*Polish Journal of Chemical Technology, 15, **4**, 24 — 27, 10.2478/pjct-2013-0062*

Extraction protocol for isolation of CNSL by using protic and aprotic solvents from cashew nut and study of their physico-chemical parameter

Tejas S. Gandhi[1], Bharatkumar Z. Dholakiya[1*], Mayank R. Patel[2]

[1]*Sardar Vallabhbhai National Institute of Technology (SVNIT), Department of Applied Chemistry, Surat-395007, Gujarat, India*
[2]*Department of Surface Coating and Technology, ISTAR, Vallabh Vidyanagar-388120, Gujarat, India*
[*]*Corresponding authors: e-mail: bharat281173.svnit@gmail.com, mmrpatel@yahoo.com, tejsvnit.ac.in@gmail.com*

Cashew nut shell liquid (CNSL) represents the largest readily available bioresource of alkenyl phenolic compounds. (CNSL) and its derivatives are widely used in polymer-based industries, synthesis of chemicals and intermediates, including bactericides, insecticides and surface active agents. In this work extraction of cashew nut shell liquid from cashew nut shell (CNS) was carried out by using the Soxhlet extraction method in the presence of polar & non-polar solvents. From the extracted CNSL, anacardic acid was selectively isolated and acid free CNSL was treated with liquor ammonia to separate the cardanol and cardol in the stepwise manner. Comparative study for the extracted CNSL and S-was performed. Higher amount of extracted CNSL was obtained from polar solvents. They were all characterized using quantitative analysis by HPLC.

Keywords: Cashew nut shell, Cashew nut shell liquid, Cardanol, Soxhlet apparatus.

INTRODUCTION

Nowadays researchers work towards replacing petroleum based raw materials for a synthesis of polymeric materials. An alternative route for polymer synthesis by using a renewable plant based source was developed[1]. Using plant based raw material would contribute to global sustainability without the depletion of source resources.

Cashew nut shell liquid (CNSL), an agricultural by product, is a source of long chain m-substituted phenol which promises to be an excellent monomer for polymer production. CNSL and their major four components such as anacardic acid (60–65%), cardol (15–20%), cardanol (10%) and traces of methyl cardol, the byproduct of cashew industries, are cheap and abundantly available renewable resource materials. CNSL occurs as a reddish brown viscous fluid in the soft honeycomb structure of the shell of the cashew nut. Extraction of CNSL from the shell includes the artisanal method of roasting, thermal--mechanical method (Hot oil bath), steam processing at 270°C, and quick roasting at 300°C, Cold method and solvent extraction[2, 3, 5]. In the cold method, the CNSL can be obtained by extrusion, in solvents or by pressing. The cashew liquid obtained by the cold is denominated as natural CNSL and when extracted in hot is denominated technical CNSL. The present research for the extraction of CNSL from CNS is done by using the soxhlet method. Polar and non-polar solvents were used in the extraction of CNSL from the CNS and comparison was made between them[4]. The ideal approach would be the one retaining the advantages of soxhlet extraction (namely, the sample fresh solvent contact during the whole extraction step, the no filtration step, simple manipulation) while circumventing its shortcoming by accelerating the process and minimizing environmental pollution. In view of its biological and industrial applications it was considered necessary to develop a simple and efficient method for the isolation of all the major phenolic constituents of CNSL. Because of the thermo-stability of the carboxylic group of anacardic acid (tendency to get converted to cardanol), CNSL constituents cannot be separated by fractional distillation[6].

We report a novel method for isolation of anacardic acid from CNSL to obtain a stable salt with Barium and separation of cardanol and cardol. They were all characterized using quantitative analysis by HPLC and comparison with standard samples[7]. CNSL and its derivatives have been reported to be useful in innumerable applications in polymer-based industries like friction linings, paints, primers, and varnishes[8], laminating resins, and rubber compounding resins, surfactants, epoxy resins, wood preservatives and polyurethane-based polymers[5]. Cardanol is a phenolic compound with a C15 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 the form of dye stuffs, plasticizers, and ion-exchange resin. Chlorinated products of cardanol were found to have pesticidal action. Sulfonated derivatives of cardanol, tetra hydro cardanol, and their Phenolic ethers are used as surface-active agents[9].

