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Review on Applications, Extraction, Isolation and Analysis of Cashew Nut Shell Liquid (CNSL)

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Abstract

India is the largest producer and processor of cashews (*Anacardic occidentale* L). Cashew nut shell liquid (CNSL) is a dark brown viscous liquid present inside a soft honey comb structure of the cashew nut shell and is a byproduct obtained during the processing of cashew nuts. The present review discusses various application of CNSL as well as the applications of constituents of CNSL. Various methods of extraction of CNSL are available in the literature. They are 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 can properly be extracted by methods like cold extraction, hot solvent extraction using Soxhlet extractor, supercritical Carbon dioxide extraction and vacuum pyrolysis. The review focuses on various methods of extraction, their merits and demerits. CNSL mainly consists of anacardic acid, cardol and cardanol in various proportions depending upon the type of extraction. This review also highlights various methods of isolation of these major constituents. The quantitative and qualitative analysis of CNSL is also presented in this review. Scope for future work is also discussed.

Key words Cashew nut shell liquid, Anacardic acid, Cardanol, Cardol

Introduction:

Cashew (*Anacardium occidentale*) is one of the well known species of the Anacardiaceae family. Cashew nut ranks third in the world production of edible nuts. India has a comparative advantage in the production and processing of cashew nuts on account of its skilled labor force. The nuts have gained popularity as 'nature's vitamin pill'. Cashew kernels have the highest protein content among tree nuts (19.5%). This protein content matches soybean and is higher

than peanut. The nut was reported to have been used in place of soyabean meal in finishing broiler chickens². The nut also represents a major source of alkenyl phenolic compounds³. The fruit of the tree consist of an outershell (epicarp), a tight fitting inner shell (endocarp), testa and kernel. The pericarp of the fruit consists of a strong vesicant liquid known as cashew nut shell liquid (CNSL). The CNSL destiny is either the overseas market if the price is convenient, or used internally as fuel, if the international price is

low. Better extraction methods and isolation of the components make value addition.

Applications:

Cashew nut shell liquid (CNSL) is a by-product of the cashew industry. It is a naturally occurring substituted phenol which can take part in a variety of reactions. It is a cheap and renewable substance and can be employed for the manufacture of a multitude of useful products. It can replace phenol in many applications with equivalent or better results.

It was mentioned that⁴ CNSL reduced the extent of the electrochemical processes taking place on carbon steel surface undergoing corrosion. The corrosion rate of the carbon steel was reduced by over 90% with just 300 ppm of CNSL under static conditions. A better performance at very low concentration was registered under dynamic conditions. High inhibitor performance of about 96% was observed with just injection of 20 ppm of CNSL. Rotation was found to have a positive effect on the inhibitor performance suggesting that the formed protective inhibitor film to be resistive against flow (shear stress). The results also indicated that very low concentration is required on dynamic systems to attain the maximum efficiency as compared to the stationary system. Furthermore, the results revealed that CNSL inhibitor is temperature sensitive. Its performance decreases with increasing temperatures. This inhibitor was found to work more efficiently at room temperature. .

CNSL and its derivatives have anti-oxidative characteristics⁵. The order of antioxidant activity was reported as: CNSL >> cardanol > hydrogenated and alkylated cardanol > hydrogenated cardanol. This effect of CNSL could be attributed to the extra contribution of the other components besides cardanol and to the unsaturation on the long side chain. This greater activity is important because CNSL is much more cost effective than its derivatives.

Similar conclusions were drawn by Oliveira et al⁶. Antioxidant property was measured by DPPH and ABTS (+) tests. Their results suggested Cardanol to be most active, followed by cardol and anacardic acid.

Poly(methyl methacrylate) films 1% additivated with new thiophosphate esters antioxidants derived from technical Cashew Nutshell Liquid (CNSL), were investigated by Lomonco et al⁷ using thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) measurements and concluded that thermal stability of the films is increased in presence of the thiophosphate ester additive. It is mentioned by some authors that Olefin metathesis (OM) reaction on cardanol is an important class of reactions that allows for the synthesis of new olefins that are sometime impossible to prepare via other methods⁸.

Cardanol based polyhydriens were used as sensitizers for improving the photo-catalytic activity of bare TiO₂. The porphyrins are brown-red sticky solids, very soluble in CHCl₃ or CH₂Cl₂, have been characterized by FT-IR, UV-Vis, ¹H- and ¹³C-NMR, and MALDI-TOF techniques⁹.

Work was also reported for use of CNSL in fuel blends and fuel mixtures with 1, 2, 5 and 10% may provide savings of 0.82%, 1.63%, 4.08% and 8.16% respectively¹⁰.

Work was also available for making diesel oil from cashew nut shell liquid¹¹. 100x10-3kg of CNSL was cracked with 20X10-3kg of molecular sieve in a 5X10-3m³ reactor at 500°C for 2 hours. All the gas came out was partially condensed in the condenser and collected as the liquid product, and the rest was collected as the gas product. The purified liquid product obtained was brown in color and gave strong smell. Analysis of this product with GC resulted as chromatogram, which some in parts looked nearly like the diesel.

Since phenolic resins are among the most commonly used materials, CNSL was also used for making asbestos of free friction composition for brake linings 12.

Work was reported for converting CNSL into valuable chemicals by pyrolysis process at high temperatures (450 to 7500C) and short residence times¹³ and the products of pyrolysis are shown in the following table (Table-I).

Table I: Products of pyrolysis of CNSL

Product (wt%)	Low temperatures	High temperatures
Tar	0.20	Traces
Phenols	0.44	0.43
Hydrocarbons	0.30	0.37
Gaseous fraction	0.06	0.20

The pyrolysis reaction was carried out in a down flow reactor with a pattern close to plug flow reactor. The authors also concluded that high temperature and short residence times reduced the extended polymerization.

Sanger et al¹⁴ reported work for carbonization of cashew nut shell liquid by direct and indirect methods in a prototype kiln. The authors reported maximum CNS temperatures obtained inside the kiln during direct and indirect methods were 452.20C and 458.80C respectively. Maximum oil percentage obtained in direct and indirect methods is 21.1% and 23.8% respectively suggesting indirect method to be more suitable for carbonization.

