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# Experimentation on solvent extraction of polyphenols from natural waste

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**Abstract** The main commercial product of the cashew tree is the cashew apple and nut. Cashew nut is regarded as lost crop in the content of agricultural produce of India despite its industrial and export potentials. After separation of nut from the cashew fruit, the nut shell is disposed into the environment and this is acting as a waste. The nut shell containing a dark reddish brown viscous liquid is called cashew nut shell liquid (CNSL) and consists of 70% anacardic acid (polyphenol), 18% cardol, and 5% cardanol. This waste material is having twofold advantages: CNSL is a low-cost phenol, which is having many industrial applications and after extraction of CNSL from the shell, the shell is acting as a fuel for many boilers. Cashew nut shell liquid was extracted from cashew nut shell by indirect leaching process using soxhlet extraction equipment. Different solvents were used in the extraction of CNSL from the cashew nut shell (CNS) and a comparison was made between them. Among all the solvents acetone gives more amounts of CNSL and its properties rely with the industrial CNSL. The operating conditions for the extraction were 60 °C and 1 atm; in every 25 g of cashew nut shell used for the extraction, 8.75 g CNSL was obtained. The CNSL was further separated into cardol, cardanol, and anacardic acid (polyphenol) using an extractant, ammonium hydroxide, with the aid of mechanical shaker equipment. Subsequently, the polyphenol was further separated into dihydric phenols (resorcinol) and monohydric phenol (phenol).

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## Introduction

The cashew tree (*Anarcardium occidentale*) is a native of Brazil and the Lower Amazons. The cashew has been introduced and is a valuable cash crop in the Americas, the West Indies, Madagascar, India, and Malaysia. Cashew nut is a high-value edible nut. It yields two "Oils" of which one, found between the seed coat (or pericarp) and the nuts, is called the cashew nut shell liquid**.** It is not a triglyceride and contains a high proportion of phenolic compound. The cashew tree is evergreen. It grows up to 12 m high and has a spread of 25 m. Cashew nut is regarded as lost crop in the content of agricultural product of Nigeria despite its industrial and export potentials. The major by-product of cashew nut is the liquid from the pericarp known as cashew nut shell liquid. CNSL is one of the sources of naturally occurring phenols. CNSL is an amber-colored, poisonous, viscous oil obtained as a by-product of the cashew nut shells during extraction. It is often considered as the better and cheaper source of unsaturated phenols. CNSL has innumerable applications in polymer-based industries, such as friction linings, paints, varnishes [3], laminating resins, rubber compounding resins, polyurethane-based polymers, surfactants, epoxy resins, wood preservatives [2]. It offers much scope and varied opportunities for the development of other tailored polymers. More so, resins based on the reaction products of cardanol, phenol, and formaldehyde is used to improve the resistance of rubber articles to cracking and ozone degradation. Raw cashew nut shell contains around 20% oil. When cashew nuts are processed by oil extraction process, about 50% oil is extracted. Balance oil (or liquid as it is known) can be further extracted with the help of expellers. This note primarily deals with this kind of processing.

There are three different methods generally used in extracting cashew nut shell liquid from cashew nuts,