EXPERIMENT SECTION

Materials

Cashew nut shell was obtained from Gujarat Cashew industry (Kutch). The experiment can be set up with a required round bottom flask, bubble type condenser, heating mantle with the temperature range of 0–200°C, and simple distillation unit for solvents recovery from CNSL. Water was removed from the mixture by using dean-stark assembly. The solvents were purchased from Merck (India) and Thin layer chromatography (TLC) plates (silica gel GF254). All the components were characterized by using quantitative analysis by HPLC in the Centre of excellence (India).

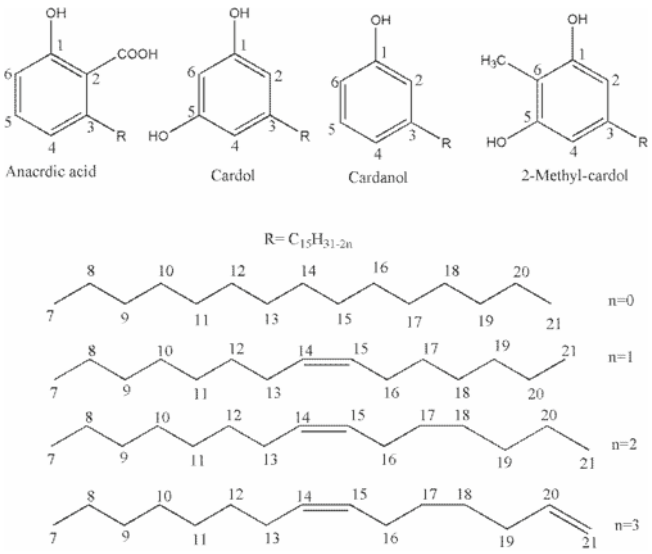

Figure 1. Structure of main components of Cashew nut shell liquid[10]

Method

Extraction of cashew nut shell liquid from cashew nut shell

The extraction of CNSL from CNS was carried out with the help of the soxhlet apparatus using polar--non-polar solvents. The Soxhlet apparatus which was equipped with two hundred and fifty milliliters (250 ml) of solvents 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 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, it depends on the category of solvents and the time cycle. 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 solvents were recovered from a simple distillation method[16].

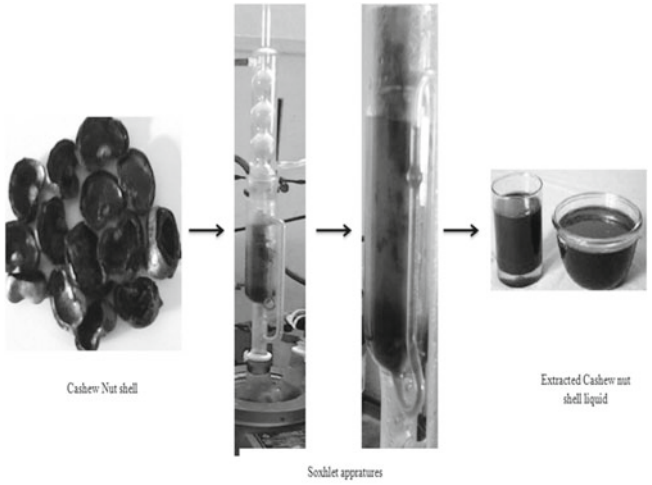

Figure 2. Extraction of CNSL by using the Soxhlet method

Isolation of anacardic acid from CNSL

Extracted CNSL (50 g) was soluble in polar solvents in MIBK (methyl isobutyl keton) (300 ml), and Barium hydroxide (30 g) was added in portions under stirring. After completing the Barium hydroxide, the temperature was raised up to 60°C and stirring was continued for 3.5 h and the TLC was checked for the absence of acid peak (Anacardic acid). After the completion of the reaction, the precipitated Barium anacardate was filtered and washed with MIBK (160 ml), and dried at 2 h. The filtrate was preserved for a subsequent isolation of cardol and cardanol. Barium anacardate (50 g) treated with distilled water (200 ml) and concentrate HCL (33–35%) (40 ml) was added and constant stirred for ½ h. The resultant solution was extracted with petroleum ether (2 x 150 ml). The combined organic layer was washed with distilled water (2 x 100 ml), dried over anhydrous sodium sulfate, and evaporated to dryness to get anacardic acid 26 g.

