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**CHARACTERIZATION OF UNMODIFIED AND MODIFIED CASHEW NUTSHELL LIQUID (*ANACARDIUM OCCIDENTALE*) USING INFRARED SPECTROMETRIC TECHNIQUE**

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## Abstract

*Cashew nutshell liquid (CNSL) (90 % Anacardic acid) extracted from cashew (Anacardium Occidentale) using Soxhlet extraction was characterised using Fourier Transform Infrared Spectroscopy (FTIR) to ascertain the functional groups contained in the liquid. Results obtained shows the presence of hydroxyl group, aromatic ring, phenyl group, carboxylic group and substituted $C_{15}$ alkyl chain indicated by their vibration bands eluted at their respective wavelengths as shown in the infrared spectrum. The hydroxyl and phenyl groups in CNSL gives it the properties of phenols as such can be used as an appropriate substitute for liquid phenols whereas the additional presence of carboxylic group is responsible for the phenolic characteristics of CNSL which makes it very useful in the production of drugs and other pharmaceutical products. The extracted CNSL was modified by esterification at the carboxylic group with the use of acidified butyl alcohol to obtain a carboxylate product indicated by two carbonyl groups (C-O) for the ester and carboxylic functional groups respectively. The modified derivatives of CNSL have a great deal of distinctiveness which gives them a wider range of uses compared to the unmodified CNSL, for instance modified CNSL are very important in oil field operations as surfactants, demulsifiers, flow improvers and corrosion inhibitors.*

## Key Words

Functional group, esterification, anacardic acid, infrared, extraction

**Introduction**

Cashew represents an evergreen tree majorly cultivated in tropical regions especially in South America, it falls in the family of *anacardiaceae* with the botanical name *Anacardium Occidentale*, it is the second to almond in commercial importance. Cashew (*Anacardium Occidentale)* is the source of the cashew nut, oil, liquid and apple (*Olife et al., 2013*) Almost every part of the cashew is useful in various industrial applications. Cashew nuts have a lot of health benefits such as boosting immunity, weight management, improves brain function, promote healthy skin, regulate blood sugar etc. Cashew nuts contains appreciable number of tocopherols, squalene and phytosterols which exhibit cardio-protective qualities (*Copini et al.,2020; Suganya and Dharshini, 2011*). Activated charcoal obtained from the bark of cashew tree has proven to be effective in the recycling of spent lubricating oil. Cashew nutshell liquid (CNSL) is a versatile by-product obtained from cashew, it is the outer shell of the cashew nuts which are part of the cashew nut fruit along with the cashew apples, these shells contain viscous liquid released on steaming raw cashew nuts. Cashew nutshell liquid (CNSL) is as useful as the nuts, apple, and the bark of the cashew tree, they are used in polymer-based industries for friction linings, paints, laminating resins, surfactants and varnishes etc *(Adeigbe et al., 2015*). Cashew nutshell oil (CNSO) can be used as a raw material in the development of antioxidants, drugs, biomaterials, and fungicides. Cashew nutshell oil are rich in vitamin E and so are essential oil used in anti-aging and can improve skin complexion. There is a difference between CNSL and CNSO, whilst the former represents a specific liquid component of the nut with characteristic chemical components the latter is a more general term that encompasses the entire oil extracted from the cashew nut shells *(Copini et al.,2020)*. CNSL can be extracted from the cashew nut by solvent extraction. Solvent extraction is an analytical technique used in determining the contents of various inorganic and organic species, it is a process in which compounds are separated based on their relative solubilities in two different immiscible liquids usually water and an organic solvent *(Hammed et al., 2008).* Infrared Spectrometric technique unveils the specific functional groups attributed to different vibrational bands present in the spectrum. The aim of this study is to characterize CNSL using infrared spectrometric technique. An in-depth knowledge of the functional groups present in CNSL is very critical in broadening its uses when compared with the functional groups present in synthetic products of specific applications. For instance, to verify the effectiveness of CNSL as a demulsifier or surfactant, the functional groups in the CNSL can be compared with those of a synthetic demulsifier or surfactant. Further studies will be the direct application of the CSNL in areas of interest under controlled laboratory conditions after the functional groups have been verified to ascertain its effectiveness. A picture of cashew (*Anacardium Occidentale),* cashew nuts and nutshells are shown in figures 1, 2 and 3 respectively.

