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Characterization of Chemically Modified Cashew Nut Shell Liquid

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Authors' contributions

This work was carried out in collaboration among all authors. Author HND designed the study, carried out the experiment and characterization, wrote the protocol, performed the analyses and wrote the first draft of the manuscript. Authors AD, BK and OA supervised and managed the analyses of the study. Author OA managed the literature searches and chemistry aspect of the study. All authors read and approved the final manuscript.

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ABSTRACT

The need to convert waste-to-wealth motivated this research. Huge amount of by-products generated in the processing stage of cashew nut is treated as waste and dumped in the environment. The waste contains a dark liquid rich in natural and renewable phenolic material known as cashew nut shell liquid (CNSL). Owing to the phenolic composition and structural features of CNSL, different types of naturally occurring as well as modified natural cellulose based polymers have been synthesized and used to substitute synthetic and petroleum based polymers for various applications. In this study, naturally occurring liquid from cashew nut shell was extracted, modified and characterized as additive for drilling fluid formulations. The study adopted solvent extraction technique using soxhlet apparatus, acetone and cashew nut shell. The liquid

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extract was further modified using amines respectively. In the condensation reaction, 100 mls of the cashew nut shell was used to react with 7.3 ml ethanol-amines, 27.58 ml diethanol-amine (DEA) and 38.2 ml triethanol-amine (TEA) respectively. The mixtures were sulphonated with sulphamic acid as catalyst at a temperature ranging from 100ºC to 140ºC. The reaction mixtures were stirred continually for an hour (1hr.) and water of esterification was collected as by-product of the reaction which was an indication of complete reaction. Biodegradable, cheap and renewable esters were obtained. To elucidate on the chemical structure, the esters were subjected to elemental analysis using the FTIR instrument. The results of the FTIR analysis revealed that N-H and C-H stretching vibrations which were absent in CNSL, were present in the modified compounds, attesting that in deed new compounds have been formed. The physico-chemical properties of the extract was analysand the result showed an agreement with existing literature. These products, in combination with the right additives, and conditions could be potential multi-purpose additives in drilling operation. This will help to reduce the cost of importing synthetic oilfield additives, creating job opportunities and boosting the local content goal.

Keywords: Agro-waste; CNSL extract; synthesis; characterization; oilfield-chemical additives; drilling operation.

1. INTRODUCTION

Agriculture is a major economic activity in Nigeria [1]. The industry generates huge tons of wastes from its processes and biomasses each day. This is attributed to the continuous increase in agricultural activities. Such agro-wastes have remained largely under-utilized owing to lack of technology to convert them to useful commodities [2].

The environmental challenges posed by these wastes have made our environment untidy, the lands where they are dumped are unfit for certain economic activities and the numerous dump sites across the country have also turned a breeding place for some disease-causing agents [3]. Nwankezie and Ogbeide [4] observed that waste generated from agro processes and seeds of plant that are unproven to be edible are neglected as they are always dumped on the ground and trampled upon thereby making them useless. The usual disposal mechanism of this menace in Nigeria has been burning or leaving them to decompose [3,5]. Agro-wastes in recent times have gained tremendous attention occasioned by the calls for green chemistry to achieve greener environment. These wastes most often composed of natural phenolic materials and other useful compounds that can be synthesized to obtain products that serve as raw materials for diverse applications. Again most of the industries rely on non-renewable resources especially minerals as sources for their raw materials but these minerals are currently been depleted. The need to bridge the gap between renewable and non-renewable sources brought agro-waste into focus as potential alternatives [2].

Cashew industry is one of the leading producers of edible nuts in the world. Cashew tree with botanical name Anacardium occidentale belongs to the Anacardaceae family. It is made up of 20-25% edible nut, 2-5% testa, and the outer hard skin shell occupies 65-75% [6]. This tree is abundantly scattered in Nigeria and is grown mainly for processing and exporting of the edible nut while the shell is dumped as waste. According to FAO [7], Nigeria recorded an increase in cashew production from thirty thousand (30,000) in 1990 to one hundred and seventy six thousand, eight hundred (176,800) tons in the year 2000. This is over one hundred percent (100%) increment and it shows an increase in demand which expected to be constant over a period of time. On that premise, Federal Government of Nigeria through the ministry of Agriculture (2019) has announced establishment of four (4) more processing plant to handle the excess production. It therefore means that more of these wastes are expected and so alternative utilization of the wastes becomes very imperative.