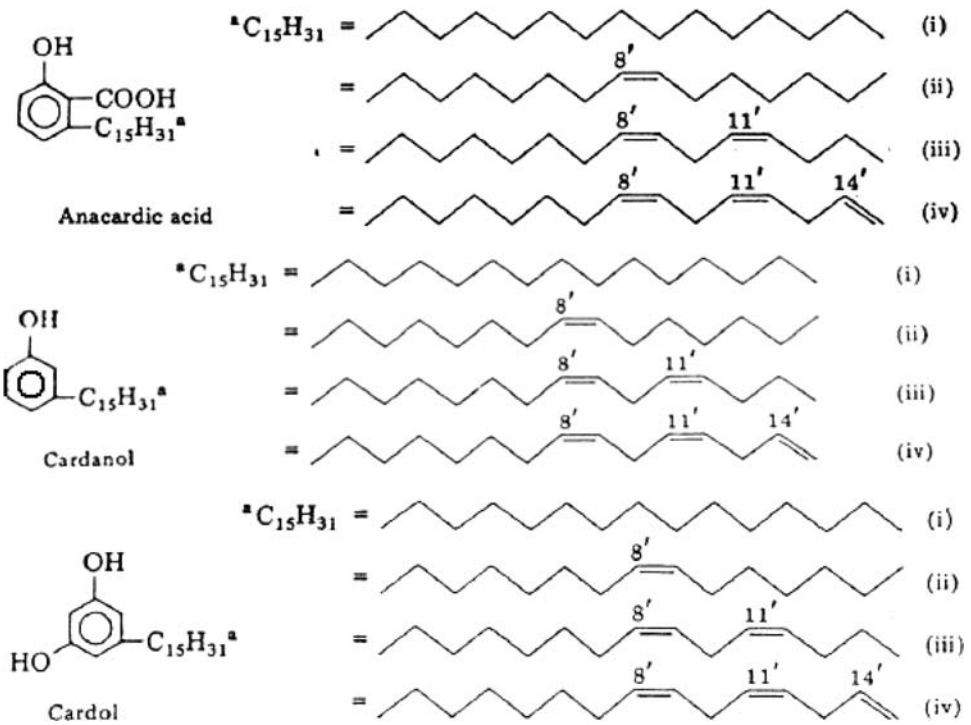
namely mechanical, roasting, and solvent extraction. The processes used are mainly hot-oil and roasting in which the CNSL oozes out from the shell. The traditional method of extracting CNSL is by roasting of the nuts over an open fire. This removes the CNSL by charring/degradation thereby wasting the liquid which is a valuable source of natural phenols. CNSL, if properly extracted, has a lot of industrial applications. Cardanol is a phenolic compound with a $C_{15}$ aliphatic chain in the meta position, obtained from cashew nut shell liquid, that find many applications in the form of phenol formaldehyde resins in vanishes, paints, and brakes linings. Derivatives of cardanol find applications in form of dyestaaffs, plasticizers, and ion-exchange resin. Chlorinated products of cardanol were found to have pesticidal action. Sulfonated derivatives of cardanol, tetrahydrocardanol, and their phenolic ethers are used as surface-active agents.

The industrial significance of CNSL are its use in producing low cost phenol, possibilities in the development of high performance polymers, versatility in polymerization and chemical modification and good impact resistance, flexibility etc. Some of its uses are in manufacturing CNSL resins, anticorrosive mortars, paints and enamels, laminates, foundry oil. It has been established that the dark colors formed during the polymerization of CNSL are attributable to the presence of polyhydric phenols, primary cardol, the dihydric component, accounts for CNSL a vesicant activity and toxicity; however, the application of CNSL in the surface-coating industry has been limited. Cashew apples are sometimes made locally into fruit drinks, wines, and pickles. In some countries they are also Osmo-Sol dried to produce a date-like caramel.

The CNSL is one of the sources of naturally occurring phenols. About 30–35% CNSL is present in the shell, which amounts to approximately 67% of the nut. Natural CNSL contains 70% anacardic acid, 18% Cardol, 5% Cardanol, with the remainder being made up of other phenols and less polar substances. Anacardic acid, cardanol, and cardol consists of mixtures of components having various degrees of unsaturation in the alkyl side chain.

The present study aims to extract CNSL from cashew nuts so as to determine its proportional constituents cum characteristics with the help of different solvents like acetone, hexane, toluene, and methanol. Specifically, the objective is to characterize as well as separate the CNSL into anacardic acid and cardol using an extractant, ammonium hydroxide, with the aid of mechanical shaker equipment.

**Structures of Anacardic acid, Cardanol and Cardol**



## Materials and methods

### Pretreatment of samples

Some basic physical operations were carried out on the samples (cashew nuts) before extraction to ensure high degree of purity and quality of product. These operations include washing, drying, and shelling as well as size reduction. The nuts were first washed thoroughly with detergent and subsequently rinsed after removing the fruit parts, so as to remove any dirt and contaminant that might have been attached. Subsequently, the nuts were dried for easy removal of the shell. This was done by spreading them under the sun for several days that made the nuts moisture free. The nuts were then shelled to remove the shells using a plier-like knife while wearing hand gloves. Finally, the dried shells were properly crushed to small sizes with the aid of mortar and pestle to create a better surface area for the shell and solvent to contact for easy removal of the CNSL.

### Apparatus required

The modified soxhlet apparatus was used for the extraction of CNSL from cashew nut shell (CNS). The experimental setup consists of round bottom flask, reflux extractor, bubble type condenser, heating mantle with the temperature range of 0–150 °C, and also a simple distillation unit for the separation of solvents from the CNSL and solvent mixtures. The mechanical shaker equipment was used to separate the polyphenols from the CNSL. All the chemicals used were of analytical grade.

