Cashew nutshell liquid and its derivatives in oil field applications: an update

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ABSTRACT
The oil and gas industry is often challenged with serious problems like high cost of oil field chemicals and environmental toxicity issues of commonly used synthetic oil field chemicals, and this has dragged the attention of researchers to the search for more cost effective and environmentally friendly oil field chemicals. Oil field chemicals formulated from various renewable sources (such as plant extracts) have been recognized as an alternative with great environmental advantages, cost advantage, and availability compared to their synthetic counterparts. Cashew nut shell liquid (CNSL), a byproduct of the cashew industry, stands out as a unique renewable starting material amongst others due to its peculiar structural feature, low cost, and availability. It consists of naturally occurring substituted phenolic compounds that can participate in diverse reactions for the manufacture of numerous useful products. A large number of chemicals and products have been developed starting from CNSL by taking advantage of the reactive sites namely phenolic hydroxyl, aromatic ring, the acid functionality, and unsaturation(s) in the C15 alkyl side chain. This update gives highlights on the composition, extraction, isolation, and reactivity of CNSL. It also focuses on the oil field application of CNSL and its derivatives.

1. Introduction
The cashew tree (Anacardium occidentale L.) (Figure 1(a)) is a self-renewing nut-bearing tropical plant that is engendered to Brazil (1). It is a multipurpose tree crop with vast economic value to third world countries such as Ghana, India, Mozambique, Nigeria, Philippines, Sri Lanka, Tanzania, Benin Republic, Brazil, Cote d’Ivore, Guinea Bissau, and Vietnam. Structurally, the arrangement of cashew tree makes it a paramount tree crop for recovering of land area to facilitate fertility, through its soil erosion control ability (1). Cashew tree is economically cultivated for its apple (Figure 1(b)), nut, and wood; from which other products are derived as shown in Table 1 (2, 3). The most economically valuable part of the cashew tree is the nut; it generates foreign exchange revenues for producer countries. In Nigeria, cashew nuts export has been estimated to be approximately 7–8% of the non-oil export revenue with a postulated export value ranging from 25 to 35 million US Dollar per annum (4). Cashew farming and its nut processing
activity provide job and livelihood for women and small-scale farmers in Nigeria (5, 6).

CNSL (Figure 1(c)) is a dark brown viscose liquid containing a mixture of phenolic lipids, that is obtained from the spongy mesocarp of cashew nutshell (5). This cashew nutshell (Figure 1(d)) is of low commercial value, but with relatively high technological significance due to its phenolic constitution. CNSL, with its cost-benefit and renewable nature, can be a replacement for phenol in many industrial applications, which is an excellent case of management of a synthetically derived substance and the utilization of a cheap agricultural byproduct (7). It is usually used in its technical form in various industrial applications such as brake linings, surface coatings, paints, varnishes, lacquers, adhesives, or laminates (8). Cardanol and cardol and their derivatives have been intensively worked on and used as polyethoxylate surfactants (9, 10), ammonium salt surfactants (11), carbonate surfactant (12), sulfonate surfactant (13, 14), phenalkamine curing agent (15), plasticizers (16–18), antioxidant (19, 20) and anticancer agent (21). This update highlights the foundational aspects of CNSL chemistry such as its extraction, isolation, composition, and its reactivity. Furthermore, this update focuses on oil field application of CNSL and its derivatives; with emphasis on using CNSL as a starting material for the production of countless products such as surfactants, resins, polymers, antioxidant, pour point depressant; and as a precursor for a range of value-added additives for the oil field chemical operations.

### 1.1. Composition of CNSL

The likely first investigations on the composition of CNSL ever reported was by Staedeler, 1847 (7). Since then, many researchers have investigated and reported various claims on the composition of CNSL. Naturally, CNSL contains four major components, which are anacardic acid, cardanol, cardol, and 2-methyl cardol (Figure 2) (22). Depending on the method of extraction, these constituents vary in concentration. Commercial-grade CNSL may contain little or zero percentage of anacardic acid due to decarboxylation of the anacardic acid constituent during the roasting process, which converts anacardic acid to cardanol or 2-pentadeca-diethyl phenol; this roasting process may also result in polymerization, which accounts for 20–25% of polymeric substances in the oil (7). These components of CNSL are themselves mixtures of four constituents differing in varying degrees of unsaturation in C15 alkyl side-chain unsaturation levels, namely saturated, monoene, diene, and triene (Figure 2) (23, 24). Intensive investigation on the individual composition of CNSL reports the components of anacardic acid as 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.