Work was also reported for the use of CNSL as bioadditive in engines and it was mentioned that it increases the durability of pieces and equipments¹⁵. Hence, the production of CNSL as bioadditive will replace imports, besides preserving the environment with lower pollutant residues.

Technologies are available for converting rice husk +CNSL into eco-wood¹⁶. CNSL and cardanol found extensive use in automotive break-lining applications¹⁷. CNSL/cardol based surface coatings possess excellent gloss and surface finish with a high level of toughness and elasticity¹⁸. Cashew nut shell crude extract was used for control of golden apple snail¹⁹.

Cardanol polysulfide (CPS) was also used as vulcanising agent for natural rubber as reported by Khaokhum et al²⁰. The authors also mentioned that the optimum cure time of rubber containing CPS was reduced and the mechanical properties were improved. Moreover, the CPS rubber was found to have lower reversion.

Cardanol-aldehyde condensation polymers containing Boron-Nitrogen co-ordination bond showed excellent physio mechanical properties, good anticorrosive properties and stable at high temperatures²¹.

Cardanol based novolac-type phenolic resins, capable to form thermo set polymers when blended to commercial epoxy or isocyanate monomers were successfully developed by Amioco and co-workers²².

Work was also available²³ for the conversion of cardols (6-alkenylresorcinols) into lasiodiplodin, a naturally occurring 12-membered orsellinic acid type macrolide, which exhibits plant growth regulating and antileukemic properties.

It was also reported that immature CNSL (iCNSL) has excellent protective activities in strains of *S. cerevisiae* against oxidative damage induced by hydrogen peroxide and inhibits acetylcholinesterase activity²⁴. It was mentioned that iCNSL may have an important role in protecting DNA against damage induced by reactive oxygen species, as well as hydrogen peroxide, generated by intra- and extracellular mechanisms.

The high in vitro antibacterial activity of cashew nut shell liquid (CNSL) has been attributed to its anacardic acid content 25-26. There is also a suspicion that anacardic acids inhibit the growth of cancer tumors such as breast cancer 27.

Gram positive bacteria, which cause tooth decay, acne, tuberculosis, Streptococcus pneumoniae, Francisella tularensis, and leprosy are killed by anacardic chemicals 28. There was a claim that one part to 200,000 to as high as 2,000,000 parts of solution of anacardic acid is lethal to gram positive bacteria in 15 minutes.

Study was also available²⁹ for evaluating the effect of anacardic acid (6-pentadecyl salicylic acid), a natural histone acetyltransferase inhibitor, on pituitary adenoma cells. Anacardic acid also reduced the expression of survivin and X-linked inhibitor of apoptosis protein, antiapoptotic proteins associated with cellular survival and radio resistance, and radio sensitized pituitary adenoma cells.

It was also mentioned that quaternary nitrogen compounds derived from monophenolic components of cashew nut shell liquid were very stable, soluble in water, odorless, possess high bacterial activity and act as surface active agents³⁰. These properties made them especially useful as germicides, disinfectants and sanitizing agents especially in food and dairy industries.

The sodium salts of anacardic acid are anionic surface-active agents 31--32. It was suggested that disodium anacardate could be a useful bactericidal surfactant. The surface tension showed a minimum in the range of 0.2-0.1 percent concentration. The authors also established a relation between conductance and concentration and found out critical micellar concentration 0.053%. They also established a relation between surface-activity and unsaturation. They concluded that as unsaturation increases,

emulsifying and foaming characteristics increase and followed by a slight fall. Neither the saturated nor the most saturated gives the best surface-active and bulk properties; optimum hydrophilic-lipophilic balance lies near the mono and di-unsaturated anacardate. It was reported that the monosodium salt is more potent as a bactericide, particularly against Staphylococcus aureus, since it possesses a wider spectrum of antibacterial activity than that generally exhibited by anionic surface-active agents, and that this activity is largely independent of pH over the range of pH 5 to 9 25. The sodium salt was also reported to destroy snake venom 33. Literature was also available for use of sodium anacardate for control of vector mosquito which was responsible for causing dengue fever 34.

3. Extraction of CNSL:

CNSL is classified into Technical CNSL and natural CNSL depending upon the type of extraction. Technical CNSL is rich in Cardanol (also known as Decarboxylated CNSL) where as Natural CNSL is rich in Anacardic acid.

There are three main methods generally used in extracting cashew nut shell liquid from cashew nuts namely thermal, mechanical and solvent extraction 35. Solvent extraction in turn can be carried out by cold extraction, hot extraction by different solvent using Soxhlet extractor, Ultrasonication and super critical carbon dioxide extraction. Cashew nut shell liquid was also extracted using vacuum pyrolysis.

1. Thermal extraction :

A1) Roasting method:

This is the traditional method of removing CNSL 36 and it involves roasting the nut in drums or baths. The roasting process not only removes the corrosive CNSL, but also makes the shell brittle, thereby aiding the cracking process. This method causes the loss of

most of CNSL. In order to extract the retained CNSL, the nuts are roasted in baths at a temperature of 180–185°C. Vents in the equipment dispel the unpleasant fumes. This method recovers 85–90% of the liquid.

Some authors reported work 37 of scrapping the shell in a rotary apparatus with sand and steel wool, heated at 100–300°C for 1 h and then roasted at 400–700°C in an inert atmosphere, when the oil again oozes out.

A2) Hot oil bath method:

By and large, this is the most common method of commercial extraction of CNSL in practice nowadays. The technique can be different depending upon the raw material, which is either raw cashew nut shell or cashew nut. For the first, cashew nut shells were collected in the cylinder, where steam heating was applied at temperatures around 200-250°C for 2-3 minutes. CNSL was then released from the shells and the process was repeated. This method yields CNSL of around 7-12% by weight. For the latter, the raw nuts are passed through a bath of hot CNSL itself, when the outer part of the shell bursts open and releases CNSL. This method produces CNSL which was around 6-12 % by weight of nut.

A3) Using Solar cooker :

Cashew nut shell oil was extracted using concentrating solar cooker 38 of 1.4 kW capacity and a diameter of 1.4m. The focal point diameter of the cooker was 30m and was used to collect the reflected heat from reflector and achieved a temperature of 225-300°C. Solar cooker of the following specifications was used for carrying out the extraction.