### Methodology

The extraction of CNSL was carried out using a Soxhlet extractor and acetone as solvent. Five hundred milliliters (500 mL) of solvent was charged into the round bottom flask of soxhlet apparatus. Subsequently, 25 g of crushed cashew nut shell was charged into the thimble and fitted into the soxhlet extractor. The apparatus was assembled. The solvent in the set-up was heated to its boiling point and the vapour produced was subsequently condensed by water flowing in and out of the extraction set-up. This process of heating and cooling continued until a sufficient quantity of CNSL was obtained. At the end of the extraction, the thimble was removed while the remaining solvent in the extractor was recharged into the round bottom flask for a repeat of the process. Finally, the set-up was then re-assembled and heated to recover the solvent from the oil. The flow sheet for this process is shown in the Fig. 1.

The extract (CNSL) was separated into various constituents namely anacardic acid, cardanol, and cardol using ammonium hydroxide with the aid of mechanical shaker equipment. Subsequently, the polyphenol was further separated into dihydric phenols and monohydric phenol.

## Results and discussions

### Characteristic properties of CNSL

The different solvents like acetone, hexane, methanol, and toluene were used in solvent extraction method to extract CNSL from the CNS. The comparative studies were carried out on the properties of CNSL obtained using the different solvents mentioned above. By comparing all the above determined properties of CNSL using different solvents, acetone was concluded efficient in obtaining the CNSL close to that of the industrial values. The results of determining the characteristic properties of the CNSL are given in Table 1. Table 1 gives the pH result (5.96) of the CNSL and is indicative that it is acidic. The acidity of the CNSL is attributable to the presence of anacardic acid ($C_6H_3OH$–$C_{15}H_{31}$–COOH). From the available information in the literature, the specific gravity of CNSL is 1.07 g/cm$^3$ [1], whereas the specific gravity of the present work is 0.93 g/cm$^3$. The slight variation in the specific gravity may be attributed to the extraction technique cum operating conditions employed during the experiment. More so, CNSL is a natural product that contains a number of chemical species and is of variable composition depending on its source. Nevertheless, it still falls within the literature range [1]. Overall, the properties of the present finding fall within the standard specifications of CNSL. The composition of the CNSL is approximately 10% cardol (dicarboxy-pentadica-dienylbenzene), 50% cardanol, and 30% anacardic acid (carbopenta-dica-dienyl-phenol), with the remainder being made up of other substances.

### Physicochemical properties of polyphenol

Table 2 gives the physicochemical properties of the recovered polyphenol. From Table 2, it can be seen that the resorcinol component of the polyphenol is more acidic than that of phenol component of the same polyphenol. In the aqueous solution of the CNSL, polyphenol exists partly as non-dissociated molecules and partly as dissociated ions known as quinoid structures. The greater the acidity of the phenol species the more dissociated and the higher the concentration of quinoid ions implying that the resorcinol (pH 3.21) is majorly of quinoid ions which is plausibly explained by the more acidic nature of the resorcinol than the phenol. Thus, in a solution containing polyphenol,