This research considered waste generated from cashew nut processing. The choice of this waste is premised on availability, cost and biodegradable nature of products because of their natural sources. The processing of the edible nut is increasing because of the economic importance of the nut, meaning additional tons of waste shall be generated and neglected in areas of operation, increasing microbial activities that may be harmful to the environment.

Cashew nut shell is a major by-product of the cashew nut processing which is normally discarded as waste. In areas of operations where these wastes are not properly managed, environmental pollution is eminent. As documented in literature, cashew nut shell contains naturally occurring liquids with phenolic and carboxylic compounds [8,9]. It is a dark or redish- brown coloured liquid, viscous in its crude form and found in the soft honey comb structure of the shell of cashew nut [10,11]. Unlike the conventional phenols that are synthesized from petroleum sources, natural CNSL is not limited by environmental restriction hence, eco-friendly products are derived from it. Again, because it is natural and renewable, its synthesised products are biodegradable and could sustain the environment. CNSL has been reported to have some special structural features; have long chain alkyl structure similar to benzene ring, unsaturated molecules attached to side chain which, enables them undergo many reaction that results to variety of products utilized as source of raw material for diverse applications [12]. Composition of CNSL is well established [13,14]. The rich liquid is a source of Anacardic acid (60-70%), Cardanol and Cardol having the remaining percentage [9,15]. The percentage yield of any of the component depends on the interest and mode of extraction. For the purpose of this work, the anacardic acid component was utilized. Cashew nut shell liquid potential have been tested and utilized for some application; friction and brake lining, special type adhesive cement, manufacture of insulating varnishes in the electrical industry, production of particle board when blended etc [2,16]. In spite of the success achieved in converting this menace into useful products, more and more alternatives for the utilization of the liquid are been sort.

2. MATERIALS AND METHODS

2.1 Preparation of Nuts

The cashew nut shells obtained from Uturu area of Abia State, Nigeria were de-hulled with kitchen knife, to remove the edible kernels. Both the de-shelling and other experimental works were carried at research laboratory, department of chemistry, University of Port Harcourt. All the regents, (ethanol-amine, diethanol-amine, triethanol-amine and sulphamic acid as catalyst) chemicals were ANALAR grades obtained from BDH chemicals, while, laboratory glass wears were provided by the same research laboratory.

2.2 Extraction

Solvent extraction method was used to extract oil (liquid) from the cashew nut shell [17,18,19]. For this study, acetone was utilized as the solvent while Soxhlet extractor apparatus Fransz, (1879) was used. Different sizes of the shell was measured in gramms (40, 70 and 400) respectively and rapped with filter paper. The samples were then loaded into the main chamber of the soxhlet extractor, while 350 ml of acetone was poured into 500 ml bottom flask. The process continued with the placement of the chamber into the flask containing the acetone and connecting it to the condenser, pipes and the heating mantle. After completing the set-up, the heating mantle was turned on and the system was allowed to attain a temperature between 68ºC and 70ºC temperature within which the solvent boils. During the process, the vapour from the heated solvent travelled up the distillation column, enters the condenser and the condensed vapour flows downward through the samples in the chamber and enriching it to get out the oil discharged into the flask. The process was done in circle and the extract collected as mixture in the glass reagent bottle. The solvent was thereafter recovered by simple distillation.

2.3 Determination of Physicochemical Properties of the Extract

The physiochemical properties of the crude extract was analysed following standard techniques in a PVT lab using the ASTM procedure [8]. The aim was to ascertain the suitability of the extract as raw material for the synthesis of esters as additive for drilling mud formulation. The properties of interest include: Specific gravity, Viscosity at 40ºC, pH, Iodine value, Acid value and Temperature.

