Cashew Nut Shell Oil (CNSL) as a reliable replacement of petroleum products: A Critical Review

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Abstract – *As a result of the growing world population, the consumption of petrochemical and petroleum resources is also abruptly increasing. Such an abrupt increase results in increased global warming and also causes fast depletion of the petroleum reserves. Therefore, an immediate, eco-friendly and cost-effective alternative is required in order to meet the necessary demands and also reduce the harmful environmental impacts. Cashew nut shell is a byproduct that we throw off as an agro-industrial waste after obtaining the edible cashew in a cashew processing industry. But due to the phenolic lipid content, Cashew Nut shell liquid (CNSL) can be a potential replacement of the fossil fuel.*

Since the shell is generally thrown off as a waste, CNSL will be comparatively much cheaper. Cardanol and other CNSL derivatives find their applications in a varied range of disciplines including production of biodiesel, larvicides, vulcanized rubber, brake linings, foundry chemicals, surface linings, surfactants and the list is yet to be continued and discovered. This critical review has been conducted to throw some light on the chemical composition, extraction procedure and various applications of Cashew Nut Shell Liquid (CNSL).

Key Words: Cashew Nut Shell Liquid (CNSL), Cooking oil, biofuel/biodiesel, green fuel, petrochemical feedstock, sustainable energy, CNSL as larvicide

1. INTRODUCTION

The cashew tree, whose scientific name is *Anacardium occidentale L.*, belongs to the Anacardiaceae family that also includes mangoes and pistachios. Cashew nut is generally the false fruit or the accessory fruit of the cashew tree which is used for making sweets and beverages and also used in a varied range of food products. But still cashew nut is the most economical product of the cashew tree. The pericarp which contains the cashew nut, is commonly known as the cashew nut shell. The cashew nut shell consists of a dark and abrasive liquid known as the cashew nut shell liquid (CNSL) which can be obtained during the industrial processing of the cashew nut. Cashew nut shell oil generally is a reliable element of the cashew fruits. This CNSL is generally composed of phenolic lipids which makes it a noteworthy replacement of petroleum products.

With the growing world population, the demand to supply ratio of the petrochemical resources is increasing by a large-scale day by day. This if continued, can exhaust our petrochemical feedstock and as a result affect the life of our future generation. In order to maintain the human living standards and keep up the industrial economy, scientists are in search of an alternative source of fuel. The cashew nut shell is generally thrown off as an industrial waste of the cashew nut processing industries. Scientists, through their research have recently found that Cashew nut shell liquid (CNSL), due to its content of phenolic lipids and other comparable chemicals, can be a substantial replacement of the petrochemical products and as a result it will help us to maintain our global petroleum reserves.

2. CHEMICAL COMPOSITION OF CASHEW NUT SHELL OIL

CNSL is a red, brown, abrasive and darkish oil with a strange odor. Cashew nut shell oil is the prime source of non-isoprenoid phenolic lipids and is mainly comprised of chemical compounds namely: (1) mono-unsaturated anacardic acid, (2) mono-unsaturated and saturated cardanol, (3) cardol (mono-unsaturated, saturated, di-unsaturated), (4) Stigmasterol, (5) β-sitosterol, (6) Octacosene, (7) Triacontene and some other unknown hydrocarbons, depending on the type of CNSL we obtain, whether it is Natural CNSL or Technical CNSL.

These phenolic derivatives may possess complicated organic structure along with a long alkyl sidechain which consists of 15 carbons. The hydrocarbon chain is located at the meta position with respect to the hydroxyl group in the organic structure. The hydrocarbon chain may be saturated with no double bonds or unsaturated with 1 to 3 double bonds at 8^{th}, 11^{th} or 14^{th} Carbon. Some basic structures of the components in CNSL have been shown below in Fig-1.