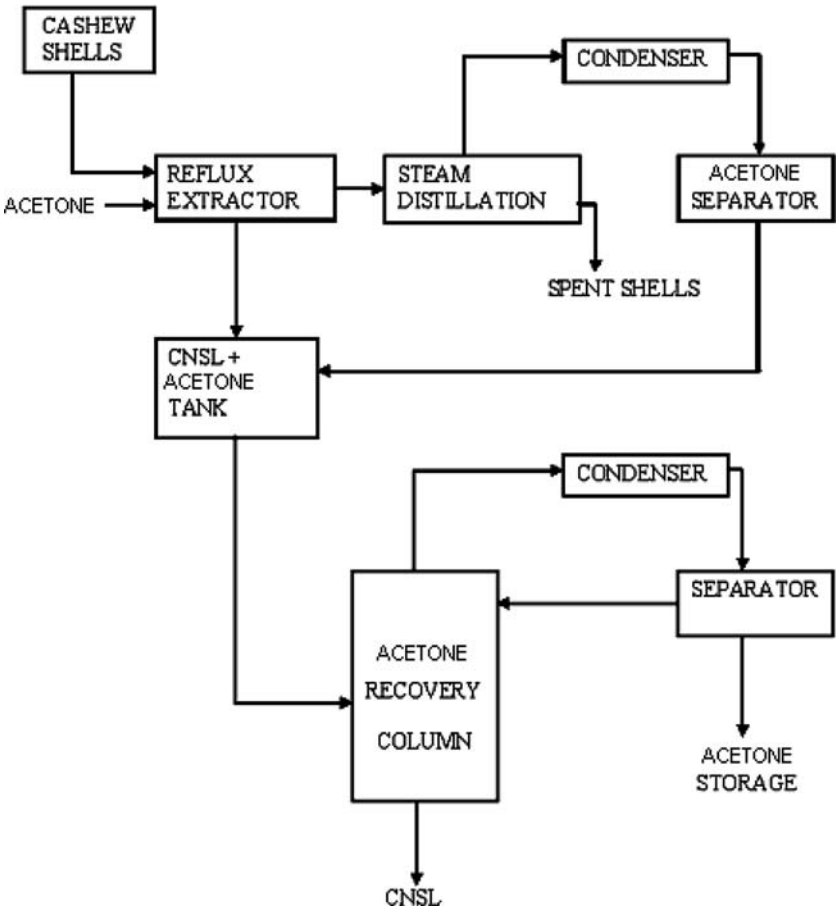



**Fig. 1** Recovery of CNSL from cashew shells

**Table 1** Characteristic properties of CNSL extracted at 65 °C and 1 atm

| Properties | Acetone | Hexane | Toluene | Methanol |
|---|---|---|---|---|
| pH | 5.96 | 5.53 | 5.68 | 5.32 |
| Viscosity (poise) | 57.5 | 56.5 | 54.5 | 52.1 |
| Specific gravity (g/cm$^3$) | 0.93 | 0.91 | 0.87 | 0.89 |
| Refractive index | 1.41 | 1.39 | 1.35 | 1.37 |

**Table 2** Physicochemical properties of polyphenol

| Properties | Polyphenol | |
|---|---|---|
| | Phenol | Resorcinol |
| pH | 6.0 | 3.21 |
| Viscosity (poise) | 57.2 | 285.5 |
| Specific gravity (g/cm$^3$) | 0.89 | 1.2 |
| Refractive index | 1.43 | 1.35 |

because of the higher level of quinoid formed in the dihydric polyphenol, there is preferential extraction of the monohydric polyphenol.

The results of the present study are supportive of the fact that cashew nut shell is a potential substitute for the more petroleum-dependent phenol, which is, as of now the major and/or sole source of phenol.

## Effect of contact time

The results of determining the percentage recovery of CNSL for varying time intervals, acetone was used as solvent. The operation is carried out for 1 h duration with the time interval of 2, 5, 10, 20, 30, 40, 50, and 60 min. Figure 2 shows the percentage recovery of CNSL increase with increase in time. The maximum percentage recovery was found to be 96%. Most of the maximum percent recovery was attained after about 60 min of extraction time. The increasing contact time increased the CNSL extraction and it remain constant after reaching equilibrium in 20 min.

## HPLC analysis

High-performance liquid chromatography (or high pressure liquid chromatography, HPLC) is a form of column chromatography used frequently in biochemistry and analytical chemistry to separate, identify, and quantify compounds.

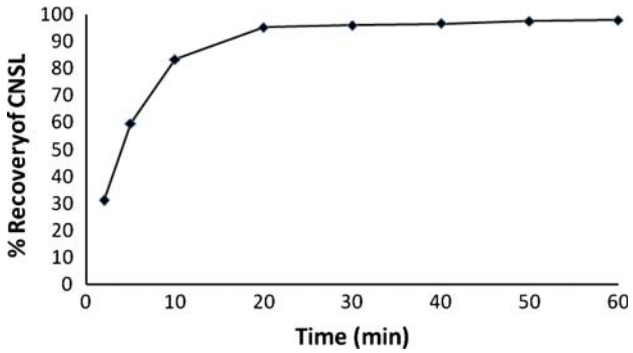



**Fig. 2** Effect of contact time

HPLC utilizes a column that holds chromatographic packing material (stationary phase), a pump that moves the mobile phase(s) through the column, and a detector that shows the retention times of the molecules. Retention time varies depending on the interactions between the stationary phase, the molecules being analyzed, and the solvent(s) used.