Specifications

Type: Parabolic Solar Cooker
Model: S K-14
Reflector: Aluminium sheet (reflectivity >75%)

Diameter: 1.4m

Reflector area: 2.2m²

Temperature: 200–215 °C

Thermal efficiency: 40%

Cooking capacity: 13 X10-3 m³/hr

the authors could achieve CNSL to the tune of 550X10-3m³ from 5 kgs of shells in 5 minutes. The composition of analysis of CNSL could not be performed. They carried out the proximate analysis of de-oiled cake. Low percentage of ash content and higher percentage of volatile matter and calorific value revealed the suitability of de-oiled cashew shell as a fuel for thermal application using the gasification route for better control and higher efficiency. Combustion of shell could be done either in a fixed bed combustion chamber which gave 50% efficiency or fluidized bed chamber which gave 85% efficiency 39.

B) Screw press method:

The raw cashew nut shells are put in the hydraulic press on screw pressing and then exert high pressure in order to release CNSL from shells. This method is rather straightforward and quick among others. Work was reported for extraction of CNSL by means of tapered compression screw, feeding rollers of transversal zigzag surface type and cylindrical casing with 2 mm diameter holes. By using screw speed of 7-13 rpm and feeding rate of 54-95 kg/h, the percentage of CNSL extracted was 20.65-21.04 percent, the percentage of CNSL purity was 85.53-87.8 wt % and the rate of extraction was 11.93-14.90 kg/h 40. However, the residue from this method still contained significant proportions of CNSL, around 10 to 15%. Moreover, this method of extraction had higher levels of impurity, higher viscosity, lower thermo-oxidative stabilities and lower ebullition temperature. The CNSL obtained by this process contained 42% cardol, 47% anacardic acid and 3% Cardanol 41.

Solvent extraction:

This method gives off most of CNSL compared to other methods. The oil remains in the residue was less than 1% by weight 42.

Extraction solvents fall into two groups; those which are less dense than water and those which are denser 43. Commonly used extraction solvents which fall into the first group include diethyl ether (the most common extraction solvent of all), ethyl acetate and hydrocarbons, such as light petroleum, hexane or toluene. The second group comprises chlorinated

solvents, such as dichloromethane and chloroform, with dichloromethane being the preferred solvent because of its lower toxicity. However, chlorinated solvents do have a greater tendency to form emulsions than non chlorinated solvents. Emulsions are suspensions of small droplets of one immiscible liquid in another. The properties of some common extraction solvents, listed in order of increasing dielectric constant, are given in the following table (Table-II).

Table-II: Common extraction solvents and their properties

Solvent	Dielectric constant	Boiling point (OC)	Density (g/ml)	Flammability	Toxicity	Suitability
Hexane	1.9	68.7	0.65	+++	+	Poor solvent for polar compounds
Benzene	2.3	80.1	0.87	+++	+++	Too toxic
Ether	4.3	34.6	0.71	+++	+	Good general extraction solvent, especially for oxygen-containing compound; dissolves up to 1.5% water.
Chloroform	4.8	61.7	1.48	Nonflammable	+++	Easily dried; toxic
Ethyl acetate	6.0	77.1	0.89	+++	+	Good for polar compound; absorbs large quantity of water
Dichloro Methane	8.9	39.7	1.31	Non flammable	++	Good extraction solvent
1-Butanol	17.5	117.7	0.81	++	+	"Last resort" for extraction of very polar compound; dissolves up to 20% water

+ = least flammable/toxic, ++ = moderately flammable/toxic, +++ = most flammable/toxic.

4. Separation of shell from the nut :

In order to extract the oil from the shell, the shell needs to be separated from the nut. Earlier method includes roasting of the cashew nut which has resulted in loss of all of the CNSL into the atmosphere from the shell leading to environmental problems. Shells can be separated from the kernel by the following methods.

1. By application of cold:

In the first method, the nuts were placed in liquid nitrogen bath when they cracked. The shells were

broken by light hammering and separated from the kernel and testa⁴¹. In an alternative method, the nuts were stored in overnight freezer to make the shell brittle. The nuts were bisected by light hammering along the axis of the junction of the two halves of the shell. The intact kernel in the testa lining was separated 42.

2. Steam roasting:

The raw cashew nuts were steamed in boiler [without steam pressurizing the cooker vessel]. The cooking time is varied depending upon the conditions of

cashew nut and atmospheric conditions. Work was done to study the effect of period of steaming and drying temperature on chemical composition of cashew nut 43. The authors considered steaming time of 20, 30 and 40min and temperatures of 50, 60 and 70°C and reported that cashew nuts processed by steam boiling at 40 minutes and drying temperature of 70°C recorded best quality as it reduced the residual CNSL and moisture content of the kernel. The steaming expands the shell, softens the nuts due to penetration of steam into the shell. After steaming,

the nuts are air-cured by spreading out on the floor in the shade. These ultimately harden the shell and make it fit enough for de-shelling in the manually operated cutting machine. The steam processing preserves the original color of the cashew kernel inside the Nut. The cut shells of steam roasting process yield quality Cashew Nut Shell Liquid [C.N.S.L.]. The structure of various components of CNSL is shown in Figure-1.

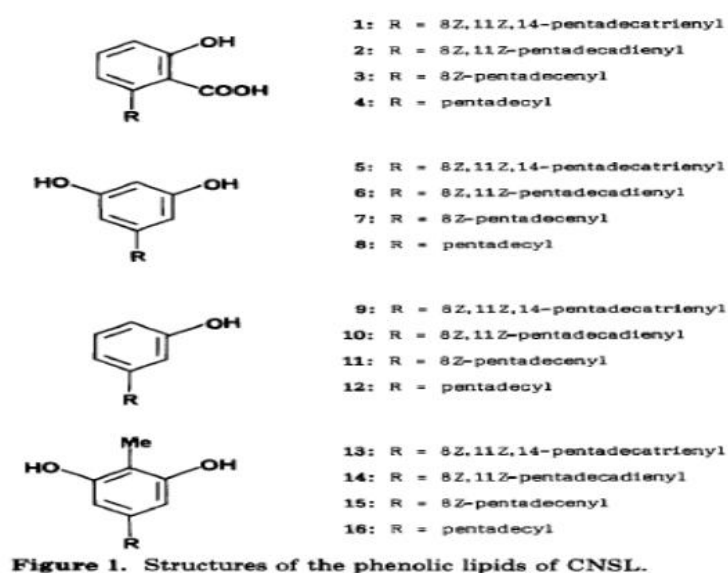


Figure 1. Structures of the phenolic lipids of CNSL.