*Fig. 1:* Cashew **(***Anacardium Occidentale)* *Fig. 2: Cashew Nut*

*Fig. 3: Cashew Nutshells*

**Materials and Methods / Experimental Procedure / Research**

**Sample Collection and Preparation**

Cashew nuts from cashew (*Anacardium Occidentale)* were obtained from a village in Okene local government area of Kogi state Nigeria. CNSL were extracted from the cashew nuts by solvent extraction using a Soxhlet extractor with acetone as the solvent. The extracted CNSL was treated with calcium hydroxide to isolate anacardic acid which is the active ingredients in the liquid. Anacardic acid (AA) from CNSL was modified by esterification reaction to obtain the ester form of the acid. The modified and unmodified AA were analysed using Fourier Transform Infrared Spectroscopy (FTIR) to ascertain the functional groups attributed to different vibrational bands present in the spectrum for both the modified and unmodified anacardic acid *(Ike et al., 2021).* The chemical structure of anacardic acid is shown in figure 4 while the reaction for the esterification of anacardic acid with butyl alcohol is shown in equation 1:

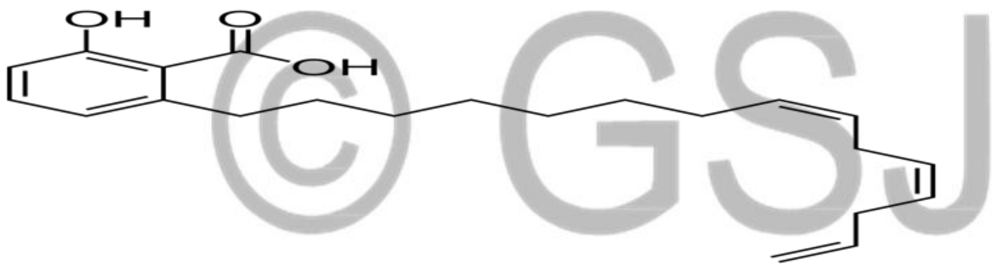


*Fig. 4: Anacardic acid (AA)*

$$\underset{AA}{C_{22}H_{30}O_3} + C_4H_9OH \xrightarrow{\text{Esterification}} \underset{\text{Modified AA}}{C_{22}H_{29}O_3C_4H_9} + H_20 \;\ldots\ldots\; (1)$$

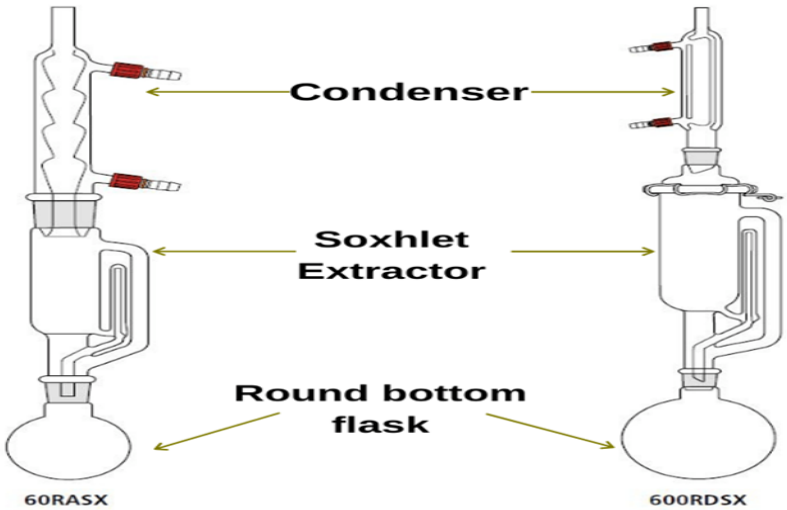


*Fig. 5: Soxhlet Extractor Set Up.*

**Extraction of CNSL Using Soxhlet Extractor**

Cashew (*Anacardium Occidentale)* was placed on a burning charcoal for about three minutes, the red-hot shell was wet with caustic oil, the shell split and the nuts were removed. The cashew nutshells were crushed into powder and 20 g of the powdery sample was introduced into the thimble of a Soxhlet extractor while 100 ml of acetone which serves as the solvent was introduced into the round bottom flask. The solvent was heated to reflux at a temperature of 68 $^{0}$C and the vapour produced was subsequently condensed by water flowing in and out of the extraction set up. The condensed solvent was mixed with the sample until the extraction thimble is filled completely with solvent. The extract from the sample (CNSL) which are the soluble components were separated from the sample and then siphoned into a beaker through subsequent solvent evaporation. The procedure was however repeated several times until the CNSL was completely extracted from the sample. The extracted CNSL was treated with calcium hydroxide solution whose quantity is 10% the volume of the extract to produce Anacardic acid (AA). Part of the AA was modified by esterification *(Idah et al., 2014).* Figure 5 shows the picture of a Soxhlet extractor set up.

