Preliminary Investigation of Kaduna-Grown Cashew Nutshell Liquid as a Natural Precursor for Dyestuffs, Pigments and Binders for Leather Finishing

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ABSTRACT

The ever-increasing cost of petroleum based products and the increasing environmental concerns and legislation worldwide are forcing industries to look for inexpensive, renewable, locally available and environmentally friendly raw materials. Cashew (Anacardium occidentale) nutshell liquid (CNSL) is one such material that can be polymerized compared to simple phenols from petrochemicals, which have restrictions. CNSL was extracted from cashew nuts purchased from local farmers in Kaduna, Kaduna state (North of Nigeria) using n-Hexane. The crude extract was analyzed for Iodine Value (88mgI_2/100g), Acid value (141mgKOH/g), Saponification Value (53mgKOH/g), Refractive Index (1.689 @ 25^{0}C) and pH (3). The results show that CNSL from the Kaduna-grown cashew nuts is a semi-drying oil and suitable for the synthesis of resins and dyestuff intermediates. It, therefore, has a great potential as a natural precursor for dyestuff, pigments and binders for leather finishing.

INTRODUCTION

The nutshell of the cashew tree, *Anacardium occidentale*, consists of the kernel (20-25%), the shell liquid (20-25%) and the testa (2%), the rest being the shell[1]. The shell is about 0.3cm thick, having a leathery outer skin and a thin hard inner skin. Between these skins is the spongy structure (mesocarp) containing the phenolic material popularly called CNSL, which is usually obtained as a by-product in the process of removing the edible cashew kernels by roasting the cashew nuts.

CNSL occurs as a reddish brown viscous liquid consisting of alkyl-substituted phenolic compounds (Fig. 1) that can be obtained by extraction in hot oil process (technical CNSL), liquid extraction (using solvents), mechanical expulsion from the shell or by vacuum distillation[2]. The composition varies with the extraction method but generally, the composition of natural CNSL is a mixture of anacardic acid, cardanol, cardol, and 2-methylcardol.

Anacardic acid and cardanol are major constituents for cold extraction and thermo extraction respectively[3]. Philip *et al*[4] reported composition of cold extracted CNSL as 85.0%, 11.3%, 2.5% and 1.2% anacardic acid, cardol, 2-methylcardol and cardanol respectively.

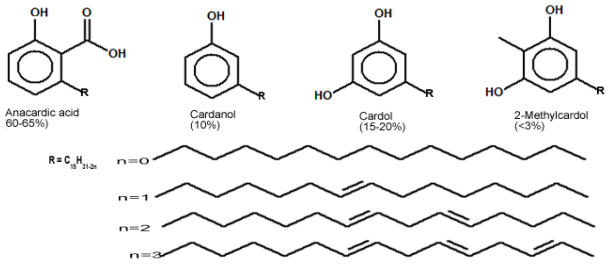
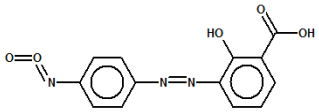


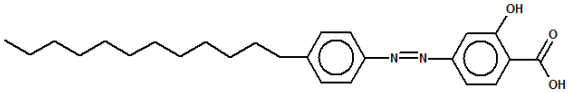
Figure.1: Chemical structures of the components of natural CNSL obtained by solvent extraction[5]

Anacardic acid has been used as an intermediate in the synthesis of dyes and pigments e.g. CI Mordant Orange I marketed as Solochrome Orange M (ICI).



CI Mordant Orange I (CI 14030)

Azo dyestuffs with large alkyl group substitution in the diazo components are listed in the Color Index[6] for application on leather; including CI Acid Red 138 (CI 18073):



Acid Red 138 (CI 18073)

On strong heating (135-140^{0}C), anacardic acid decarboxylates to cardanol[1] (a mono hydroxyl - phenol) with $C_{15}H_{27}$ side chain[7]. Cardanol has a special and unique characteristic: It contains in the *meta* position of the phenolic ring; a long alkyl chain that confers attractive properties to cardanol derivatives such as good processability and high solubility in organic solvents but also, the possibility to influence many chemical transformations; introducing novel functionalities[8].

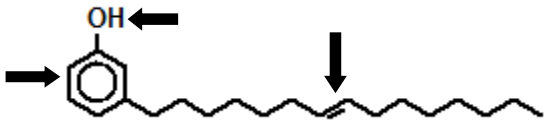


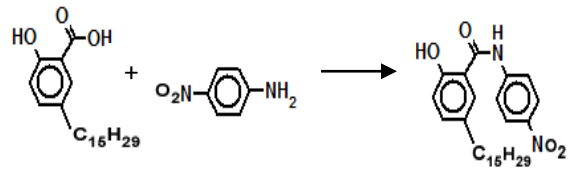
Figure 2: Possible sites for introducing functionalities on the cardanol molecule

With these characteristics, CNSL can be polymerized to give resins in both aliphatic and aromatic hydrocarbons and possessing very good resistance to acid and alkali. CNSL emulsion primers have been shown to possess good physical, mechanical and storage properties[9] when prepared by refluxing the CNSL with formaldehyde followed by addition of a phenolic resin, which could also be a CNSL derivative.