Solvent extracted CNSL, especially of Indian origin is rich in anacardic acid as shown in the following table.

(Table-III) 44 as reported by Shoba and Ravindranath.

Table III: Percentage compositions of phenolic lipids of CNSL from different sources

Structure	a	b	c	d	e	f	g
1	30.60	30.00	20.50		30.02	27.17	27.26
2	12.60	13.60	12.82		12.72	11.01	11.16
3	25.80	28.50	24.10		16.98	23.15	22.85
4	0.71				0.96	1.21	1.27
total (1-4)	69.71	72.90	57.42		60.68	62.54	62.56
5	16.20	13.20	11.38	12.20	17.26	13.76	14.26
6	3.5	4.20	5.60	3.78	5.68	4.51	4.24
7	0.80	0.28	3.70	1.90	1.90	2.37	2.29
8							
total (5-7)	14.50	17.68	20.68	17.88	24.84	20.64	20.81
9	1.60	1.61	2.38	26.60	2.33	2.48	2.94
10	0.71		1.20	11.60	1.25	1.17	1.27
11	1.15	1.50	3.10	19.40	1.13	2.04	1.95
Total (9-11)	3.46	3.11	6.68	57.60	4.71	5.96	6.16

a) Supercritical carbon dioxide extraction of Indian cashew nut shell b) Pentane extract (cold extraction) of raw Indian cashew nut shells c) Pentane extract of steamed Indian cashew shells d) Indian technical CNSL e) Brazilian CNSL f) Kenyan CNSL g) Mozambiquan CNSL.

5. Methods of extraction:

The table suggests higher percentage of anacardic acid in solvent extraction of raw cashew nut shells compared to extraction using supercritical carbon dioxide. Hence, if anacardic acid of high percentage is required, cold extraction using solvent extraction seems to be the possible feasible solution. More over, the CNSL obtained by cold solvent extraction preserves the original properties of the liquid. Anacardic acid percentage in steam roasted shells is less compared to raw cashew nut shells suggesting decarboxylation during the separation of kernel from the shells by steam roasting.

The table also suggests higher percentage of unsaturated constituents in pentane extract of Indian

raw cashew nut shells compared to all other sources. This compositional difference is reflected in the resultant technical CNSL (rich in cardanol) obtained from industrial processing. The table also shows lower percentage of % Cardols in Kenyan and Mozambique CNSL.

It can also be seen from the table that there is compositional variation of CNSL obtained from different geographical locations. The extraction and chemical composition has been the subject of investigation 45. Methods of Soxlet extraction using different solvents were also available in the literature 46-50. This was not referred to in the table. Extraction using vacuum pyrolysis was also reported in the literature 51.

The table also suggested that there are two methods of isolation of CNSL from the shells. They are

- Cold solvent extraction
- Supercritical carbon dioxide extraction

These methods along with the other methods of extraction available in the literature are discussed in the following paragraphs.

- **Cold extraction:**

In one method of cold extraction method, pentane was used as a solvent 44. The broken shells were placed in Erlenmeyer flask and were covered with the pentane. After 12 hours, the extract was filtered off; the shells were again covered with solvent. Five such extracts were combined and evaporated on rotary evaporator under reduced pressure, below 300C. The solute to total solvent ratio was maintained at 1:10. The authors have carried out only the analysis of CNSL and no quantification of CNSL was done. In another method of cold extraction 45, diethyl ether was used as solvent. The broken shells were placed in 0.1X10⁻³m³ of diethyl ether containing 0.1% anti-oxidant. After 24 hours, the ethereal solution was decanted and the ground-up residual shell material re-extracted with another 0.1X10⁻³m³ of diethyl ether during a further 24 hours. The combined extracts were filtered and evaporated to constant weight. Solute to solvent ratio was not mentioned in their work.

Experiments of cold extraction with carbon tetrachloride, light petroleum and diethyl ether were carried out by soaking the shell material (0.1Kg) is soaked in 0.4 X10⁻³ m³ of solvent for one week⁴⁷. The authors performed extraction using Ultrasonication and concluded the solvent requirement is less compared to other methods of extraction.

Cold extraction was also carried out using hexane where extraction time was reported to be 14 days. The authors did not report the solute to solvent ratio in their work 41.

In the above methods of extraction, the extraction

time is very long. To reduce the time of extraction, hot extraction using Soxlet extractor was carried out.

b) Soxlet extraction:

Extraction using Soxlet extractor was carried out using light petroleum oil at a solute to solvent ratio⁴⁷ of 1:3.75. Work was also reported using hexane as solvent for extraction of CNSL⁴⁸ from Shells. 35X10⁻³Kgs of CNSL for every 100X10⁻³kg of Shells charged into the extractor was obtained. The CNSL obtained consisted of 10% cardol, 50% cardanol and 30% anacardic acid. The physical properties like pH, viscosity, refractive index and specific gravity were also determined. The solute to solvent ratio maintained was 1:17.5. This ratio was much lower than that reported⁴⁹. The authors carried out work using different solvents like acetone, hexane, methanol, and toluene in solvent extraction method. They have considered a solute to solvent ratio of 1:20. Their study suggested that of all the solvent used, acetone gave more amount of CNSL and the properties rely with industrial CNSL. The authors studied the effect of time on extraction of CNS and mentioned that maximum percentage recovery of 96% was obtained after one hour of extraction. The time of extraction seems to be too less, since possible mechanism for extraction is that the solvent has to diffuse into the matrix of the shell, dissolution in the oil and then diffusion back into the solution. This mechanism coupled with the shape of the shells gives long extraction times. Their studies also suggested the methanol extract to be slightly more acidic than other extracts. They reported a maximum yield of 8.75X10⁻³ kg of CNSL for 25X10⁻³kg of shells taken. They also studied the effect of temperature on extraction performance in the range of 30 to 500C and reported that the effect of temperature in the range considered was not significant. The yields of anacardic acid were reported as 45.2%, 43.7% and 44% respectively for the three solvents considered. Since, on heating Anacardic acid undergoes decarboxylation; the authors might have