### Table 1. Products derived from cashew – apple, nut, and wood.

| S/N | Cashew tree part | Derivable products | Reference |
|-----|-----------------|--------------------|-----------|
| 1   | Apple           | Juice, jelly, syrup, fenny, jam (using osmotic dehydration) and wine | (2, 3) |
| 2   | Nut             | Kernel snack, kermel oil and CNSL | (2) |
| 3   | Wood            | Furnitures, logs/lumbers for constructions, fishing boats fuel | (1, 2) |

**Figure 1.** (a) Cashew tree (b) cashew fruit (c) CNSL and (d) cashew nutshell.

**Figure 2.** Chemical composition of CNSL: (a) anacardic acid, (b) cardanol, (c) cardol and (d) 2-methyl cardol (23, 24).
cardanol as 3-pentadecylphenol, 3-(8-pentadecenyl)phenol, 3-(8,11-pentadecadienyl)phenol, and 3-(8,11,14-pentadecatrienyl)phenol; cardol as 5-pentadecyl resorcinol, 5-(8-pentadecyl)resorcinol, 5-(8,11-pentadecadienyl)resorcinol, and 5-(8,11,14-pentadecatrienyl)resorcinol (26, 27). The composition of 2-methylcardol was established as 2-methyl-5-pentadecyl resorcinol, 2-methyl-5-(8-pentadecenyl)resorcinol, 2-methyl-5-(8,11-pentadecadienyl)resorcinol, and 2-methyl-5-(8,11,14-pentadecatrienyl)resorcinol (28, 29).

1.2. Extraction method

Extraction processes can be carried out either in the hot or cold, those that involve heating (technical) and those that are done at room temperature (cold). The oil so obtained from extraction in the cold is called natural CNSL, while that obtained by techniques that involve heat is known as technical CNSL (30). Several methods have been unveiled in the literatures for the extraction of CNSL, and the extraction efficacy differs with the method employed. It has been estimated that the raw cashew nut contains approximately 20% of the nutshell oil. Basically, three main extraction methods have been established for the extraction of CNSL from cashew nuts namely thermal, mechanical, and solvent extraction. Nevertheless, Other methods such as pyrolysis (31–33), use of supercritical carbon dioxide (34, 35), supercritical water (36), ultrasonication (37, 38), etc. have also been reported.

1.2.1. Thermal extraction

This method involves roasting and hot oil bath.

(a) Roasting: Traditional method of removing CNSL, which basically is the roasting of the cashew nutshell in drums or baths (Figure 3) at a temperature of 180–185°C (39).

(b) Hot oil bath: This is the most frequently used commercial extraction method for CNSL in recent times. The technique involves either the heating of the raw shell with steam at a temperature of 200–250°C to release the oil, or heating of the raw nut in a bath (Figure 3) of the oil itself at high temperature to the outer part of the shell to burst open and extrude the oil. The first method yields oil of approximately 7–12% by weight; whereas, the second gives an approximate 6–12% yield (38).

(c) Solar Cooker: Cashew nutshell oil was reported to be extracted using a 1.4 kW capacity concentrating solar cooker (Figure 4) of 1.4 m in diameter. The focal point diameter of the cooker is 30 m and was used to collect the reflected heat from a reflector to achieve a temperature of 225–300°C (38, 40–42).

1.2.2. Mechanical extraction

This involves the use of a screw press. Raw cashew nutshell-shells are put in the hydraulic press on screw pressing, and then a high pressure is exerted on it to force out the oil from the shells. This method is direct and quick, among other methods of extraction (38).

1.2.3. Solvent extraction

This method gives a high yield of the oil compared to other methods of extraction. This method involves the use of a solvent and the oil is extracted from the shell either by Soxhlet technique (Figure 5) or by maceration.

1.3. Isolation

The components of CNSL can be isolated via several techniques such as HPLC (33–42), GC-MS (29), solvent
1.4. Reactivity of CNSL

Cashew nutshell, an agricultural byproduct has little economic importance but CNSL, which is of high technical value, is a rich and economic spring of naturally occurring phenolic compounds with long-C15 alkyl chain substituted at the meta position, and can be valued as a multipurpose and most treasured raw material for polymer production (45). It is difficult to synthesize via regular chemical processes due to the long C15 alkyl side chain substituted at the meta position with respect to the phenolic hydroxy group. CNSL possesses diverse functionality for a different sequence of chemical reactions; hydroxy group for esterification, epoxidation, ethoxylation, alkylation, etc., carboxylic acid group for decarboxylation, esterification, etc., meta C15 alkyl side chain (which directs all further substitution to ortho and/or para positions) for metathesis reaction, phenylation, epoxidation, hydroxysilylation, hydrogenation, etc. and the aromatic ring, a site for hydrogenation, nitration, sulfonation, halogenation, etc.