2.4 Synthesis of Cashew Nut Shell Liquid for Production of Polyesters as Drilling Fluid Additives

The syntheses were carried out in stages;

Firstly, 100 ml of the CNSL was poured into a 250 ml of flat bottom flask. 17.3 ml of ethanolamine was added into the flask. The reaction proceeded in the presence of 0.05 g sulphamic acid as the catalyst and was heated to temperature 100ºC -140ºC using paraffin bath on magnetic stirrer and was stirred continually for period between 40 mins and 1 hour until water (by-product) of the reaction was distilled out and collected using dean and stark apparatus.

Secondly, 100 ml anacardic acid component of the cashew nut shell liquid was added to 27.58 ml diethanol-amine (DEA) at mole ratio 1:1 in a flat bottom flask equipped with Dean and Stack apparatus in the presence of 0.05 g of sulphamic acid as catalyst and paraffin oil as the solvent. The temperature of the reaction was gradually increased from 100ºC to 140ºC with continues stirring. The reaction mixture was heated continually until water of condensation was collected as by- product of the reaction.

Lastly, we reacted 100 ml of the anacardic acid with 38.2 ml triethanol-amine in a 250 ml flat bottom flask equipped with dean and stack apparatus. The mixtures were reacted at mole ratio 1:1 and were further esterified in a paraffin bath which served as the solvent in the presence 0.05 g of sulphamic acid as a catalyst. The reaction proceeded with gradual increase to temperature of 140ºC. The mixture was reflux between 40 mins and 1hour until the required water been the by-product of the reaction was obtained, indicating the end of the reaction and result.

2.4.1 Characterization of cashew nut shell liquid esters

The Characterization of the CNSL and products derived were carried out using Fourier Transform Infra-red (FTIR) Agilent Technologies Spectrophotometer (4000-650 cm range) to elucidate its structure and functional groups and result represented in (Table 2).

3. RESULTS AND DISCUSION

3.1 Results

The results from the FTIR characterization of the raw cashew nut shell liquid (CNSL) and its derivatives are shown in the Figs. 1 to 4 (Table 2) while some specific characteristics of the extract (CNSL) is presented in Table 1.

Table 1. Physio-chemical characteristic of extracted CNSL (100-140℃ and 1atm P)

Parameter	Experimental value	Literature values	Source of Literature values
pH	4.49	4-6	Dholakiya et al. [20] Eke et al. [8]
Temperature (℃)	27.6	-	-
Specific gravity	0.874	0.9-1.2	Dholakiya et al. [20] Eke et al. [8]
Iodine Value	71.8	110	Eke et al. [8]
Acid value (mgKOH/g)	1.64	-	-
Kinematic Viscosity (40℃)(cSt)	20.5	20.5	Eke et al. [8]
Kinematic Viscosity (100℃) (cSt)	5		Eke et al. [8]
Colour	Dark-Brown		Dholakiya et al. [20]

Table 2. (Figs. 1-4) FT-IR characterization of CNSL and Derivatives for modified and unmodified

Samples	Functional groups						
	Major peaks and functional groups present in each sample						
	N-H	O-H	C-H	C=O	C=C	C-N	C-O
CNSL	-	3011.7	2922.2 and 2855.1	1643.8	1602.8	-	1207.7
CNSL+EA	3160.8	3011.7	2922.2 and 2855.1	1580.4	1453.7	1323.2	1271.0
CNSL+ DEA	3220.4	3011.7	2922.2 and 2855.1	1580.4	1453.7	1323.2	1271.0
CNSL+TEA	3276.3	3011.7	2922.2 and 2855.1	1580.4	1453.7	1323.2	1274.7