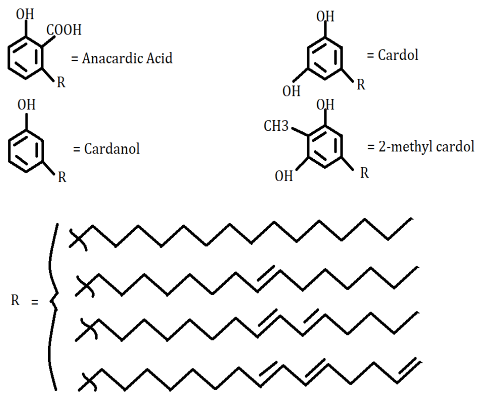

Fig-1: Basic structures of components in Cashew nut shell oil (CNSL)

EXTRACTION OF CASHEW NUT SHELL OIL

It has been studied and reported that raw Cashew nut shell consists about 20% of oil. Oil bath processes leave about 10% of the oil content as a by-product along with the used shell. By using expellers for oil extraction, we can utilize more of the oil content. Based on the process of extraction Cashew nut shell oil (CNSL) can be classified into Natural or actual (solvent extracted) CNSL and Technical CNSL.

Technical CNSL can be obtained by hot methods like hot oil roasting, open pan roasting and drum roasting whereas cold methods like cold extrusion, solvent extraction and pressing are used to obtain the Natural CNSL.

Natural CNSL can generally be prepared by using different solvent extraction techniques that commonly include Soxhlet, supercritical carbon dioxide (SC-CO_2), or subcritical water (SCW) in order to obtain the components of the cashew nut shell oil under mild conditions or at room temperature, without any chemical change taking place. In this way, natural CNSL signifies the chemical composition that is naturally present in the shell of the cashew nuts, which is basically composed by anacardic acids (about 60–70 %), cardol (about 10–20 %), cardanols (about 3–10 %), 2-methylcardols (about 2–5 %), and minor percentages of some other constituents.

The exact percentage however depends on the type of extraction method used. It has been reported that more percentages of mono-unsaturated cardanol from SCW and Soxhlet extraction methods. Additionally, operating conditions like temperature and pressure and time also affect the percentage of chemicals present in the extracted oil. So, the selectivity of different compounds during the extraction processes depends on a varied range of factors. Unlike the natural CNSL, the Technical CNSL can be obtained from the industrial processing of the cashew nuts where we only require the edible cashew or the fruit kernel and cashew nut shell is obtained as a by-product or secondary product there. Previously technical CNSL was considered as phenolic source to help in the manufacturing of Bakelite (phenol-formaldehyde resin). After conducting a lot of researches, the Technical CNSL has been recognized as an economically viable source of phenolic compounds. Industrially, CNSL can be obtained by extraction through high temperature processes in order to crack open the cashew nut shell and obtain the edible cashew kernel. In these processes, more commonly known as 'hot-oil processes', the cashew nut shells are generally kept in an immersed condition in the previously extracted technical CNSL or even in natural CNSL and heated to a temperature of about 180–190 °C. Under this temperature range, the anacardic acid present in natural CNSL of the nut shell undergoes a decarboxylation reaction and the anacardic acid gets converted into cardanol, generating technical CNSL as a result. The chemical composition of technical CNSL is much different from natural CNSL. Technical CNSL is mainly composed of cardanol (about 60–70 %), cardol (about 10–20 %), 2-methylcardol (about 2–5 %) and other polymeric materials (about 5–10 %). Minor percentages of few other components might be present depending upon the operating conditions and ambient conditions. A flowchart of the technical CNSL generating process has been drawn below in Fig-2. Refining and purification of CNSL includes the vacuum distillation of the raw liquid obtained upon pressing. However, the operating parameters may play an important role in the extraction process.

Cleaning and soaking of the cashew nut shell
↓
Shells from shelling process
↓
Shell heating or Roasting
↓
Shell pressing
↓
Filter
↓
Refining
↓
Purified CNSL (Technical CNSL)

Fig-2: Extraction process of Technical CNSL

3.1 Characterization of extracted cashew nut shell oil

Dean and Stark Apparatus can be used to determine the moisture content of the sample.

A capillary viscometer (maintained in a water bath at 30°C) can be used to determine the viscosity.

A calibrated pH meter model can be used to diagnose the pH of the sample.

A Pycnometer can be used to determine the specific gravity of the oil sample.

An Oxygen Bomb Calorimeter can be used to get the calorific value of the CNSL sample under adiabatic conditions.

An electrolyte can be used to regulate the heat of the system.