Cardanol, the major fraction of commercial cashew nutshell liquid (technical CNSL), differs from phenol only in the meta C15 alkyl substituent, but undergoes all regular reactions of phenols and even more (24). CNSL may be polymerized via the following sequence; additional polymerization at the C15 side chain unsaturation in the presence of cationic initiators such as sulfuric acid or diethyl sulfate (46), or condensation polymerization at aromatic ring using any aldehydic compounds such as the formaldehyde (47). It is also possible for CNSL to be polymerized after chemical modification to bring in peculiar characteristics (48).

CNSL displays great susceptibility to structural modification, to effect desirable change or specific properties of high value. This structural change can be achieved via chemical modification on the hydroxyl group, aromatic ring, carboxylic group, and on the side chain (Figure 6). Natural cashew nutshell oil contains anacardic acids as a major fraction and this is usually transformed to cardanol during extraction or refining processes that involve heating, also during distillation of the oil at high temperature, and deliberate heating of the oil at a very high temperature to decarboxylate the acid functional group (Figure 6(a)) (49). Direct nitration of CNSL gives the nitro-derivatives, which are useful precursors for azo dye synthesis (51). Nitration of cardanol was reported to be achieved by its reaction with sodium nitrate in the presence of sulfuric acid at low temperatures (Figure 6(b)) (51). The sulfonation of cardanol (the major fraction of CNSL from heat extraction) has been reported to yield an alkyl aryl sulfonic acid or their metal salts (Figure 6(c)) (7, 13).

Reactions with halogens are simple and easy to achieve. 15% (w/w) chlorination of CNSL is made possible by passing chlorine gas through a solution of CNSL and kerosene (52). Esterification of CNSL can occur either at the carboxylic acid end or at the hydroxyl end; esterification at the hydroxyl may be achieved by reaction with carboxylic acid or reaction with acid halides. Cardanyl esters were reported to have been obtained by reaction of acid chlorides with cardanol in the presence of alkali or any strong base (53). Esterification of the carboxylic end of CNSL was reported to be
achieved by reaction with alcohol amines in the presence of sulfamic acid (Figure 6(d)) (23).

Etherification of CNSL has also been reported via its reactions with alkyl halides (Figure 6(e)) (21, 24, 54). Etherification of cardanol has also been reported via the hydrolysis of epoxy product (55). Epoxidation of CNSL is carried out by reaction with epichlorohydrin in the presence of a base catalyst. The reaction of cardanol with epichlorohydrin in the presence of caustic soda as a catalyst has been reported to give a great yield of epoxy cardanol (Figure 6(f)) (55–57). Hydrogenation of unsaturation is often performed directly with hydrogen in the presence of metal catalysts such as copper, nickel, palladium, or platinum (Figure 6(g)) (50–58). CNSL has been hydrogenated using Pd/C catalyst and was applied for the synthesis of an azo dye (58).

1.5. Conventional uses of CNSL

CNSL and its structurally modified derivatives have numerous peculiarities which make them useful for many applications (22). As a naturally occurring substituted phenolic compound mixture, which can participate in varieties of reactions, naturally occurring CNSL offers advantages over synthetics phenolic compounds. Its outstanding applications come from the phenolic structure of its constituents, with treasured functionality for transformation into great value specialty chemicals (59). The industrial applications of CNSL-based products are numerous; and include fungicide, pesticide, insecticide, brake linings, paints and primers, foundry chemicals, lacquers, cements, specialty coatings, resin, surfactants, etc. (60). The use of cashew nutshell oil in the production of bacteriostatic antibiotics is an advancing area of research, its influence on the growth of plant, acid level, wood preservation, and pressure treatment activity have been and is still being explored. From studies thus far, much of the biological effect of cashew nutshell oil is owed to its anacardic acid component (31, 59–61), while its application in polymer and other areas of science is generally owed majorly to its cardanol substituent (24).