## Esterification of Anacardic Acid from CNSL

An excess of 500 ml of butyl alcohol was added to 100 ml anacardic acid from CNSL with 5.0 ml sulphuric acid ($H_2SO_4$) in a reaction vessel. The mixture was brought to boiling and refluxed for about two hours and then subjected to fractional distillation. The distillate formed separates into two layers of alcohol and water. The upper layer which contains alcohol was returned to the reaction vessel to produce further esterification while the lower layer which contains water was discarded. The esterification process was completed when no more water was separated from the distillate, the distillation was however continued beyond this point to expel the excess alcohol and retrieve the ester (modified anacardic acid). Care was taken to ensure that the temperature of in the reaction vessel is not too high resulting in resinification (ability to form resin) of the ester *(Gandhi et al., 2012).*

## FTIR Characterization of Modified and Unmodified Anacardic Acid

The modified and unmodified anacardic acid were subjected infrared characterization using FTIR Spectroscopy. Potassium bromide (KBr) equivalent to 100 mg was properly mixed with the sample. The KBr-sample mixture was added to the sample compartment and further mixed for transparent disc formation and then introduced to the equipment for analyses. A beam of infrared light was passed through an interferometer which splits into two separate beams. Each of the beams passes through the sample and reference respectively. The distribution of the infrared light that passes through the interferometer was altered using a moving mirror placed inside the apparatus. The signal directly recorded, called an "interferogram", represents light output as a function of mirror position. The beams pass through a splitter and then reflected back towards a detector. The splitter alternates the beams that enter the detector. A data-processing technique called Fourier transform turns this raw data into the desired result which is the sample's spectrum. The functional groups present in the sample was interpreted from the spectrum *(Chikwe and Ogbole, 2019).*

## Results and Discussion

**Table 1: Functional Groups Obtained from IR Spectrum of Anacadic Acid from CNSL**

| Peak | Wavelength (cm-1) | Mode of Vibration | Functional Group |
|---|---|---|---|
| P1 | 3410-3400 | OH Stretch | Hydroxyl group |
| P2 | 3100 - 3000 | =C-H symmetric stretching | Aromatic and phenyl |
| P3 | 2999 - 2950 | =C-H Stretch / Combination band | alkene |
| P4 | 2940 -2910 | $CH_2$-symmetric stretching | Long chain alkane |
| P5 | 2900 - 2850 | $CH_2$**-** symmetric stretching | Long chain alkane |
| P6 | 1610 - 1600 | Combination band / C=C Stretch | alkene |
| P7 | 1460 - 1450 | CH2 Scissors deformation | alkane |
| P8 | 1020 - 990 | C-O Stretch | Carboxylic group |
| P9 | 710 - 650 | C-H Out of plane bending / difference band | Aromatic and alkene |

**Table 2: Functional Groups Obtained from IR Spectrum of Modified Anacadic Acid from CNSL**

| Peak | Wavelength (cm-1) | Mode of Vibration | Functional Group |
|---|---|---|---|
| P1 | 3400-3300 | OH Stretch | Hydroxyl group |
| P2 | 3100 - 3000 | =C-H symmetric stretching | Aromatic and phenyl |
| P3 | 2900 - 2950 | =C-H Stretch / Combination band | alkene |
| P4 | 2900 - 2850 | $CH_{2-}$ symmetric stretching | Long chain alkane |
| P5 | 1610 - 1600 | Combination band / C=C Stretch | alkene |
| P6 | 1460 - 1450 | $CH_2$ Scissors deformation | alkane |
| P7 | 1300 - 1000 | C-O Stretch | Esters |
| P8 | 990 - 920 | C-O Stretch | Carboxylic group |
| P9 | 710 - 650 | C-H Out of plane bending / difference band | Aromatic and alkene |