confined themselves to the temperature range mentioned, even though higher temperatures to the tune of boiling points of respective solvents may have given more amount of CNSL. This was the procedure adopted by some authors with their work using ethanol as a solvent for extraction of CNSL in a Soxhlet extractor 50. The authors performed experiments at different temperature using different types of impellers at various agitation speeds. The use of 4 pitched turbine blade, the agitation speed of 400 rpm and a temperature of 70°C for extraction of CNSL using 95% commercial ethanol were recommended by the authors. They reported an optimum solute to solvent ratio of 1:10. The CNSL was reported to contain 36.3% anacardic acid and 33.7% Cardanol. The reported a yield of anacardic acid was 3.85 X10Kg/L and that of Cardanol was 2.01 Kg/l. The optimum time of extraction reported by the authors was however 6 hours. Extraction was done using hexane, methanol and ethanol as solvents 51. The authors varied the solute to solvent ratio from 1: 4 to 1:10 and mentioned that the ratio of 1: 8 was adequate for extracting anacardic acid. It can be inferred from the above that there is still some debate about the optimum solute to solvent ratios. Even though, the solvent extraction is generally employed to get higher concentration of phenol, the limitations with solvent extraction of CNSL are that they give rise to colored impurities 52. More over, the solvent extraction has a serious problem of elimination of polluting organic solvent from the extract. To improve the quality of CNSL, to reduce the extraction time, to make the extraction process more environment friendly, supercritical carbon dioxide was contemplated even though earlier work using supercritical carbon dioxide reported an extraction time of 17.5 hours 47.

- **Extraction using supercritical carbon dioxide:**

Recently, carbon dioxide near critical and supercritical states (scCO₂) has drawn much attention as solvent, especially in food and pharmaceutical industries. This is particularly for the interest of avoiding the use of organic solvents that are economically and environmentally unfriendly, besides the difficulties of completely eliminating organic solvents from the desired end products⁵³. Literature was also available for use of supercritical fluids in the extraction (SFE) of bioactive compounds from plant matrices with focus on essential oils, phenolic compounds, carotenoids, tocopherols, and tocotrienols 54. They mentioned that the most important advantages of SFE is the possibility of changing operational conditions of pressure and temperature to facilitate the extraction of specific compound leading to not only extraction, but fractionation. Selection of these conditions depends on the specific compound or compound family to be extracted.

The authors also mentioned that the kinetics of SFE can be represented by the overall extraction curve (OEC). Generally, OECs are characterized by three time periods: (1) a constant-extraction rate period (CER); (2) a falling-extraction rate period (FER); and (3) a diffusion controlled rate period (DCR).

Supercritical Extraction was carried out at a pressure of 250 bar and a temperature of 40°C for 16 hours 42. They reported that extraction rate was maximum between 5 to 10 hours. Though the yield was only 60% of that obtainable, the product was nearly colorless. The flow rate of carbon dioxide was set at 5 kg/hr (80 kg for the entire extraction process). They obtained 0.7X10-3Kg of CNSL for every kg of Carbon dioxide. The amount of carbon dioxide was reduced in subsequent works by Smith and co-workers 53. They carried out extraction by two methods. First method was typical extraction method during which the yields obtained were much less than the theoretical yields. However, the yield was at 10X10-3Kg/Kg of CO₂.

Second method was based on Pressure profile extraction method with intermediate depressurization steps. This not only reduced the amount of carbon dioxide, but also increased the yield of CNSL. However, they discussed the quality and quantity of CNSL and no attempt was made to separate the components of CNSL.

Based on pressure profile method, CNSL was separated from cashew nut shell 55. The shells were contacted with high pressure carbon dioxide at elevated pressures of 30 MPa for 1 hour and the pressure is released before separation process begun. Extraction yields of CNSL to the tune of 10 times those obtained by supercritical fluid extraction were obtained. It was found that the temperature has different effects on the solubility depending on the pressure. At low pressures (<12 MPa), increasing temperature results in a decrease in CO₂ solubility in the CNSL phase. At pressures higher than 20 MPa, increasing temperature results in an increase in CO₂ solubility in the CNSL phase. Conditions that resulted in higher CO₂ solubilities in the CNSL gave high extraction yields. The extraction mechanism of pressure profile method seems to occur by (i) penetration of the CO₂ through the shell material, (ii) dissolution of the CO₂ into the CNSL, (iii) expansion and rupture of the shell matrix due to depressurization that increases mass transfer and phase contact area.

The effect of time of pressurization-depressurization (PD) on CNSL extraction was also carried out 56. In initial stages of the trials, before a PD step was performed, the extraction temperature did not have a significant effect on the yield. This means that probably only a very small amount of CNSL was available to the solvent. After a PD step was performed, however, the results for the various temperatures changed greatly with the higher temperature giving the higher yields for a given amount of CO₂ than for yields obtained at lower temperatures. Once that the CNSL was in good contact with the CO₂, the temperature influence on

the CNSL-CO₂ phase behavior became more important. The PD step is thought to break the oil-bearing membranes and to create channels in the cashew shell honey-comb matrix. They also carried out extraction of ground shells and concluded that grinding the shell breaks the CNSL-bearing membranes and allows good contact between CO₂ and the CNSL. Further, it can be implied that the PD step plays a similar role as grinding since the PD step must promote contact between CO₂ and CNSL. In the extractions, it was found that a pressurization-depressurization step that was approximately 1 h gave extraction yields as high as 60%. Extraction of ground shell material gave extraction yields as high as 90%.

Processing of Cashew nut using supercritical fluid technology was available in the literature 57. The authors explained the two possible mechanisms for extraction. The first mechanism is the permeation and diffusion of the carbon dioxide into the matrix and subsequent diffusion of CNSL into the bulk phase. The second possible mechanism is that the carbon dioxide penetrates into the natural matrix and partially dissolves into the oil phase. This causes the oil to swell and its viscosity to become gradually reduced. This allows the oil to flow out of the honeycombed matrix and then diffuse into the bulk phase. Work was carried out for extraction using supercritical carbon dioxide and the effect of pressure, temperature and mass flow rate of carbon dioxide on yield of CNSL 58. It was reported that total yield increased four times when the pressure was increased from 200 bar to 300 bar at 333 K and 1.0 kg/hr flow rate. The rate of extraction was reported to be high in the initial stages of extraction. With increased temperature, the yield of CNSL increased at a given mass flow rate. With increased solvent ratio, the total CNSL yield increased. However, due to lower retention time, loading of solvent was lower, there by reducing the capacity of utilization of the solvent. The calorific value of the oil was found to be 39Mj/Kg for all extraction conditions. The calorific value was 49

Mj/kg in case of vacuum pyrolysis.