2. Oil field applications

2.1. CNSL as corrosion inhibitors

CNSL has found great application in an electrochemical cell process, as it mitigates the extent of the electrochemical corrosion processes that take place on a carbon
steel surface. This inhibition capacity is outstanding for both static and dynamic conditions (60–62), this inhibition capacity (or antioxidative effect) of CNSL can be attributed to its electron-donating nature (owing to the free lone pairs of electrons on the oxygen atoms and electron-rich aromatic ring) and steric effect of the substituents (heavy substitutes at the ortho, para, and meta positions of the aromatic ring). The electron-donating ability often increases the electron density at the phenolic oxygen of the cashew nut oil, thereby promoting the trapping of the radicals that initiates oxidation reaction (33, 61). Cashew nutshell oil is a mixture of bulkily substituted phenols with long C15 alkyl substitution at the meta position. The unsaturation at the long side-chain substituents is a paramount factor that enhances the great antioxidant activity of CNSL and the formation of thermally stable films that increases in the presence of thiophosphate ester additives (33, 62). The corrosion inhibiting properties of CNSL on carbon steel in 3% aqueous NaCl solution at a pH of 6.0 saturated with carbon dioxide at 30°C under steric conditions using ac-impedance and potentiodynamic polarization technique was investigated, and reported that CNSL reduced the rate of corrosion on the carbon steel by over 92% for 300 ppm dosage applied (63). Cardanol-based porphyrins improve the photo-catalytic activity of bare TiO2. The porphyrins are brown-red sticky solids that are soluble in CHCl3 or CH2Cl2. This substituted cardanol-based porphyrin and their metallic complexes have found great application in the photodegradation of toxic and bio-refractory 4-nitro phenol in water, which is dangerous to the ecosystem and human health (64).

2.2. CNSL as fuel

Cashew nutshell oil has also found great vitality in fuel blends and mixtures, and also in the production of diesel oil (65, 66). The cracking of CNSL with a molecular sieve at 500°C for 2 h generates brown colored liquid that can be used as diesel fuel (66). The viscosity of CNSL is 30–35 times higher than diesel, leading to a difference in properties and applications of different blends. In addition, any adjustment in the property of the oil and/or in its application procedures such as injection pressure, injection timing, and preheating; will also affect the performance of the engine (67). It was reported that preheating of CNSL25 blends at 200 kg/cm² injection pressure and 28°C injection timing gives encouraging results suitable for commercial purposes (67). CNSL as a bio-additive in engines improves the durability of the equipment.

Comparison of some properties of diesel, biofuel, and ethanol against CNSL was studied (60). It was reported that CNSL shows a higher density than diesel and can be reduced by degumming and transesterification; cetane for CNSL is very poor due to the presence of aromatic compounds. The normal C:H:O ratio of vegetable oils is 78:12:10, while that of CNSL is 80:12:8, justifying the higher calorific value of CNSL (40 MJ/kg) and that of diesel is 42 MJ/kg (33, 60). CNSL presents a flash point of 164°C, which is higher than that of diesel; it also showed higher starting ignition temperatures and compression compared to diesel (67).

Deviating from the conventional practice of using unprocessed CNSL directly as a substitute for diesel, an investigation on the use of specially processed CNSL as a substitute for diesel was carried out, and in the study unlike the regular methods of extractions, CNSL was extracted from the nutshell by steam treatment followed by mechanical crushing (Figure 7) (68). This method was found to give CNSL with low viscosity (43.1×10⁻⁶ m² s⁻¹) compared to the conventional methods and at a yield of 20%. This low viscosity makes it the best fit for direct application on a diesel engine. Also moving away again from the normal trans-esterification processing method that help in promoting its fuel viscosity (10.3×10⁻⁶ m² s⁻¹) only (69), a catalytic cracking method using zeolite catalyst (owing to its better material properties such as high porosity, increased ionic conductivity, and better heterogeneity), was employed on the extracted CNSL to yield 90% catalytically cracked CNSL (CC-CNSL) that showed a better fuel viscosity (4.1×10⁻⁶ m² s⁻¹) and improves calorific value (42,500 kJ/kg). Furthermore, on investigation of the composition and properties of the CC-CNSL using GC-MS, it was noted that the major component of CC-CNSL was 2-methylphenol; an aromatic oxygenate that is known to promote combustion process and fuel oxidation. Contrasting to the conventional trans-esterification product that yields majorly methyl ester of fatty acids with possesses innate oxygen and several unsaturation, thereby increasing its viscosity and lowering its calorific value (34,300 kJ/kg) (70,71).