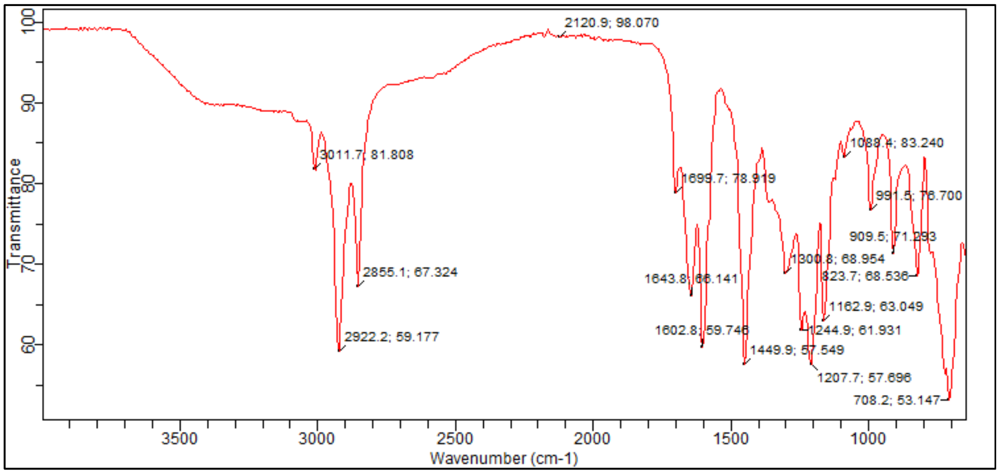

Fig. 1. FTIR spectrum of raw CNSL

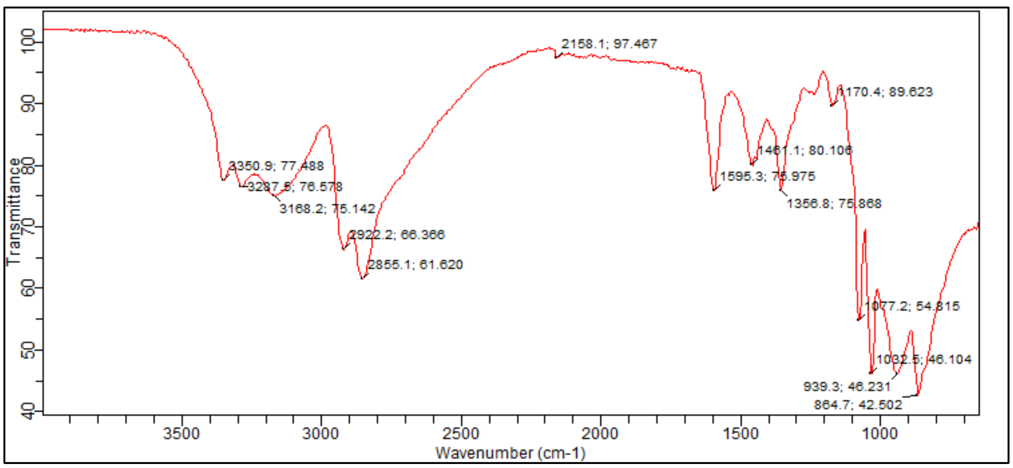

Fig. 2. FTIR spectrum of Ethanolamine (EA)

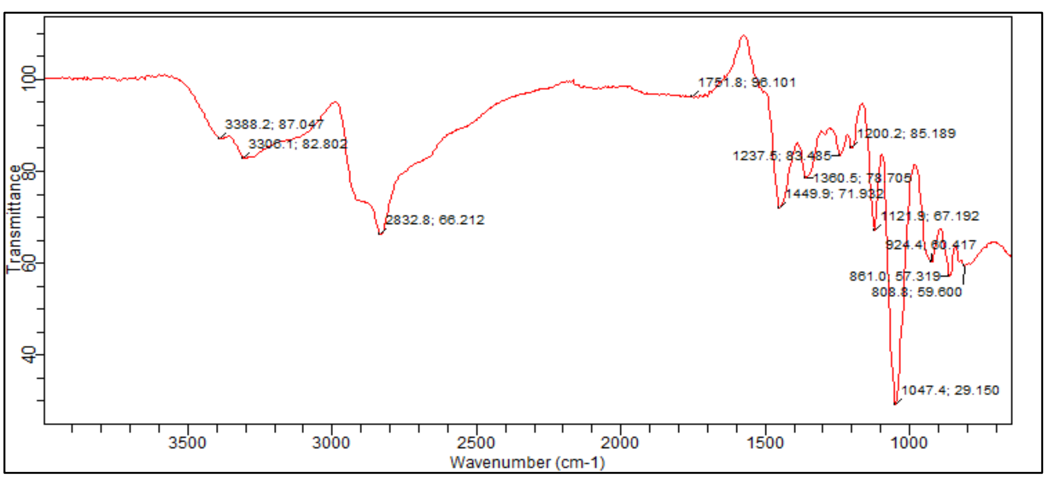

Fig. 3. FTIR spectrum of Diethanolamine (DEA)