*Operation*

The sample to be analyzed is introduced in small volume to the stream of mobile phase. The analyte's motion through the column is slowed by specific chemical or physical interactions with the stationary phase as it traverses (passes through) the length of the column. The amount of retardation depends on the nature of the analyte, stationary phase/ and mobile phase composition. The time at which a specific analyte elutes (comes out of the end of the column) is called the retention time; the retention time under particular conditions is considered a reasonably unique identifying characteristic of a given analyte. The use of smaller particle size column packing (which creates higher backpressure) increases the linear velocity (speed) giving the components less time to diffuse within the column, leading to improved resolution in the resulting chromatogram. Common solvents used include any miscible combination of water or various organic liquids (the most common are methanol and acetonitrile). Water may contain buffers or salts to assist in the separation of the analyte components, or compounds such as trifluoroacetic acid which acts as an ion pairing agent.

*Analysis*

A sample is extracted with an acetone–water mix and then prepared and cleaned with chloroform. Subsequently, the reduced extract is placed onto a polyamide cartridge. The solid phase extraction is carried out with methanol or alkaline methanol, respectively. Both fractions are reduced and membrane filtered prior to injection.

It is recommended to use as eluents for the HPLC a water–formic acid mixture (95/5) as eluent A and a methanol–acetonitrile–formic acid mixture (95/5) as eluent B. The process continues from 100% eluent A via several steps through to 100% eluent B. The gradient run takes about 70 min. It is recommended to use a column of type C18, e.g., Beckman-columns ODS ultra sphere. The detection is done in a UV diode-array-detector (DAD). The DAD allows a classification of individual groups of substances by permanently recording the spectra. In this way, known peaks can be compared to peaks of the sample. In addition, it is possible to show concurrently data at several wavelengths (e.g., at 265, 280, 310, and 360 nm). In a slightly modified method, one can analyze polyphenols in both wort and beer.

Figure 3 shows the polyphenols of the CNSL from the fraction of the polyamide cartridge solid phase extraction at two wavelengths. Table 3 shows the most important substance groups with bandwidths according to the individual contents. The specific HPLC method results in the sum of the contents of 0.5–2.0 vol.% which is significantly less than the sum of the total polyphenols values of 3.0–6.0 vol.%. The reason for this difference is the fact that the HPLC method focuses exclusively on low-molecular components, while the colorimetric method includes all medium- and high-molecular components.

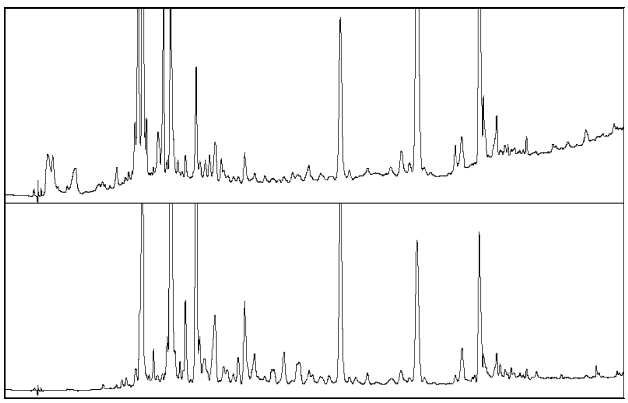


**Fig. 3** HPLC-chromatogram of the polyphenols at 265 and 310 nm

**Table 3** HPLC analysis of the polyphenols

| Group of substances | Contents (mg/100 g) |
|---|---|
| Salicylic acid | 1–10 |
| Coumaric acid | 100–450 |
| Flavonoid | 100–600 |
| Flavanoles | 30–200 |
| Quercetine | 50–250 |

## Conclusion

It can be concluded that cashew nut shell has the potentials of yielding polyphenols, present in the form of anacardic acid, a carboxypenta-dica-dienyl phenol, which is very blistering to the skin. This makes up 30% of the CNSL using an extractant (ammonium hydroxide). Whereas the remainder is 10% cardol, a dihydroxy-penta-dica-dienylbenzene, and 50% cardanol as well as other in identified components. The use of the ammonium hydroxide extractant has facilitated the separation of monohydric and dihydric phenols within the process of extraction as well as offered effective means of removing polyhydric phenols from the raffinate more than is possible with the commonly used conventional solvents.

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