A CC-CNSL20 (20% CC-CNSL and 80% diesel) fuel blend was tested at different fuel injection pressure such as 200, 235, 270 and 300 bar to ascertain its use in a single-cylinder diesel engine. Analysis of the engine performance characteristics based on the Brake specific fuel consumption (BSFC), Brake thermal efficiency (BTE), and Exhaust gas temperature (EGT) parameters showed that CC-CNSL20 exhibited lower BSFC values relative to those of diesel (control), which can be attributed to the excellent combustion process owing to the subjoining of oxygen in CC-CSNL, and
the BSFC values decrease with increasing injection pressure due to increase in fuel atomization process. Also observed was an excellent flow property conducive for effective fuel atomization and air/fuel mixing processes that resulted in a great combustion process and decreased fuel consumption. As a norm, biodiesels used in diesel engines are expected to give high BSFC values to affect great engine performance due to their low energy density. But deviating from this norm, CC-CNSL with a calorific value similar to that of diesel (42,700 kJ/kg) and a unique combustion process gave better performance irrespective of its low BSFC value, which was less than that of diesel. This observation, though striking but could be backed up with previous reports where biodiesel from pine oil showed similar behaviour (72, 73). On BTE, in regards to engine power output at various fuel injection pressures. It was detected that CC-CNSL20 showed increasing in values that slightly higher than those of diesel (control). From conventional knowledge, on optimizing fuel injection pressure, it is established that an increase in injection pressure results in fuel droplets been finely atomized, and consequently improves the fuel evaporation rate and its mixing capacity with air, resulting in a better combustion process (74, 75). In acquiescence with this, combustion is alleged to have been enhanced for CC-CNSL20, as the fuel injection pressure is increased and as such, the performance of the engine is improved. In addition, CC-CNSL possessing inherent oxygen is a crucial factor which besides improved fuel properties of CC-CNSL, also uplift engine performance (68). Finally, a decrease in EGT values with the increasing fuel injection pressure was observed, signifying the enhancement in the combustion process and zero possibility of late burning in a tail pipe (68). Also, from the engine experimental study, CC-CNSL20 was found to demonstrate better composite emissions of CO (carbon monoxide), HC (hydrocarbon), NOx (oxides of nitrogen), and smoke, computed based on ISO 8178 D2 standard test cycle, were found to be better than diesel and incompliance with the legislative norms for genset (68).

2.3. CNSL as flow property improver in drilling mud

Drilling is simply the excavation of the earth in order to obtain natural resources (such as hydrocarbons). The cost of drilling was estimated between $34,000 and $42,000 million (US Dollar) for normal wells (76, 77). This may increase to more than double the cost in situations with peculiarities like deeper and inclined wells (76). Drilling to a desired depth successfully requires the formulation of a suitable drilling mud with the right additives to achieve well stability. Rotary drilling operates by circulating mud down the geological formation via a drilling bit. Drilling mud is a complex fluid and has numerous definitions designated to it by various researchers (78–80). It comprises of water/solids and oil or solids with varying amounts of other chemicals called additives; and formulated drilling mud with the right additives maintains wellbore stability (81). There are three main types of mud: water-based
mud, oil-based, and synthetic-based mud (82); and the selection of the mud type for the operation depends on the well condition, safety of personnel, cost, logistics, and environment (83). Usually, muds are evaluated based on their capacity to effectively administer these functions, which depends strongly on its flow properties to achieve a stable well (78). For this reason, additives are incorporated into mud formulation to give it the peculiar flow properties desired for operation.