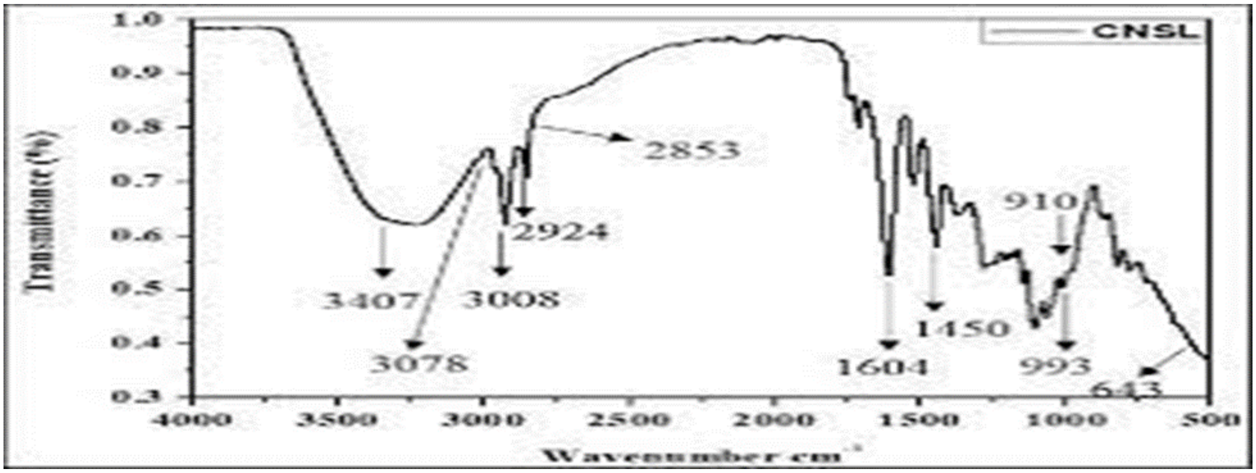


*Fig 6: Infrared Spectrum of Anacardic Acid from CNSL*

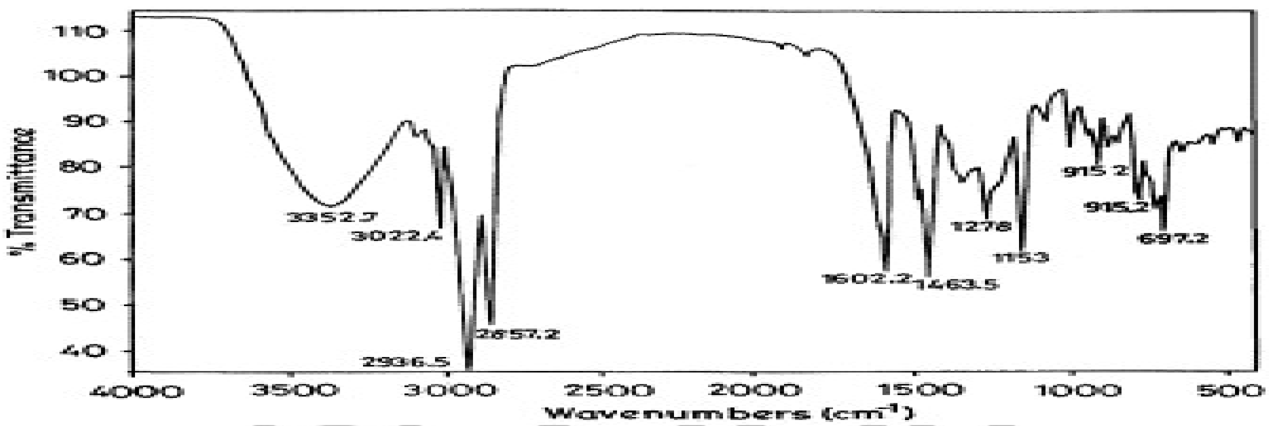


*Fig 7: Infrared Spectrum of Modified Anacardic Acid from CNSL*

## Discussion

Cashew nutshell liquid (CNSL) contains four major components in the natural state, these components are anacardic acid, cardanol, cardol and 2-methyl cardol, it is also a rich source of phenolic lipids. The concentration of the individual components that makes up the CNSL depends on the method of extraction. The use of Soxhlet extraction in extracting the liquid leaves the liquid with 90 % anacardic acid whereas modification of the liquid through processes such as decarboxylation or esterification produces a more commercial grade CNSL *(Ike et al., 2021; Gandhi et al., 2012)*. The industrial and commercial use of any component is to a large extent dependent on the functional groups that makes up the component. Comprehensive investigation of anacardic acid which constitutes 90% of the extracted CNSL showed that the component contains 1-hydroxy-2-carboxy-3-pentadecylbenzene, 1-hydroxy-2-carboxy-3-(8-pentadecenyl) benzene,1-hydroxy-2-carboxy-3-(8,11-pentadecadienyl)benzene and 1-hydroxy-2-carboxy-3-(8,11,14-pentadecatrienyl)benzene *(Braga et al., 2021)*. The individual functional groups contained in the liquid were obtained by infrared spectroscopic technique as shown in Table 1. Results obtained shows the presence of the hydroxyl functional group, an aromatic and a phenyl group which is responsible for the phenolic compound present in CNSL. Cashew nut production is one of the major economic sources of naturally occurring phenol, CNSL is a low cost and renewable material that can be used to replace phenol *(Victor-Oji et al., 2019)*. Phenol has a wide range of industrial uses which includes production of plastics, explosives and drugs. The common phenol hydroquinone is the component of developing photography because of its ability to reduce exposed silver bromide crystals to black metallic silver *(Tyman and Bruce, 2003)*. The presence of carboxylic group with phenol in CNSL is responsible for the phenolic characteristics of CNSL which makes it very useful in the production of drugs and other pharmaceutical products due to its anti-aging, anti-inflammatory, antioxidant and anti-proliferative characteristics *(Tyman and Bruce, 2004)*.

The presence of $CH_2$ symmetric stretching confirms the presence of long-$C_{15}$ alkyl chain substituted at the meta position which is a very important component for polymer production. The presence of different functional groups in CNSL makes it possible for it to undergo different sequence of chemical reactions for instance the hydroxyl functional group undergoes esterification, epoxidation, ethoxylation, alkylation reactions etc while the carboxylic acid group undergoes decarboxylation, esterification etc *(Ike et al., 2021*). The meta $C_{15}$ alkyl side chain directs all further substitution to ortho and/or para positions for phenylation, epoxidation, hydrosilylation, hydrogenation and metathesis reaction. The aromatic ring is a site for hydrogenation, nitration, sulfonation and halogenation etc . It is therefore