous fibrosis [65]. In addition, its phenolic components exerted several biological activities, including antioxidative properties [66, 67], inhibition of acetyl cholinesterase and membrane perturbation [68, 69].

There is no direct evidence regarding the toxicity of CNSL or its major phenolic components. However, the effluent generated during the processing of the cashew nut could be considered potentially harmful to the environment due to its high phenol content. The hazardous effects of phenolic compounds have been extensively studied. According to [70], a concentration above 1 mg/L can affect aquatic life, while [71] recognizes deleterious effects at concentrations as low as 1 µg/mL.

As previously mentioned, data on the chemical composition of the cashew nut industry effluent are scarce, but preliminary analysis showed high phenol content due to the cardol, cardanol and anacardic acid of CNSL. The high toxicity observed for the isolated phe-

nols, cardol and cardanol potentially contribute to the toxicity of the cashew nut industry effluent [72].

5. Conclusion

The report has highlighted various chemicals obtainable from CNSL both directly and indirectly. This inexhaustible listing presents CNSL as a very important, reliable source of raw material for petrochemical industry. It is a good, promising supplement and/or alternate to petroleum, which is currently facing depletion globally.

Varied CNSL compositions with varying modes of extraction are a vantage opportunity with potential for multiple applications.

Though CNSL contains phenolics, its products are highly environmental friendly. However, efficient treatment strategy may be inevitable to reduce environmental impact associated with the production industry.

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