They proposed the following model for extraction $C=C_{inf} - C_{inf} \exp(-kt)$, where C is the mass fraction of the solute in supercritical fluid over given period of time t, C_{inf} is the total amount of solute present in the solid, and k is the rate constant. The authors also reported maximum daily profit at 145 minutes and 13% oil extraction corresponding to optimum time of extraction.

d)Vacuum pyrolysis :

Work was also reported for extraction of oil from CNS using vacuum pyrolysis [52]. Pyrolysis is generally used to describe processes in which preferred products are liquid oils especially those with desirable chemical composition and physical attributes for liquid fuels, fuel supplements and chemical feedstock. The liquid pyrolysis fuels apart from being energy rich are easier to handle, store and transport in combustion application and can be upgraded to obtain light hydrocarbons for transport fuel. In the method described, CNS on removal of oil at 1500C is termed as Bio-oil CO1 and this is pyrolysed for study of product distribution in a packed bed vacuum pyrolysis unit. The reaction conditions are maintained at, initial reactor vacuum pressure of 5 kPa and at various maximum temperatures between 400–6000C, with an increment of 500C for each experiment. The total condensable collected in the condensing train is termed as total liquid. Among the total liquid, first three fractions, which are directly combustible without any further treatment, are termed as bio-oil CO2. The total liquid percentage varies from 37% (4000C) to a maximum of 42% (500–550 0C) and dropping to 36% (at 6000C). However, the liquid to oil ratio was reported to be independent of maximum temperature of pyrolysis in the temperature range of 400 0C to 5500C. The calorific value of Bio-oil CO1 was reported to be 33 MJ/kg while that of Bio-oil CO2 was reported to be 40 MJ/kg which is unusually high like petroleum fuels. Their physical properties analysis showed high miscibility with diesel and methanol in a useful factor

for consideration as a fuel. They also reported the viscosity data which is even though high at 30 0C, reduces drastically at higher temperatures. The ash content for both oils was reported at .01% while that of moisture content for CO1 was reported at 3.5% while that of CO2 was mentioned as 3%. In addition to the possibility of some of the CNSL polymerizing at elevated temperature, thermal extraction can adversely affect the quality and color of the obtained CNSL.

This oil is rich in cardanol and the liquid samples obtained from pyrolysis were reported to contain 59% to contain higher percentage of polymeric material and difficult to load the sample in to the extractor for isolation of phenols using supercritical carbon dioxide extractor. To overcome this problem, pyrolysis oil was mixed with the inert material like saw dust (1:1 by weight) and then it was placed in the extractor. This solid inert material was essentially used as a surface support for the bio-oil. CNSL obtained after decarboxylation of CNS at 1800C and after pyrolysis was used for the studies. Extraction kinetics for CNSL at different operating pressures and operating temperature of 323K and at a solvent mass flow rate of 1.2 kg/hr were reported. The batch time was taken as 150 minutes. The increase in yield of CNSL to the tune of 50% was observed with increase in pressure from 225 to 300 bar, keeping other operating parameters constant. It was also interesting to note from GC-MS results that the total concentration of phenols and Cardanol has also increased with increase in pressure.

Extraction was also carried out in the temperature range of 303-333 K, pressure range of 120- 300 bar and mass flow rate of 0.7-1.2 kg/hr. The yield of Cardanol rich oil from both pyrolysis CNSL and 1800C CNSL at 300 bar and 333 K was found to be 63% and 45% respectively. The Concentration of cardanol by this technique was found to be 86% with 5% of phenols.

The kinetics of pyrolysis of CNS was also reported in the literature⁶¹. Some of the conclusions of the work were

- High hydrocarbon and less char in CNS
- Moderate activation energies (130 to 216 kJ/mol) which enable the respective reactivity to be high.

6. Separation of major components of Cashew nut shell liquid:

The CNSL components are hydrophobic and aqueous solvent systems are not useful for their separation. Efforts were made to isolate the anacardic acid by making a sodium salt of it which is stable at room temperature³¹. Subsequently, some authors reported work of treating the sodium salt with an organic solvent and to remove non acid materials and then treated with an acid to liberate crude anacardic acid. This procedure is tedious and gave anacardic acid fairly contaminated with non-acidic phenols. Further, if reasonably pure anacardic acid is required, the yields are low⁶². This procedure is modified by precipitation of the acids from an alcoholic solution with freshly prepared lead hydroxide and decomposing the lead salt with ammonium sulfide⁶³. The draw back of this process is ammonium salt of anacardic acid is so thick and viscous that it is difficult to filter it from fine suspension of lead sulfide. This method was modified by extracting the lead salt into ethereal solution⁶⁴. The ethereal salt containing lead anacardate is repeatedly shaken in an inert atmosphere and with dilute hydrochloric acid followed by water. The solution is dried and then distilled to give anacardic acid as brown oil.

A process for the separation and isolation of anacardic acid from Ginkgo biloba leaves and cashew nuts was reported by some authors⁶⁵. In this method, the fatty acids are separated from anacardic acid by selective methylation. The fatty acid esters and anacardic acids are separated on silica gel. In the

next step, anacardic acids are separated from other phenolics by treating with a calculated amount of diazomethane under mild conditions. The dimethyl derivatives are separated by GLC.

A practical column chromatographic method for the isolation of anacardic acid was also reported in the literature. In this method, the cashew nut shell oil was portioned with water and hexane. The hexane layer was subjected to column chromatography. The components were eluted with ethylacetate-hexane-acetic acid (10:90:1 to 20:80:1 v/v) and further separated into component phenols by HPLC⁶⁶.