important to note that the greater the possibility of a reaction sequence due to the presence of functional groups in a compound the more the number of products realizable from the compound hence CNSL is a precursor for the manufacture of several industrial and commercial products *(Idah et al., 2014)*. Table 1 also indicates the presence of the alkene functional group at a couple of wavelength bands. Alkenes are essential in the synthesis of polyolefins such as polypropylene. Polyolefins are essential components of several plastics and can be used in the manufacture of pellets, bottles, jars, hot beverage cups, food packaging etc, they are also frequently used in the automotive industry to produce batteries, bumpers, instrument panels, trims of doors and elements for interior decorations *(Smith et al., 2003; Perdriau et al., 2012)*. The functional groups of modified Anacardic acid obtained from CNSL by esterification is shown in Table 2. The modification of CNSL gives the liquid an extra carbonyl (C-O) functional group for esters in addition with the carbonyl functional group of carboxylic acid and this gives it more commercial and industrial value. Owing to the presence of carboxylic and hydroxyl groups in CNSL, esterification can occur at both ends with either a suitable base or an acid respectively *(Lubi and Thachil, 2000)*. Esterification of the CNSL was achieved at the carboxylic end with the use of butyl alcohol in the presence of $H_2SO_4$ acid. The modified derivatives of CNSL have a great deal of distinctiveness which makes them more useful compared to the unmodified CNSL. Modified CNSL are essential assets in oil field operations, the carboxylate functional groups make them very good surfactants that facilitates the recovery of residual oil by reducing the interfacial tension between two immiscible fluids *(Balgude and Sabnis, 2014)*. Modified CNSL can be used as flow improvers for waxy crude oil and drilling muds, demulsifiers to separate water from crude emulsions, lubricants for engines and corrosion inhibitors in oil and gas installations *(Victor-Oji et al., 2019)*.

## Conclusion and Future Scope

CNSL is a cheap agricultural waste product obtained from cashew (*Anacardium Occidentale)* with a wide range of industrial and commercial importance owing to the functional groups it possesses. CNSL extracted from cashew (*Anacardium Occidentale)* through Soxhlet extraction comprises of 90 % Anacardic acid with functional groups such as phenolic hydroxyl group, carboxylic acid group, amines and olefinic linkages in the $C_{15}$ alkyl chain with aromatic ring. The presence of these functional groups increases the possibility of several reaction sequences thereby making CNSL a precursor for the synthesis of various products such as plastics, dyes, drugs, explosives etc. Modification of the carboxylic group in CNSL by the process of esterification broadens its industrial

use as surfactants, demulsifiers, flow improvers for waxy crude as well as building blocks for oil field operations.



## Conflict of Interest

The authors wish to declare no conflict of interest with respect to all that concerns this study.

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