The calorific value of the spent cake of Cashew nut shell can be measured by placing the spent cake in a capsule which can then be put in the calorimeter crucible.

The calorific value can be calculated by the following equation:

$$\text{Calorific Value (kcal/kg)} = \frac{(W+w)(T1-T2)}{X}$$

where,

W = weight of the water in the calorimeter in kg,

w = water equivalent with respect to the apparatus,

T1 = initial temperature of the water in degree Celsius,

T2 = final temperature of the water in degree Celsius,

X = weight of the fuel sample (CNSL sample in this particular case) taken in kg

4.CASHEW NUT SHELL LIQUID AS A REPLACEMENT OF FURNACE OIL AND LIGHT DIESEL OIL (LDO)

Light Diesel oil (LDO) and furnace oil mainly belong to the intermediate boiling range products of crude oil distillation. As a result, LDO and furnace oil have a high metallic content along with other impurities which is detrimental to our daily usage and additionally the petroleum reserves are stiffly exhausting. Prices of petrochemical derivatives are rising. So, an urgent replacement is needed in order to maintain the stability of our economy.

In an experiment, the properties of both LDO, furnace oil and CNSL were tested and the results were compared. According to obtained results, CNSL was found to have a higher ash content as compared to both LDP and furnace oil, but that is only more by 1%. So, this little amount of difference can be tolerated in our industrial heating applications. The Gross Calorific Value (GCV) and relative density of the LDO, furnace oil and CNSL are the same. Moisture content is same for CNSL and furnace oil but is lower for LDO. So, the moisture of CNSL needs to be removed to some extent before being used in replacement of LDO. The moisture content can easily be removed.

The most notable point of difference is that the flash point for CNSL (170°C) is much higher than that for LDO (66°C) and furnace oil(66°C). The pour point of CNSL (2°C for both summer and winter) is much lower than LDO (120 °C for winter and 20 °C in summer). The comparatively higher flash point and lower pour point indicate that the CNSL in much safer to use and will be much more commercial if used in place of LDO and furnace oil.

5.CASHEW NUT SHELL LIQUID AS A COOKING OIL

Studies and researches have reported over and over again that CNSL upon being consumed, raises high-density lipoproteins (HDL) and lowers the low-density lipoproteins (LDL). Tus CNSL indirectly helps the HDL in removing excess cholesterol from our hearts and carrying it to liver for getting oxidized in the liver. Thus, CNSL reduces excess cholesterol and also positively and efficiently controls the oxidative stress, swelling and inflammatory issues and the cardiac functions. The lipids in CNSL have anti-inflammatory, heart protecting and anti-cancer characteristics.

Zea-Xanthine is an antioxidant pigment that is present in CNSL. The retina in our eyes rapidly and immediately absorbs the Zea-Xanthine that provides a protective shield to our eyes against the harmful ultraviolet radiation. CNSL thus contributes to our eye health and the Zea-Xanthine also prevents muscular degradation due to ageing in an elderly adult.

6.CARDANOL IN CASHEW NUT SHELL LIQUID AS COMPRESSION-IGNITION ENGINE FUEL (BIOFUEL/BIODIESEL)

Cashew Nut Shell Liquid (CNSL)'s main components are Anacardic acid, Cardanol, Cardol and some small amounts of other phenolic derivatives. Cardanol, which is separated from CNSL can be used in diesel engine as a biofuel. Biodiesel on being blended with petroleum diesel, is commonly referred to as a biodiesel blend. It can be used as fuel in unmodified diesel engine. The Cardanol biofuel/biodiesel is hydrophobic and remains flexible and liquid at very low temperatures. Cardanol improves flexibility and good drying after baking. It also significantly improves electron insulation properties and thermal stability. Cardanol also has a low freezing point of about -20°C. All these characteristics of cardanol make cardanol an effective substitute for the petroleum-based phenol. Viscosity which is a major drawback for every biomass can be reduced while blending with diesel or in addition to the ethanol. Flash and Fire point of CNSL are higher than diesel. Flash point and Fire point of Cardanol are approximately 92°C and 96°C. Higher Flash and Fire point indicates the oil is well suited for storage, transportation and handling. Calorific value of Cardanol is very closer to diesel, which enables higher quantity of heat liberation during combustion. Cardanol is added to diesel without any additives. Biodiesel is a green energy source and ecofriendly due to its phenolic contents, which reduces environmental pollution. The use of biodiesel is good for the environment because it made from bioresources and has lower emission compared to petroleum diesel. Besides, India is 2nd largest producers of cashew in the world, which is the raw material of CNSL. CNSL can be used in diesel generators and vehicles in the form of effective biodiesel blend. Performance of an engine when run with CNSL was found to be poorer compared to diesel and it can be improved by modifying the fuel by blending, preheating, using fuel additives etc.