Separation of Cardol and Cardanol

The ketonic solution obtained after the filtration of the Barium anacardate. Liquor ammonia (80 ml) was added and stirred for 15 min. This solution was extracted with hexane/ethyl acetate (98:2) (3 x 100 ml). The combined organic layer was washed with NaOH solution (2.5%, 200 ml) followed by 5% HCl solution (100 ml) and distilled water (100 ml). The organic layer was dried over anhydrous sodium sulfate and concentrated to get pure cardanol (7 g). Aqueous ammonia solution was extracted with ethyl acetate/ hexane (80:20) (100 ml). The organic layer was washed with 5% HCl (50 ml) followed by distilled water (50 ml), dried over anhydrous sodium sulfate, and concentrated to yield pure cardol (14 g). The identity of cardanol and cardol was confirmed by HPLC and comparison with standard samples [11].

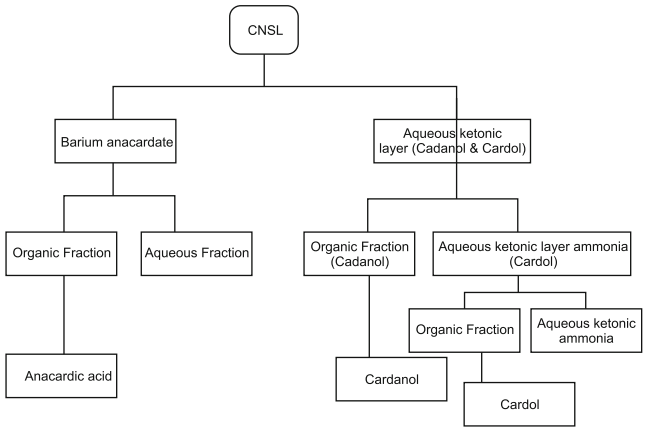

Figure 3. Flow diagram for separation of anacardic acid, Cardanol and Cardol from CNSL

Direct separation of Cardanol from CNSL (Decarboxylation Process)

The extracted CNSL (50 g) was mixed with toluene (100 ml) in a round bottom flask and refluxed for 3 h by using dean-stark apparatus and the TLC was checked for the absence of anacardic acid. Then the decarboxylated CNSL and 100 ml methanol were placed in a 500 ml round bottom flask. Then 10 ml of 40% formaldehyde solution and 1.5 ml diethylenetriamine were added to this solution. This mixture was heated until boiling under reflux for 2 h. After the solution was allowed to reach room temperature, the separation phase occurred,

showing a slightly reddish upper solution, and a dark brown solidified lower phase. The upper phase was subsequently decanted, and treated with distilled water (40 ml) followed by petroleum ether. The Petroleum ether layer was evaporated to dryness, yielding a reddish residue of cardanol (15 g) [12–13].

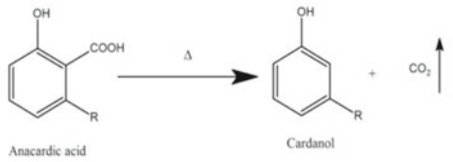

Figure 4. Decarboxylation of Anacardic acid

RESULT AND DISSCUSSION

Physicochemical characteristic of extracted cashew nut shell liquid and yield of the products

The different types of polar and non- polar solvents were used in solvent extraction method CNSL from CNS. The comparative studies were carried out on the properties of CNSL obtained with the use of different solvents. On the basis of physico-chemical parameter of the extracted CNSL, we concluded that ketonic solvent was more efficient than other solvents. S-CNSL gives the pH result (5.7) of the CNSL and indicted the presence of anacardic acid. From the available information in the literature, the specific gravity of CNSL is 1.07 g/cm^3 [14–15]. The slight variation in the specific gravity may be attributed to the extraction technique cum operating conditions employed during the experiment. Comparative study for the extracted CNSL and S-CNSL and their Physico-chemicals characteristics which is shown in Table 1. Using water as a solvent for extraction of CNSL from CNS, extraction was done but isolation product remain sticky and tar-like in nature. So, future modification will be required and work proceeds in this direction.

High-performance Liquid Chromatography (HPLC) Analysis

High-performance Liquid Chromatography (HPLC) Analysis was done on a modular HPLC instrument comprising two 510 reciprocating pumps, a 481 variable--wavelenght detector, and a Rheodyne injector, all from waters (Milford, MA.) A supelcosil LC-18 (150 mm x 4.6 mm i.d., 5 μm particle size) column was used and the mobile phase was acetonitrile/water/acetic acid (80:20:1) at 1.80 mL/min, absorbance was monitored at 280 nm. Each analysis was carried out dissolving 25 mg of sample in 5 ml of acetonitrile, passing that through a C18 sep-pak cartridge (Water Associates, Miilford, MA) and injecting a 20 μL sample[13].

