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Extraction of Polyphenols from Cashew Nut Shell

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Abstract

Cashew nut shell liquid (CNSL) was extracted from cashew nut shell by indirect leaching process using soxhlet extraction equipment. Normal hexane (n-hexane) was used as solvent. The operating conditions for the extraction were 680C and 1 atmosphere in every 100g of cashew nut shell used for the extraction, 35gCNSL was obtained. The CNSL was further separated into cardol, cardanol and anacardic acid (polyphenol) using an amine extractant (alanine) with the aid of shake-out separation equipment. Subsequently, the polyphenol was further separated into dihydric phenols (resorcinol) and monohydric phenol (phenol).

The physical separation of the CNSL showed that it consisted of about 10% cardol (dicarboxy- pentadica-dienylbenzene), 50% cardanol and 30% anacardic acid (carbopenta-dica dienylphenol) (with the remainder being made up of other substances) whose boiling points and specific gravities were 900C and 0.9g/m³ 1750C and 1.1g/m³ and 1790C and 1.2g/m³.

Keywords

Extraction, Cashew nut shell, Cashew nut shell liquid, Cardol, Cardanol
Anacardic acid (Polyphenol)

Introduction

Cashew nut is regarded as lost crop in the content of agricultural produce 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). (CNSL) is one of the sources of naturally occurring phenols. CNSL is amber-colored, poisonous, viscous oil obtained from the by-product shells of the cashew nut by 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, vanishes, laminating resins, rubber compounding resins, polyurethane based polymers, surfactants, epoxy resins, wood preservatives (Dupont et al., 1991). 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 are used to improve the resistance of rubber articles to cracking and ozone degradation.

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 as has been highlighted in the preceding paragraph.

This study, therefore, aims at extracting CNSL from cashew nuts so as to determine its proportional constituents cum characteristics. Specifically, the objective is to characterize as well as separate the CNSL into anacardic acid and cardol using an amine extractant (alanine) with the aid of a shake out separation equipment.

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 with distilled water that was 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.

Extraction of CNSL

The extraction of CNSL was carried out using a Soxhlet extractor and n-hexane as solvent. Three hundred and fifty milliliters (350ml) of hexane was charged into the round bottom flask of soxhlet apparatus. Subsequently, 20g 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 680C 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 extract (CNSL) was separated into various constituents namely anacardic acid, cardanol, cardol using alanine with the aid of shake - out separation equipment. Subsequently, the polyphenol was further separated into dihydric phenols and monohydric phenol.

Characterization of the CNSL

The following characteristic properties of the CNSL were determined namely, pH, viscosity, specific gravity and refractive index using standard equipment /apparatus following standard methods.

Results and Discussions

The results of determining the characteristic properties of the CNSL are given in Table 1.

Table 1. Characteristic Properties of CNSL Extracted at 65 - 700°C and 1 atm

Properties at 320°C	Value
pH	5.79
Specific gravity (g/cm ³)	0.95
Viscosity (poise)	58.9
Refractive index	1.48
Total dissolved solids heated at 90°C (g)	1.53
Molecular weight	5030.74

Table 1 gives the pH result (5.79) of the CNSL and is indicative that is acidic. The acidity of the CNSL is attributable to the presence of anacardic acid (C₆H₃OH-C₁₅H₃₁-COOH). The molecular weight of the sample is 5030.74, which falls within the molecular weight range of polymer (Tagar, 1972). From available information in the literature, the specific gravity of CNSL is 1.07 g/cm³. (Klimisch H. J. et al., 1997), whereas the specific gravity of the present work is 0.95g/m. 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 (Klimisch et al., 1997). 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.

Table 2 gives the physicochemical properties of the recovered polyphenol

Table 2. Physicochemical Properties of Recovered polyphenol

Property	Polyphenol	
	Phenol	Resorcinol
pH	6.7	2.57
Viscosity (posie)	58.89	301.2
Specific gravity (g/cm ³)	0.91	1.1
Refractive index	1.48	1.39



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 2.57) 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, 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.

Conclusions

It can be concluded that cashew nut shell has the potentials of yielding polyphenols, present in 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 amine extractant (alanine). 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 amine 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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