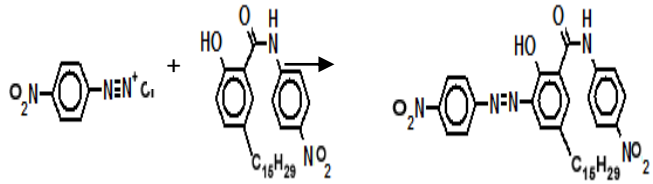
CNSL-based paints containing small amounts of lead silicochromate have been used on mild steel panels because of their anticorrosive properties, good scratch resistance, flexibility, impact resistance and abrasion resistance[10, 11]. Formaldehyde – CNSL and linseed oil – resin condensate binders have been shown to provide antifouling paint compositions to prevent marine growth on structures[12].

A technique for the synthesis of polymer-coated pigment described by Perronin and Gurtner[13] has become commonly used in the surface coatings industry today. The monomer, anacardic acid from CNSL, can be reacted in a medium in which it is soluble plus a polymerization catalyst and a colored specie. The end product is a copolymer which can be used as a colored specie and as a resin.
As an intermediate compound for the synthesis of polymeric azo pigments, anacardic acid can

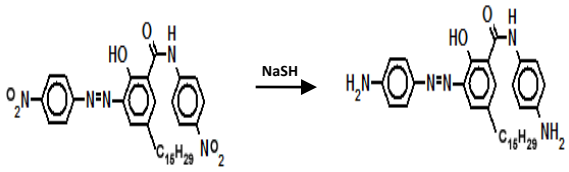
be condensed with a suitable amine having reducible nitro groups to form a benzanilide:



The benzanilide now forms the coupling component in the formation of a simple pigment molecule:



The nitro group can be reduced to amino groups using a suitable sulphide:



The amino azo pigment molecule now forms the real intermediate for the several syntheses of several macromolecular pigments of high colour value[14]. Such pigments have found application in paint and printing inks formulations, mass coloration of plastics and pigmentation of leather. The synthetic route to these pigments is rather lengthy and costly but the high colour value obtainable compensates for these shortcomings.

Nigeria is one of the major producing countries of cashew[15]. World Bank data[16] estimates that 97% of production is from wild trees and only 3% is from established plantations. This study, therefore, preliminarily investigates the CNSL obtained from cashew nuts grown in Kaduna for possible indicators towards the aforementioned potentials of CNSL.

MATERIALS AND METHODS

Sample Collection and Preparation: The cashew nuts were purchased from local farmers in Kaduna, Northern Nigeria. The nuts were air-dried and the nutshell separated by hitting the nuts with a pestle until the shell broke; just freeing the kernel. The nutshell was then ground into powder using pestle and mortar; and stored in polyethene bags.

Extraction of CNSL: The cashew nutshell liquid was thermo extracted with n-Hexane (BDH) using Soxhlet extraction method[17]. 6.60g of the ground nutshell sample was weighed into the extraction thimble and closed with a fat-free cotton wad. The thimble was inserted into the Soxhlet extractor and the spigot for solvent drain closed. The solvent vessel was filled with n-Hexane and extraction carried out at 70^0C for 4hrs. The solvent was then evaporated and the oil residue oven-dried at 103^0C to a constant weight.

Analyses of CNSL: The CNSL obtained was analyzed for acid value, iodine value, saponification value, pH and refractive index using standard method by the Association of Official Analytical Chemists[17]. Fourier Transform Infra Red (ATI Mattson) analysis of the CNSL was carried out using NaCl cells.

RESULTS AND DISCUSSION

The results of the analyses are presented in Table 1. Iodine value is a measure of the degree of unsaturation of oils. The iodine value of 88.0

mg/100g obtained for the CNSL sample shows that it is a semi-drying oil. This suggests the suitability of the Kaduna-grown CNSL for the synthesis of resins and also as a dyestuff intermediate. Separated into various constituent fractions containing triglycerides of different levels of saturation, the fractions of higher iodine value than the original oil would be more desirable for coatings applications[17].

Table 1: Characteristics of the cashew nutshell liquid (CNSL)

Parameters	Results
Acid value (mgKOH/g)	141
Saponification value (mgKOH/g)	53
Iodine value (mg/100g)	88
Refractive index (25^0C)	1.689
pH (25^0C)	3

In the coatings industry, acid value is important and deviations from the standard could lead to challenges. Too high acid value in a resin formulation could lead to excessive water uptake and ultimately emulsification while too low acid value will result in poor pigment wetting, lack of gloss, poor flow, etc. Thus, the CNSL obtained in this study with an acid value of 141.0 mgKOH/g would need to be neutralized or alkali-refined[19,20] to a manageable level to be useful as an intermediate for coatings materials. Alternatively, decarboxylation of the free acid (anacardic acid) in the oil to cardanol would ease this challenge. The low pH of 3 confirms that the CNSL contains very strong acid. The saponification value (53mgKOH/g) is low and suggests that CNSL contains high molecular weight fatty acids and unsuitable for use in the soap industry.