Medium scale separation of anacardic acid was carried out from 100X10⁻³ kg of CNSL using chromatography and is based on the difference in acidity of anacardic acid and other phenolics⁶⁷. Anacardic acid, being more acidic, selectively forms salts with weakly basic amines. Cardols and Cardonls being phenolic and weakly acidic, are unretained on weakly basic surfaces. A column of silica gel was prepared by slurring 0.5kg of gel in 1.5 L of hexane containing 30ml of triethylamine, and 0.1 L of hexane was loaded into the column, using a separatory funnel as the delivery system and the column was irrigated with 4 L of ethyl acetate and hexane mixture in the ratio of (25:75v/v), containing 0.5% triethylamine. The column effluent was evaporated in rotary vacuum evaporator yielding 27X10⁻³kg of cardols. The column was then irrigated with 1.5 L of ethyl acetate-hexane mixture (25:75v/v) containing 1% acetic acid (formic acid can also be used with comparable efficiency). The effluent on evaporation yielded 70X10⁻³ kg of anacardic acid. Among variety of bases used like ammonia, a primary amine and a tertiary amine and an aromatic amine, triethyl amine was found to be more effective. This method of separation separated the four components of anacardic acid as a group. The anacardic acid contains saturated anacardic acid, mono, di and tri olefins. These four components were separated using low temperature crystallization in the

temperature range of 0 to -80 °C. The procedure for preparation of anacardic was same as that reported by earlier researchers 63-64. However, the authors observed some solubility in ethanol which was not reported earlier.

A solution of 0.200 kg of anacardic acid in 3 L of acetone was prepared and cooled to 40°C for 10 hours, the crystals removed and washed with acetone and marked as fraction A. The filtrate was diluted to 3.5 L with acetone and crystallized at -79 °C for 14

hours, the crystals designated as B. The filtrate was freed of the solvent the residue was dissolved in 2.5 L of methanol and crystallized at -79°C for 14 hours and the crystals marked as C. The residue from the final filtrate was designated as D. Each of the above fractions was subjected to further fractional crystallization in appropriate solvents and at different temperatures. The fractions are further classified into I containing Ac, II, Af and Bc, III, Cf and Dc, and IV Df. The following table (Table-IV) gives the details of crystallization of anacardic acid.

Table: IV : Various fractions of anacardic acid separated based on crystallization.

Stage	Fractionation	Appearance	Yield (Kg)X10 ³	Iodine number	No of double bonds	Remarks
Ac	Crystals from A	Light color solids	13	104	0.41	The filtrate from B was added to C and the resulting mixture was crystallized and the crystals are designated as Cc and Cf
Af	Filtrate from A		10	174.8	1.37	
Bc	Crystals from B		18	177	1.4	
Cc	Crystals from C	Brown liquid	21	225	2.05	
Cf	Filtrate from C		54	247.1	2.35	
Dc	Crystals from D	Brown liquid	38	249.4	2.38	
Df	Filtrate from D		40	277.4	2.76	

Using column chromatography, CNSL was separated into Cardol, Cardanol and 2 methyl cardol with an aim to recover Cardanol 69 which can be used in the synthesis of cation-exchange resins. The separation was effected using a mixture of benzene and chloroform as the mobile phase in a column packed with silica gel adsorbent of particle size 60-120 mesh as the stationary phase. The authors dissolved 80mL of CNSL in 60mL of Chloroform to make it less viscous. Then, they added 0.170kg of silica until the solution became paste like. The paste was dried in an oven at a temperature of 110 °C for three hours to obtain the CNSL cake. Drying of CNSL cake affected the decarboxylation of anacardic acid to cardanol. However, no tests were performed to ensure the absence of anacardic acid while heating. The mean RF value of Cardanol was reported to 0.516, for cardol it was 0.173 and for 2 methyl cardol, it was 0.148. The pH of CNSL and Cardanol was found to be 6.69 and 3.43 respectively suggesting Cardanol is more acidic than raw CNSL. This pH value suggested less percentage of anacardic acid in the CNSL. Cardanol was also isolated from CNSL using vacuum

distillation method 70. CNSL of pH 4.3 was used indicating the anacardic acid in the liquid was very dominant. The effect of temperatures and heating time on pH of CNSL was carried out. Based on the pH response curves, it was indicated that the higher the heating temperature and the longer the heating time, the higher the pH of the CNSL. Statistically, the heating temperature contributed 65% to the pH changes, while heating time contributed only 35%. They also reported that heating decreased the specific gravity of CNSL due to decarboxylation leading to release of carbondioxide. Data on characteristics of CNSL showed that heating also reduced the substrate viscosity, but increased both iodine and hydroxyl values. The increases in iodine and hydroxyl values were due to reduction in amount of CNSL masses and release of CO₂ and water during the decarboxylation. The decrease in viscosity was due to the formation of cardanol which has got lower viscosity. An optimum heating temperature of 140°C and heating time of one hour was reported by the authors for decarboxylation of anacardic acid. Cardanol was isolated from the CNSL by vacuum

distillation (4-8 mmHg) at high temperature, with an optimum temperature of 280°C, and the rendement 74.22%. They carried out the feasibility studies and reported construction of Cardanol production industry and reported values of IRR as 45.79% and PBP as 2.22 years. The method of distillation can only be used for isolation of cardanol.

Work on isolation of anacardic acid from solvent extracted CNSL using supercritical carbon dioxide was also reported recently 71. The authors studied solubility data of CNSL under different operating conditions of temperature, pressure and flow rate. The best operating conditions were reported to be 500C, 300 bar and flow rate of 5X10-3kg/min. Since there is a possibility of anacardic acid undergoing decarboxylation, this method may not recover all the anacardic acid present in solvent graded CNSL. The authors have not reported the yield of anacardic acid. The methods of isolation of the other two major components were not discussed by the authors. Moreover, the yield of anacardic acid reported by the authors was only 82% in 150 minutes. Work was also reported for isolation of all the three major components of CNSL 72. This method even though was based on use of chemicals, recovers all the three major components of CNSL. Commercially available solvent extracted CNSL was dissolved in 5% aqueous methanol and calcium hydroxide was added while stirring, leading to precipitation of calcium anacardate. The calcium anacardate was suspended in distilled water and 11M HCl was added. The resultant solution was extracted with ethyl acetate. The combined organic layer was washed with distilled water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. This gives high purity of anacardic acid at a recovery of 95%. The authors reported the composition of aqueous methanol was crucial in obtaining anacardic acid of high purity and in good yield. The mother liquor obtained after filtration of calcium anacardate was stirred with liquid ammonia and extracted with a

mixture of hexane/ethyl acetate (98:2).Cardol remained in the liquid ammonia where as while the cardanol was extracted in to the organic layer. Subsequently, extraction of ammonical solution with a mixture of ethyl acetate/hexane in the ratio of 80:20 gave cardol of high purity. This method separated all the three major components of natural CNSL. Moreover, the solvent is water soluble, removed all the other impurities.