The main objective of drilling operation is to drill to a desired depth at possible minimal cost with a mud system of zero or less negative environmental impact, especially in this era of advanced novel technologies and techniques such as deviated well, high-pressure-high-temperature (HPHT), and extended reach wells. This has triggered up a new chapter in the choice and nature of additives used in drilling mud formulation. Some additives exist in the literature, but contribute to the high cost of drilling fluids because of transportation and import charges. The application of chemical-based synthesized additives in formulating mud systems for such operations has shown great successes, but with some negative environmental impacts. They are mostly of petroleum-based sources and other dangerous materials, which may be toxic to animal or plant when these fluids are disposed to the environment (84). During formation, flow and rheological property of the mud is affected by temperature changes, thereby distorting their active component and ability to perform effectively. These additives are low carbon chain structured phenolic compounds with low molecular weight, hence they degrade easily at any alteration of temperature. The best way to curb this is by the use of biodegradable materials to synthesize cheap and eco-friendly additives with high thermal stability. Sources such as edible and non-edible vegetable oils from plants and agro-wastes containing natural phenolic liquids have been explored (84). The study on the investigation of the effects of the composition of CNSL esters [CNSL-diethanolamine (1:1), CNSL-diethanolamine (2:1), CNSL-triethanolamine (1:1), CNSL-triethanolamine (2:1), and CNSL-triethanolamine (3:1)] on the flow properties of drilling mud, showed that the esters were compatible with other mud additives utilized in the formulation. The plastic viscosity (PV) values obtained for all samples ranges from 14 to 17 cP with sample E (standard mud and 2 mol of CNSL modified with 1 mol of triethanolamine) having the greatest value with reference to based mud. Yield point (YP) for all samples were between 15 and 24 lb/100ft², with the sample F (standard mud and 1 mol CNSL modified with 1 mol of triethanolamine) having the highest value 24 lb/100ft², while sample D (standard mud and 3 mol of CNSL modified with 1 mol of triethanolamine) and G (standard mud and lube 156) gave values of 16 and 15 lb/100ft² respectively, which were lower compared to the standard mud value. The gel strength values for all mud samples were between 3 and 4 lb/100ft² for 10 s and 10 min, respectively, except to sample D (standard mud and 3 mol of CNSL modified with 1 mol of triethanolamine) with 1 lb/100ft² for 210 s. However, PV, YP, and Gel strength values for all samples were within API acceptable range except sample D with a lower value of gel strength at 10 s (84). These values prove that the formulation can actually sustain the cuttings with minimal pump pressure required for further initiation of flow after circulation stops, which therefore implies that these esters can serve as potential multi-purpose additives in water-based mud formulations, reducing cost and negative environmental impacts of using chemical-based synthesized oil field additives (84).

### 2.4. CNSL as surfactant

Surfactants are amphiphilic molecules constituted of a hydrophobic tail and a hydrophilic head. They are basically used as detergents, wetting and/or foaming agents, emulsifiers or dispersants, and demulsifiers due to their ability to lower the surface tension of a liquid, between two liquids, or between a liquid and a solid. CNSL has been examined and reported as a good precursor for different classes of surfactants such as cationic (85), nonionic (8, 9), and anionic compounds (11, 86). Sulfonation of cardanol has been reported to be readily accomplished by its reaction with excessive sulfuric acid in halogenated solvents at ambient temperature (87, 88). It has also been reported that unsaturated CNSL and saturated CNSL upon reaction with ethylene sulfate give sulfo-derivatives with magnificent surfactant properties (89). The use of ethylene sulfate with the phenoxide is an advancement taking away both the reaction with sulfuric acid and the need for an initial hydroxymethylation step (22, 89). Nowadays, several amphiphilic moieties based on CNSL have been investigated and found to be potentially useful for many industrial applications especially in the oil field (23, 56). The synthesis of sodium cardanol sulfonate surfactant from cardanol, yielded surfactant with properties of cardanol sulfonate when compared with those of dodecylbenzene sulfonate, were found to be similar; minimum surface tension for cardanol sulfonate (15% w/v) was obtained as 28 mN/m and that of dodecylbenzene sulfonate (15% w/v) was 32.25 mN/m, their critical micelle concentrations (CMC) was obtained as 0.372 and 0.435 mol/L for cardanol sulfonate and dodecylbenzene sulfonate respectively (23). Therefore, it can be used as a...
precursor for commercial detergent production. This surfactant can probably be formulated on an industrial scale because the production process is not complex, as there is no difficult step of alkylation of benzene before sulfonation, as in the case of conventional alkylbenzene sulfonate. Also, the production of cardanol sulfonate on an industrial scale is potentially of low cost in comparison with the production of common detergents. The formulation of various surfactant from raw CNSL by the modification with chemicals such as ethanolamine, diethanolamine, and triethanolamine was reported, and that these surfactants were applied as demulsifiers for water-in-crude oil emulsion, results obtained showed good demulsification efficiency for all formulated demulsifier, but when compared to those from commercial demulsifier (PT-4633) they are slightly low but owing to the cheapness, availability and eco-friendly nature of CNSL its use as a substitute to the commercial demulsifier should be encouraged (23). Some surfactants applied as demulsifier for water-in-crude oil emulsion was formulated from cardanol using epichlorohydrin, β,β-dichlorodiethyl ether, ethanolamine, diethanolamine, and tetraethylene glycol and the result obtained shows that they can be used as a substitute to conventional demulsifiers (56). Results from the above reports (23, 56) showed that the use of CNSL for the production of surfactant that can serve as demulsifier is a promising substitute for the conventional ones; since CNSL is cheap, readily available, eco-friendly, and naturally sourced.