7.CASHEW NUT SHELL LIQUID AS A LARVICIDE FOR THE PREVENTION OF MOSQUITO BREEDING

Nowadays, increasing number of the world population is getting affected with dengue fever. Some of the people are facing the more severe form of fever known is DHF (Dengue Hemorrhagic Fever). Dengue is generally caused by a mosquito type with the scientific name of *Aedes aegypti*. Despite a lot of researches and investigation, still no medicinal cure has been found out against this disease. Larvicides are used to prevent the breeding of mosquitoes. They are used at the larval stage since it is easier to control at that specific time. The commonly used larvicides have a disadvantage of giving rise to resistant insect species which will not get affected by the use of those larvicides anymore.

Cardanol and its derivatives can be a potential source for the development of larvicides in the countries which lead in cashew production. It can also be a hefty addition to the economy of that country since dengue fever is becoming a worldwide problem and we immediately need to use all kinds of alternatives to prevent the breeding of mosquitoes.

8.CASHEW NUT SHELL LIQUID AS FRICTION DUST IN AUTOMOBILE BRAKE LININGS

Automobile experts add friction dust to the brake linings in order to adjust the frictional and wear and tear properties. Records of improvised skid resistance and much less noise during brakes have been reported. Friction dust is commercially manufactured by the crosslinking of cardanol-formaldehyde resins with paraformaldehyde or hexamine and then the obtained product is powdered according to our requirements. Friction dust, on being impregnated with boric acid (popularly known as borated friction dust) finds application in air brake pads. Also, no fire catches during the transportation of CNSL-formaldehyde based resins and friction dust. CNSL-Formaldehyde (CF) resins on being used in friction dust reduces fade significantly by faster heat dissipation as compared to the phenol-formaldehyde (PF) resins.CF resins also offer a greater repellence to water in conditions of wetting. CF resins result in the production of much softer materials which are much more advantageous in cases of cold wear conditions .CF resins are also much more cost efficient as compared to PF resins. CF based friction dust also results in silent brakes which are much desired in the current situation of increased noise pollution. Tons of brake linings are manufactured for being used in automobiles every year. So, with the increasing use of automobiles, there is great opportunity of using CNSL based resins as friction dust in vehicles as CNSL is much more eco-friendly in comparison of other formaldehyde resins.

9. OTHER NOTABLE APPLICATIONS OF CASHEW NUT SHELL OIL

9.1 As a flow improver for waxy crude oil

The addition of chemical additives to crude oil in order to reduce its viscosity prevent wax formation, is becoming quite common. In the presence of asphaltenes, natural CNSL can significantly reduce the pour point of waxy crude oil. If the molecular weight of CNSL can be controlled properly then that modified CNSL can be used as a potential pour point depressant in oil industries. The modified CNSL reduces the viscosity of waxy crude oil and removes the waxy nature of the oil as a result.

9.2 As an efficient rubber compounding resin

The soaring development of rubber is increasing the requirement of new ingredients and alternatives which may be applied during the time of rubber compounding for vulcanization. Impregnation of CNSL derivatives in rubber improves the elastic strength and resistance offered against abrasion. It also reduces wear and tear and promotes self-adhesion properties of rubber. Cashew modified phenol-formaldehyde resins improve the chemical resistivity of the vulcanized rubber.

9.3 As a laminating resin

CNSL resins have the ability to decrease the brittle nature and enhance the flexibility of lamination. Cardanol and other CNSL resinous products are significantly used in laminating industries for effective outcomes. CNSL resins of this category are manufactured by condensation polymerization of Cashew nut shell liquid (CNSL), phenol and formaldehyde. These resins also impart enhanced hardening upon ageing and stronger bonding with the substrate. A huge amount of CNSL is required by the laminating industries for the manufacture of CNSL based laminating resins.