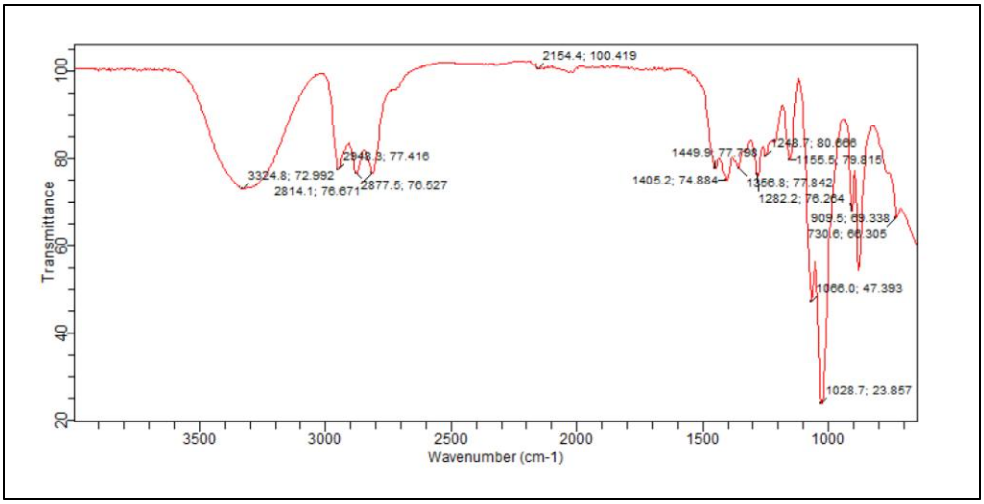

Fig. 4. FTIR spectrum of Triethanol-amine (TEA)

3.2 Discussion

CNSL was extracted using solvent extractor. The choice of acetone as solvent and the techniques was based on its ability to release 95-99% of the liquid from the solid shell [17]. The physico-chemical parameters of the CNSL was determined and presented in Table 1. From the result, CNSL has a specific gravity of 0.874 which is approximately equal to value of 0.984 of natural CNSL obtainable in literature [8]. The presence of unsaturated carbon chain in the extract was proven by the iodine value while, acid value indicates that carboxylic acid group is present the CNSL extract as seen in Table 1. The resulting pH of the CNSL is (4.49), which is an indication of the presence of anacardic acid needed for synthesis of other compounds. The value is within range of values 4.6 and 5 obtained in [8,20].The pH proved that CNSL extracted is natural owing to its method of extraction.

CNSL was further modified chemically in the presence of a suitable catalyst and products formed were subjected to FT-IR spectrum to determine functional groups present [21]. Table 2 (Figs.1-4) show the result of the FT-IR analysis on both the raw CNSL and the modified compounds. From the result, major peaks in CNSL include the phenolic O-H group stretching at 3011.7 cm^{-1}, C-H vibration at 2.922.2 and 2855.1 cm^{-1}, the C=O frequency at 1643.8 cm^{-1},and the C-O vibration at 1207.7cm^{-1}. In addition to these stretching frequencies, the modified CNSL have N-H stretching vibration at 3160.8, 3220.4, 3276.3 and 3250.2 respectively and C-N vibrations at 1323.2 cm^{-1} for all products. Spectral results also show similarity in band and frequencies obtained in [8,22]. The introduction of these groups testify that CNSL has been modified to form different compounds as shown in Table 2. (Noted; research on-going).

4. CONCLUSION

Natural CNSL was extracted and modified to other compounds. Both the physico-chemical properties sand FI-TR analysis of CNSL show an attribute or characteristic of anacardic acid-rich component. Modification of CNSL was confirmed by the presence of N-H and C-N functional groups not found originally in the raw CNSL. These products are obtained from agro-waste hence, are very cheap.

We therefore propose that these products, in combination with the right additives, and conditions could be potential multi-purpose additives in drilling operation. This will help to reduce the cost of importing synthetic oilfield additives, creating job opportunities and boosting the local content goal.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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