2.5. CNSL as flow improver for waxy crude oil

The application of chemical additives for the mitigation of wax formation and to improve flow properties of waxy crude oil is progressively adopted by oil sector operation. These additives such as pour point depressants, wax crystal modifiers, or wax inhibitors are mainly synthetic polymeric compounds, with poly acrylates and methacrylates, poly(alkylmaleate-co-α-olefin), poly(styrene-co-alkylmaleamide), and poly(ethylene-co-vinyl acetate) constituting the chemistry (80–94). The sensitive peculiarity of pour point depressant formulation to oil wells and the magnificent expense incurred by industrial operators on chemical injections have persistently increased the curiosity for the development of a better and cheaper chemical solution to the problem of wax formation (90). The pour point and low-temperature flow properties of waxy crude oil are dependent not only on the wax content but on other components particularly asphaltenes, such that crude oil with high saturates content and wax content may not necessarily exhibit high pour point and vice versa. The form and structure of wax in oils give substantial details for their wide difference in pour points irrespective of their similarity in wax carbon number distribution and the crude oil with higher wax content has a significantly lower pour point (89, 90).

Natural CNSL can reduce the pour point of waxy crude oil especially in the presence of asphaltenes. It is postulated that the pour point depression effect of CNSL is likely through its effects on asphaltene aggregation form in the oil. Natural CNSL is readily soluble in crude oil, acts as a Newtonian fluid and can impact reduction in viscosity of crude oil flowing at temperatures both below and above the wax appearing temperature, even for oils that are non-responsive to pour point depression (90). The limited effect of CNSL on waxy crude oil pour point is probably related to the relatively small size of anacardic acid compared to wax crystals, which makes it unable to efficiently perturb the wax crystal structure. Also, the absence of ester and amide groups which are essential functional groups in pour point depressant chemistry may be another deficiency. The effect of natural CNSL on the pour point and rheology of crude oil was investigated by researcher reported that the pour point of the test crude oil with 4000 ppm dose of CNSL was depressed by 6°C, the CNSL reduced the viscosity of the two waxy crude oils (from the different oil wells sampled) by 60% and 35% respectively during Couette flow at a temperature of 10°C. On the rheological characteristic of the crude oil, a tremendous improvement in the low-temperature flow properties of the crude oils was noticed. The controlled crude oils exhibited a yield pseudoplastic behavior, whereas the shear rate-shear stress relationship of the CNSL dosed oils was largely linear. The dynamic yield stress of the oils dosed with CNSL reduced by 50% and 80.8%, respectively. An investigation on the use of polycondensed CNSL with formaldehyde as a pour point depressant for paraffinic crude oils showed excellent performance with CNSL formaldehyde novalac resin, decreasing the pour point of the test crude oil by as much as 15°C, and the synthesized polymer showed an optimum molecular weight value with the ability for depression of pour point of crude oil is expected at maximum. Thus, it is believed that with proper molecular weight control, CNSL could be polymerized into a good pour point depressant for the oil field (94).

2.6. CNSL as anti-corrosion paint

The peculiarities of CNSL such as chemical stability, solubility of its resin in various solvents, profound hydrophobicity, chemical resistivity, film-forming nature, and a high degree of unsaturation make its polymers
paramount precursor for surface coating applications. Cured CNSL-formaldehyde films soften at high temperature and retain an elastic nature. Formulations of different classes of paints based on CNSL were first described by Ramanujam (7, 95). Condensates of CNSL, when reacted with alkyl ortho ester, give films of good heat resistance and great electrical characteristics. Phenolic resin coupled with cardanol (5%) has found great application in the making of coatings for cans used in food packaging. Lac–CNSL mixtures have also found application in the formulation of surface coatings with good resistance to weather change and as metal primers with anti-corrosive and water and solvent resistivity (96). Water-based CNSL–HCHO paint has been reportedly formulated by the treatment of CNSL with HCHO and cross-linking with maleic anhydride and neutralization with ammonia (97). Formulation of paints as water-based stable emulsions of oil-in-water type is possible using CNSL–HCHO resins (7). Water-based coatings with a high level of hot water and chemical resistivity have been reportedly prepared from the reaction CNSL-formaldehyde condensate with an haloacetic acid (bromo- or chloroacetic acid).