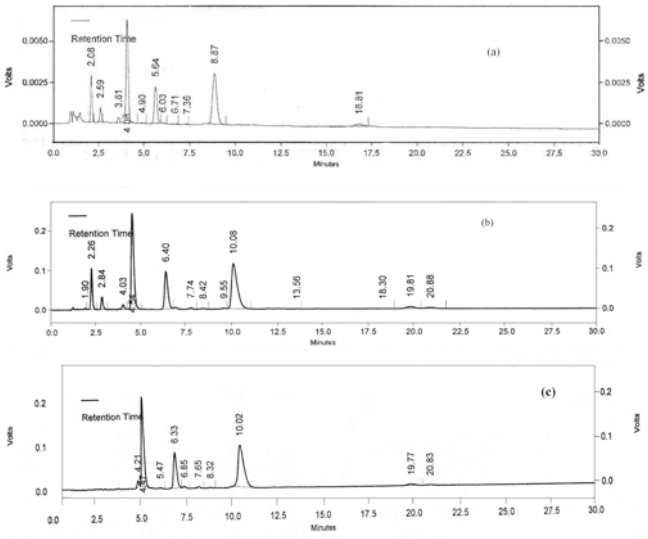

Figure 5. HPLC profiles of (a) Anacardic acid (b) Conventional cardanol (c) De-carboxylated cardanol, using Supelcosil, LC-18 and acetonitrile/water/acetic acid (80:20:1) as mobile phase at 280 nm

The purity of all compounds was confirmed by HPLC. Isplated Compounds were confirmed by being compared with the reported HPLC[13]. The resulted above averages of four experiments were performed at 100 g, 200 g, 500 g, and 1 kg scale. The purity of extracted CNSL was almost the same but the yield varied, it depends on the polarity of the solvents. As per reported process it showed the 30–32% yield. Our isolation method shows 38–40% yiels. So, our method is more convenient than the reported process.

In the initial step, anacardic acid was precipitated from CNSL as barium anacardate. Barium anacardate was isolated from CNSL using barium hydroxide. The optimum reaction condition for salt formation of anacardate was found at 50°C temperature for 3-hrs. Finally anacardic acid was isolated from mother liquor of barium anacardate.

The mother liquor obtained after the filtration of barium anacardate contained primarily the other two major phenolic constituents cardol and cardanol of CNSL. It was stirred with liquor ammonia and then extracted

Table 1. Physico-chemical parameters of extracted CNSL at 60–100°C and 1 atm

Paremeters	S-CNSL	CNSL Extracted at 60–100°C from CNS							
Tyopes of solvents		MIBK	MEK	Ethanol	Xylene	n-heptane	Iso--octane	Petroleum ether	De-ionized water
PH	5.7	5.2	5.9	6.3	4.9	5	6.8	6.8	7.2
Viscosity (Poise)	58.9	49.9	47.2	51	59.3	48.6	52.9	51.1	67.4
Specific gravity (g/c m^3)	1.07	0.9451	0.9211	0.9632	0.9725	0.9116	0.9336	0.9225	0.9996
Refractive index	1.48	1.49	1.42	1.25	1.48	1.49	1.52	1.51	1.33
Quantity (gm)	–	8.276	7.633	2.077	7.296	7.250	6.734	7.066	3.500 (Polymetric sticky material)
Color	Dark brown								

*S-CNSL = Standard cashew nut shell liquid

with a mixture of hexane/ethyl acetate (98:2). Cardol remained in the ammonical solution while the cardanol was extracted into the organic layer. Consequently, extraction of the ammonical solution with a mixture of ethyl acetate/hexane (80:20) yielded cardol in high purity. The use of the hexane-ethyl acetate mixture instead of ethyl acetate gave

HPLC. The yield of Cardanol was increased by using decarboxylated of CNSL at above 100°C for 3 h refluxed by using dean-stark assembly. The decarboxylated product cardanol was characterized by an analysis of HPLC. The decarboxylated product was treated with formaldehyde in methanol by using diethylenetriamine as a catalyst, after 30 min of stirring phase two separated. Cardanol was extracted with petroleum ether followed by water having 70% yields.