Work was also reported for separation of cardol and cardanol from technical CNSL 73. The authors in their work used different bases and observed that ammonium hydroxide formed weak complex with cardol. They dissolved technical CNSL in a mixture of methanol and ammonium hydroxide and arrived at an optimum ratio of 8:5.

7. Qualitative and quantitative analysis of CNSL:

Literature reports various methods of analysis of constituents of CNSL.

Natural and decarboxylated CNSL were analyzed by combined thin-layer chromatogrpah-gas-liquid chromatography by some researchers 74. TLC was carried out on analytical plates (10X28X0.25cm) and preparative plates (20X20cmX1mm) coated with silica gel G. Gas liquid chromatography was carried out with a Pye 104 apparatus equipped with a flame ionization detector (FID) and Fisons Vibrator integrator recorder. Acid-washed and silanized Celite (80-100 mesh) was coated with 2%polythne glycol adipate.

A thin-layer chromatographic (TLC) –mass spectroscopic procedure was devised for analysis of phenolic lipids 75. The authors experience suggested that TCL-mass spectrometry was a reliable procedure for the quantitative analysis of unsaturated constituents of long-chain phenolic lipids. Mass spectra were determined on an AEI MS9 and on a Hitachi-Perkin Elmer RMS4 instrument. Samples were used at a concentration of 20% in diethyl ether and chloroform. Corrections for different response factors lead to results a showing excellent agreement with

those from gas chromatographic analysis. Detailed investigation on the analysis of CNSL was available in the literature. The following table (Table-

Table-V: Analysis of CNSL constituents of CNSL using different methods of analysis

Source	Method	Anacardic acid	Cardol	Cardanol	2-methyl cardol
Mozambique	HPLC	a) 69.29	22.87	6.77	1.07
		b) 71.19	22.87	5.12	1.07
	TLC-UV	71.65	20.28	5.12	3.25
	GLC	71.51	22.34	3.27	2.75

The table suggests that TLC-UV method while giving good agreement with HPLC, there is a difference in analysis of minor components using TLC-UV. The internal standard used in their work was tert-butyl phenol. The column used in HPCL analysis was octadecylsilyl bonded stationary phase, acetonitrile-

V) illustrates the analysis of CNSL by different methods of analysis 45.

water –acetic acid as the mobile phase. The wave length used was 275 nm. The drawbacks of the procedure were reported to be a) each analysis required about an hour and b) the wide difference in the retention time as well as detector response as shown in the following table (Table-VI).

Table -VI : HPCL analysis of CNSL compounds

15:0 phenol	Retention time (min)	Retention volume (cm ³)	Weight (mg)	Peak areas	Relative molar response value
t-Butyl phenol	1.83	4.94	16.8		1.000
Cardol	15.39	41.55	134.4		0.749
Anacardic acid	28.83	77.84	146.1		0.535
Cardanol	43.47	117.37	127.7		1.246

Hence, to avoid delay in analysis of large number of samples, the mobile phase was changed to tetrahydrofuran 49. This enabled faster analysis with adequate analysis of all the analytes. The authors used cardol (15:0) as the internal standard because a) its retention time as mid way between various peaks b) it belongs to the same chemical class and c) it is not present in natural CNSL to any significant extent. While isolating anacardic acid from CNSL using medium scale chromatography, HPLC was used for analysis and 80% acetonitrile (v/v) containing 1% acetic acid was used as the mobile phase. The wave length considered was around 310nm. The analysis of refined cashew nut shell liquid was carried out by some authors while carrying out the

economic appraisal of supercritical fluid extraction⁷⁶. They used CNSL obtained from vacuum pyrolysis in their work. They used A Jasco V-530 UV-vis spectrophotometer at a wave length of 274 nm. FTIR system used for the analysis consists of a Nicolet Magna 550 series with an on line plotter to plot IR-spectra of the oil to provide the absorbance spectra in terms of percentage transmittance along the wave numbers 4000–400 cm⁻¹. Analysis was also carried out using Hewlett-Packard 5890A GC-MS system with a 30 cm×0.25mm I.D. capillary column coated with polysiloxane. The initial oven temperature of GC was 50 °C for 2 min and then programmed to increase at a rate of 50C/min up to 1000C. It was kept at that temperature for 2 min. Finally, temperature was

raised to 280 °C at a rate of 50°C/min. Helium was used as a carrier gas. While analyzing cashew nut shell liquid obtained from supercritical carbon dioxide, some authors used GC-MS, FTIR and UV spectroscopy. They mentioned that acid group was traced by FTIR only for CNSL obtained above 225 bar. GC-MS did not identify 'anacardic acid' as a major group and therefore was assumed to be in traces. The mobile phase used for HPLC analysis was same as above by some investigators when isolating anacardic acid from solvent extracted CNSL using supercritical carbon dioxide⁷¹. The authors also used UV-Vis, FT-IR and HNMR in their analysis. UV-vis analysis was performed using a Beckman Coulter, DU 800 Spectrophotometer. The liquid samples were dissolved in chloroform to a final concentration of approximately 1 µg/mL before the analysis. FT-IR analysis was performed on a Nicolet Impact 410 spectrophotometer equipped with a QuickIR software (Thermo Fisher Scientific). Approximately 0.2 mg of isolated anacardic acid was thoroughly mixed with 300 mg of KBr to prepare the sample pellet.

8. Scope for future work:

Work can be focused on using different solvents and combination of solvents for extraction of CNSL from Indian cashew nut shell, both for Steam roasted shells as well raw cashew nut shells and their yields at different solute to solvent ratios. This enables optimum solute to solvent ratios for extraction of CNSL. Further, the rate constant and activation energy studies for decarboxylation of anacardic acid to cardanol can also be carried out for better understanding of decarboxylation. Supercritical extraction of Cold extracted CNSL as well as CNSL obtained from Steam extracted shells can also be carried out for recovery of anacardic acid to compare the extent of anacardic acid obtained with that of chemical methods.

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