Formulations of anti-corrosive paint for ship bottoms and metal pipelines from CNSL have been extensively investigated (98, 99). Different colored coatings can be formulated from CNSL oxidized with HNO₃. HNO₃ oxidized CNSL was reported to give coatings that air-dried relatively fast. It was also reported that they were suitable for the formulation of paints, varnishes, electrical insulators, impregnating paper, woven fabrics, etc. (99). Excellent coatings have been reported to be those from CNSL cured at 150°C for 10 mins (7). Primers based on polymeric CNSL dries within 2 h. It was also reported that the introduction of lead and cobalt naphthenates or barium and potassium chromates or lead and silico-chromates enhances the corrosion resistance of CNSL-based coatings (100). Modified CNSL-formaldehyde reaction products with waste walnut kernel oil were reported to be excellent stoving enamels (7). Anti-corrosion paint useful for cleaning metal surfaces has been formulated from CNSL–salicylic acid formaldehyde resin (7). Black slate enamels have also been formulated from CNSL or CNSL distillate residue using silica and emery powder as pigments. Baking enamels were formed from the condensation of CNSL and formaldehyde in the presence of linseed oil or turpentine. The addition of unsaturated oils to CNSL improves its flexibility and drying properties (7, 101). CNSL distillation residue, when heated with castor oil, gave good surface coatings. Coating compositions have also been produced from CNSL–aldehyde products in the presence of rosin, furfural, drying oils, fatty acids, or their combinations. CNSL–aldehyde anti-fouling paints have been formulated from their reaction with copper aceto-arsenite or linseed oil rosin condensate (102). The reaction of the distillation residue of CNSL with phosphoric acid gave baking primers with improved adhesion and corrosion protection ability (103). Epoxy resins based on CNSL have found excellent application in the formulation of protective coating materials, auto-primers, linings for cans, drums, and pipes, potting and encapsulation of electrical and electronic components, and in electrical laminates. Being soluble in common solvents such as naphtha and benzene, the coatings are air-drying and do not require any expensive hardener, as in the case of conventional epoxy resins (7, 104).

2.7. CNSL as lubricant

CNSL possesses peculiar properties that validate its use as engine oils, but naturally occurring CNSL appeals weak without the addition of friction modifiers for its usage as a lubricant (105, 106). Despite the immense advantages ascribed to the use of vegetable oils as a lubricant, the fact that they are prone to oxidation and performance deterioration at reduced temperatures poses a likely setback. It is therefore expedient to use friction modifiers and other additives when using vegetable oil as a lubricant (106). Owing to this reason and to the great availability, low cost, and biodegradability of CNSL, recent researches are tailored towards the incorporation of friction modifiers and additives to CNSL for the formulation of lubricants. The tribological properties of CNSL incorporated with nano-graphene oxide (as friction modifier) as a biodegradable lubricant, was studied in comparison with a commercial mineral oil (CMO) and synthetic cutting fluid (106). It was reported that the CNSL showed similar physicochemical properties to that of the synthetic cutting fluid and CMO, CNSL incorporated with 0.5 wt% of nano-graphene oxide was observed to show a much lower coefficient of friction compared to the synthetic cutting fluid and CMO. Hence, resulting in less energy consumption due to reduced direct asperities contact of the mating surfaces. The roughness of the surfaces tested with CNSL incorporated with 0.5 wt% nano-graphene oxide was revealed to be similar to those corresponding to the synthetic cutting fluid and CMO (106).

Also, a study of the tribology properties of neat castor oil (NCO) incorporated with CNSL in comparison with a CMO reported that NCO + CNSL gave a 45.8% performance than the CMO and when incorporated with 0.5%
nano-graphene oxide as a friction modifier, it gave a better performance of 61.7% than the CMO (105).

3. Conclusion

CNSL an agricultural waste product of the cashew industry is a cheap and abundantly available versatile industrial raw material of great potential in the replacement of some phenolic products based on fossil resources. The presence of phenolic hydroxyl group, the carboxylic acid group, and olefinic linkages in the C15 alkyl chain, combined with the aromatic ring, makes CNSL an interesting starting material for the synthesis of various value-added products by taking advantage of the reactivity of each of these functionalities. Considerable attention has been devoted to transformations of the phenolic hydroxyl group, carboxylic group, and the aromatic ring in the CNSL for the production of chemical building blocks for oil field operations. This update has highlighted various chemicals obtainable from CNSL (directly and/or indirectly) as a very important, reliable source of raw material for oil field operations. It is a good promising supplement to crude oil, which is currently facing depletion globally. Varied CNSL compositions with different methods of extraction are vantage opportunities with potential for multiple applications.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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