9.4 As a raw material for cement

Nowadays, constructions widely use polymer-based cements due to their good adhesive qualities and resistance to moisture, acids and bases. The phosphorus modified-CNSL polymeric resin highly suits this requirement. This polymer sticks well onto the surface of porous bricks, concrete and steel. They can be easily set at low temperatures by the slow and gentle addition of heat. CNSL-based polymers can also be found useful in sealing leaks present in the roofs. These

CNSL-based polymers on being mixed with a curing agent forms a putty which can be filled into the cavities of the leaks in order to seal them.

9.5 As raw material for surface coating

Surface coatings which are derived from Cashew nut shell liquid (CNSL) exhibit excellent lustre and surface finish with optimized levels of toughness and elastic properties. CNSL resins are impregnated into synthetics by paint manufacturing industries to modify the paint properties and to decrease the cost. It has anti-thermite and anti- microbial properties. Due to its darkish brown color CNSL is used to make dark-colored paints and enamels. CNSL derivatives can also give a highly efficient performance as lacquers. The dry lacquer films are much better than the ordinary oil-based paints since the dry lacquers are resistant to oil damages, moisture damages and is also resistant to any kind of chemical action. CNSL resins in combination with some other polymers can contribute to a good roof protection. Anti-corrosive polymers manufactured from the cashew nut shell liquid derivatives can be used as a protective lining for the bottoms of sea ships. Zinc incorporated CNSL polymers may be used as surface coatings which are rust-proof.

9.6 In epoxy-resins

Cardanol or CNSL derived epoxy-resins offer much more stronger and efficient characteristics as compared to the common phenolics and polyesters those which we use in our daily lives. Nowadays, in many research sectors epoxy-resins are being produced from cardanol. The epoxy-resins are generally manufactured electrophilic reaction of phenol with cardanol in presence of an acid catalyst in order to obtain a bisphenol which in order to attain the final product is then further epoxidized. The side chains in the final product enhance the flexibility and the resistance offering capacity as compared to the conventional epoxy-polymers available in the markets for the consumers.

9.7 In wood composites and as CNSL based adhesives

Specialized wood products are manufactured and sold after incorporation of the CNSL derived monomers in raw wood followed by in-situ polymerization. Generally, cardanol does not get polymerized by the traditional energy irradiation methods or the free radicals. So special methods are required for this purpose. CNSL based adhesives have been studied and diagnosed to possess notable and efficient characteristics that would play a huge role in meeting the ever growing want for excellence and permanence in bonding plywood. Varied range of CNSL-aldehyde resins, upon being impregnated into woods of lower grades e.g., rubber wood, have been reported to show a significant upgradation in quality. CNSL derived composites are also equally applicable in the manufacture of wooden boards as well as boards made out of coconut leaf. Such CNSL based composites are also cost-effective and thus can be a potential efficient alternative for the mankind to use.

10. CONCLUSION

Since the modern generation faces the problem of increasing energy demand and continuous depletion of fossil fuels, alternative sustainable innovations are needed to meet the present demands and prevent the growth of new problems. The thought of using the agro-industrial waste, CNSL as an alternative raw material source has drawn the attention of scientists. Nowadays, with increasing cashew production, CNSL is becoming an efficient alternative for the production of functional outputs and a large number of research papers are being contributed to this purpose. However, isolation of pure cardanol is still a great challenge for us and since cardanol is the prime source of all these applications, researches are being conducted now to obtain the purest form of cardanol by extraction. Cardanol and other CNSL derivatives find their applications in a varied range of disciplines including production of biodiesel, larvicides, vulcanized rubber, brake linings, foundry chemicals, surface linings, surfactants and the list is yet to be continued and discovered. Thus, CNSL can perform as a promising supplement to the petrochemical derivatives obtained from petroleum reserves, that are currently getting exhausted. India, being the second largest producer of cashews, exports its cashew and CNSL to USA and China, the importing countries. So CNSL can also serve as a great source of economy.

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