FTIR analysis of the CNSL showed a broad peak at 3200cm^{-1} characteristic of free O–H stretch vibrations in phenols; =C–H stretch or Ar–H stretch in the aromatic ring at 3100cm^{-1}; C–H stretch vibrations at 2900, 2850 and 2600cm^{-1}; Ar–H or aromatic ring vibration at 1650, 1590 and 1450cm^{-1}; C–O stretch vibrations at 1250; 1200 and 1190cm^{-1} are C–C stretch vibrations; O–H bending vibrations occurred at 1100cm^{-1}; Ar–H or aromatic ring Ar–H or aromatic bending vibrations occurred at 750cm^{-1}; methylene groups $(CH_2)_n$ rocking vibrations were observed at 650cm^{-1}. The spectrum thus suggests that CNSL is phenolic and possesses carboxylic groups substituted on the benzene ring. The methylene group rocking vibrations further suggests substitution of long-chain alkyl group on the aromatic ring. These agree with reported results[1,2,3,5,8].

CONCLUSION

CNSL, a well-known by-product of the cashew industry has been successfully extracted from the Kaduna-grown cashew nuts. The results of analysis carried out on the product suggests that the CNSL is a semi-drying oil with a great potential for use as a renewable and inexpensive natural precursor for the synthesis of dyestuffs, pigments and binders for leather finishing.

REFERENCES

1. Peungjitton, P; Sangvanich, P; Pornpakakul, S; Petsom, A and Roengsumran, S (2009). Sodium cardanol sulfonate surfactant from cashew nut shell liquid. *Journal of Surfactants and Detergents*, 12:85-89.

2. Yuliana, M; tran-Thi, N.Y; and Yi-Hsu, J.U (2012). Effect of extraction methods on characteristic and composition of Indonesian cashew nut shell liquid, *Industrial Crops and Products*, 35, 230-236.

3. Buchweishaija, J (2009). Phytochemicals as green corrosion inhibitors in various corrosive media: A review, *Tanzanian Journal of Science*, 35, 84-85
.
4. Philip, J.Y.N; Buchweishaija, J and Mkayula, L.L (2001). Cashew nut shell liquid as an alternative corrosion inhibitor for carbon steel, *Tanzanian Journal of Science*, 27, 9-19.

5. Phani, P.K; Paramashivappa, R; Vithayathil, P.J; Subba, Rao P.V and Srinivasa Rao, A (2002). Process foor isolation of cardanol from technical cashew (Anacardium ociidentale L.) nut shell liquid. *J. Agric Food Chem* 50:4705.

6. The Colour Index (1973). *Soc. Dyers & Col.*, Bradford, UK.

7. Achi, S.S (1994). Modified epoxy resins as binders for cathodic electrodeposition. *Nigerian J. Tech. Educ.*, 11(142):1-8

8. Vasapollo, G; Mele, G and Sole, R. D (2011). Cardanol-based materials as natural precursors for olefin metathesis, *Molecules*, 16, 6871 – 6882.

9. Chen, L and Chen, G (1987). Cashew nutshell aqueous emulsion primer. *Tuliao Gongye*, 6:12-14

10. Selvaras, M and Guruvia, S (1987a). Performance of CNSL pigmented resins electropainted on mild steel substrates. *Paintindia*, 37(7):19-22

11. Selvaras, M and Guruvia, S (1987b). Lead silicochromate paint based on cashew nutshell liquid resin. *Paintindia*, 37(8):27-29

12. Pillai, A. G; Ravindram, K and Balasubramanyam, R (1986). An antifouling paint composition to prevent marine growth on structures, Indian IN Patent 158294.

13. Perronin, J and Gurtner, B.J.R (1977). Process for preparation of pigmentary compositions resulting there from, Brit. Pat 1, 428218.

14. Achi, S.S and Apperley, T.W.J (1986). Macromolecular azo pigments. *Dyes and Pigments*, 319-340

15. Akinhanmi, T.F; Atasie, V.N and Akintokun, P.O (2008). Chemical composition and physicochemical properties of cashew nut (Anacardium occidentale) oil and cashew nut shell liquid, *Journal of Agriculture, Food and Environmental Sciences*, 2(1)

16. Rosengarten, F. (1984). The book of edible nuts (5^{th} ed.), Walker and Co., New York, 45.

17. AOAC (1984). *Official methods of analysis* (14^{th} ed.) Arlington, VA: Association of Official Analytical Chemists.

18. Nnadi, O.M and Hymore F.K (1992). Fractionation of rubber seed oil with acetone and furfural, *Proc. Nigerian Soc. Chem. Eng. Con.*, 26-42

19. Igwe, O and Obemesi, J.A (1989). Viscometric study of film thickness effect on drying of oils. *J. Chem.. Soc. Nig.*, 14:51-56

20. Cocks, L.V and Rede, D.V (1966). *Laboratory Handbook for Oil and Fat Analysis*, Academic Press, London, 331.