CONCLUSIONS

The extraction of CNSL was obtained from CNS with the use of the soxhlet apparatus. Different types of solvents were used in the extraction of CNSL from CNS. Extraction phenomena by using different solvents exhibits the 38–40% yield. Among all of the solvents, MIBK gives the maximum amount of CNSL. Solvents having carbonyl groups show higher efficiency for the extraction of CNSL. Extraction of phenolic and acidic compounds from cashew nut shell, its more cost effective renewable raw materials for polyurethane synthesis.

LITERATURE CITED

1. Mohanty, A.K., Misra, M. & Hinrichsen, G. (2000). Biofibres, biodegradable polymers and biocomposites: An overview, *Macromol. Mater. Eng.,* vol. 276–277*,* Issue 1, pp. 1–24.

2. Patel, R.N., Bandyopadhyay, S. & Ganesh, A. (2006). A Simple Model for Super Critical fluid Extraction of Bio Oils from Biomass*, A- Bioresour Technol.,* vol*.* 97, pp. 847.

3. Mazzetto, S.E., Lomonaco, D. & Mele, G. (2009). Cashew nut oil: opportunities and challenges in the context of sustainable industrial development *J. Quimica Nova*, vol. 32, pp. 732.

4. Kumar, S.P., Kumar, A., Kumar, S.N. & Kaushik, C. (2009). Experimentation on solvent extraction of polyphenols from natural waste, *J. Mater. Sci.,* vol. 44, pp. 5894–5899.

5. Phani, P.K., Paramashivappa, R.P., Vithayathil, J.P., Subba Rao, V. & Rao, S. (2002). Process for isolation of cardanol from technical cashew (*Anacardium occidentale L.*) nut shell liquid, *J. Agric. Food Chem.,* vol. 50, pp. 4705.

6. Tyman, J.H.P., Jhonson, R.A., Muir, M. & Rokhgar, R. (1989). The Extraction of Natural Cashew Nut-Shell Liquid from *Anacardium occidentale, J. Am. Oil. Chem. Soc., vol.* 68, pp. 553–557.

7. Shobha, S.V. & Ravindranath, B. (1991). Supercritical carbon dioxide and solvent extraction of the phenolic lipids of cashew nut (*Anacardium occidentale*) shells, *J. Agric. Food. Chem.*, vol. 39, pp. 2214–2217.

8. Prabhakaran, K., Narayanan, A. & Pavithran, C. (2001). Cardanol as a Disper-sant for an Alumina/Toluene Tape Casting Slip, *J. Eur. Ceram. Soc.*, vol. 21, pp. 2873.

9. Tyman, J.H.P. (1996). Synthesis and Natural Phenolic Studies in organic chemistry, vol. 52. Elsevier, Amsterdam, pp. 518–521.

10. Menon, A.R.R., Pillai, C.K.S., Sudha, J.D. & Mathew, A.G. (1985). Cashew nut shell liquidsIts polymeric and other industrial products *J. Sci. Ind. Res.*, vol. 44, pp. 324–338.

11. Gedam, P.H,P., Sampath Kumaran, S. & Sivasambavan, M.A. (1972). Examination of components of cashew nut shell liquid by NMR, *Ind. J. Chem.*, vol. 10, pp. 388–391.

12. Menon, A.R., Pillai, C.K., Sudha, J.D. & Mathew, A.G. (1985). Cashew nut shell liquid-its polymeric and other industrialproducts, *J. Sci. Ind. Res.*, vol. 44, pp. 44–324.

13. Tyman, J.H.P. (1981). U.S. Patent application 587,058.

14. Klimisch, H.J. & Andreae, M.U. (1997). A systematic approach for evaluating the quality of experimental toxicological and ecotoxicological data. Tillmann, *Regul. Toxicol. Pharmacol.* vol. 25, pp. 1.

15. Gandhi, T.S., Patel, M. & Dholakiya, B. (2012). Studies on effect of various solvents on extraction of cashew nut shell liquid (CNSL) and isolation of major phenolic constituents from extracted CNSL, J. Nat. Prod. Plant. Resour., vol. 2 (1), pp. 135–142.

16. Gandhi, T.S., Patel, M. & Dholakiya, B. (2013). Synthesis and characterization of different types of epoxide-based Mannich polyols from low-cost cashew nut shell liquid. DOI: 10.1007/s11164-013-1034-2.