

**Evaluation of Cashew Nut Shell Liquid Based Products as Reactive
Diluents for Alkyd Coatings**

Francis Njuku Waitara

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Science in Chemistry in the Jomo Kenyatta University of
Agriculture and Technology**

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other university.

Signature.....Date.....

Francis Njuku Waitara

(SC331-1234/2011)

This thesis has been submitted for examination with our approval as university supervisors.

1. Signature.....Date.....

Dr. Patrick M. Mwangi

JKUAT, Kenya

2. Signature.....Date.....

Prof. George T. Thiong'o

JKUAT, Kenya

DEDICATION

This work is dedicated to my family. Special dedication to my dad Samuel Waitara for his love, financial support, advice and my mum Agnes Wahito for her spiritual guidance in my life.

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ABBREVIATIONS AND ACRONYMS

ACA	African Cashew Alliance
ASTM	American Standard for Testing and Materials
CNSL	Cashew Nut Shell Liquid
FAO	Food and Agriculture Organization
FTIR	Fourier Transform Infrared Spectroscopy
HAP	Hazardous Air Pollutants
HDC	Horticultural Development Center
IPM	Integrated Pest Management
JKUAT	Jomo Kenyatta University of Agriculture and Technology
KARI	Kenya Agricultural Research Institute
KEBS	Kenya Bureau of Standards
MOA	Ministry of Agriculture
NMR	Nuclear Magnetic Resonance
NUTPAK	Nut Processor Association of Kenya
USEPA	United States Environmental Protection Agency
UV	Ultra Violet
VOCs	Volatile Organic Compounds

ABSTRACT

Volatile Organic Compounds (VOCs') have aroused concern in many parts of the world especially in large cities due to their negative impacts to the environment. In the presence of sunlight, VOCs' react with NO_x gases to produce tropospheric ozone, a powerful oxidant and pollutant to the atmosphere. Although most of the VOCs' originate from petroleum products and internal combustion engine exhausts and plants, a significant amount is derived from solvent based coatings. This study reports the findings of environmentally friendly and less toxic reactive diluents synthesized from Cashew Nut Shell Liquid (CNSL) based products. CNSL is a by-product from cashew nut processing and contains anacardic acid, cardol, 2-methyl-cardol and cardanol, decarboxylated anacardic acid. CNSL is not currently utilized in Kenya. It was extracted from cashew nut shells by cold solvent extraction process using *n*-hexane solvent. The percentage yield of CNSL obtained was found to be 30.9 ± 0.2 . Cardanol was isolated using methanol and ammonia solution as the solvents in a ratio of 8:5, respectively. The percentage yield of cardanol obtained was $63.93 \pm 0.2\%$. Cardanol was modified via transesterification and methylation with acetic anhydride and methyl iodide, respectively. The percentage yield of cardanyl acetate obtained was $58.94 \pm 0.01\%$ and that of cardanyl methyl ether was found to be $52.39 \pm 0.01\%$. Cardanol, cardanyl methyl ether and cardanyl acetate were also characterized using Finnigan Gas Chromatography Mass Selective Detector 8000 and a parent peak of $m/z = 108$ observed for all the three products. The effects of cardanyl methyl ether, cardanyl acetate and neat cardanol on the properties of alkyd-based coatings film were investigated including pencil hardness which was found to be 4H for all the formulations compared to 5H for the control. Coatings formed had good adhesion, good drying time and pencil hardness and would be expected to be cheaper since Cashew Nut Shell Liquid is a renewable raw material from waste. VOCs' reduction was achieved to the extent of 39% compared to conventional commercial products. Drying time study showed that drying time can be altered variously by types and level of diluent added.

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1 Background of the Study

Environmental concern has become one of the most important topics in the coatings industry which has led researchers to continually attempt to develop coatings system with less solvent (Daniel and Scott, 2004). In the coatings industry, alkyd resins have been used for many years as renewable natural binders for various coating applications, including development of varnish and paint. Unfortunately, in order to formulate them into proper products for coatings, alkyds require the incorporation of VOCs' to satisfy the coatings application requirements, especially to reduce the viscosity which then evaporates into the atmosphere as VOCs' giving rise to regulations (Holt, 2005; Alp *et al.*, 2011). VOCs' have been recognized to cause serious problems in air pollution. The three important end effects of volatile organic compounds emissions into the atmosphere are formation of eye irritants, particulates, and toxic oxidants such as ozone. The most critical effects of coatings is ozone production and even though ozone is a naturally occurring component of the atmosphere, it is toxic to plants and animals. Also burning of cashew nut shell produces particulate matter into the environment causing air pollution. With the rapid growth of volatile organic compounds emissions from man-made sources, ozone levels especially in and around cities have exceeded the levels that many plants can withstand and have endangered human health, especially for susceptible individuals.

The largest source of man-made VOCs' emissions is from automotive and truck tail pipe emissions, along with fuel leakage during distribution. The second largest source is coatings (Paul, 1992). Photochemical reactions in the atmosphere are complex and depend on many variables such as the amount and structure of VOCs' and the concentrations of various nitrogen oxides among others (Deepak *et al.*, 2004). The principle pathways leading to the generation of ozone are by way of hydrogen abstraction from the VOCs' (Stevenson *et al.*, 2013). The problems caused by volatile organic solvent present in solvent borne coatings are driving resin and coating

producers to come up with possible solutions such as to develop reactive diluents which would function as solvent in the formulation of the coatings, but which during the cure process is converted to an integral part of the film (Renz and Bruchmann, 2001). Another solution for the VOCs' restriction problem is to employ a high technology UV-curable system which is solvent-free and low in energy consumption or develop water borne alkyds with improved properties (Van *et al.*, 2007). In this research, the work was mainly focused on either reducing or replacing VOCs' used in coatings formulations. The main objective was to evaluate neat cardanol, cardanyl methyl ether and cardanyl acetate for their suitability as reactive diluents for alkyd coatings.

1.1.1 The Cashew Tree, Cashew Nut and Cashew Apple

The cashew tree, *Anacardium occidentale*, is a botanical species native of Eastern Brazil and was introduced into other tropical regions such as India, Africa, Indonesia and South East Asia in the 16th and 17th centuries by the Portuguese (Marcionilia *et al.*, 2009). It is a small evergreen tree that grows 10 - 12 m tall, with a short, often irregularly shaped trunk. The true fruit of cashew tree is the nut, a kidney shaped structure approximately 2 - 3 cm in length. The nut is attached to the end of a fleshy pulp called the cashew apple as shown in Fig1.1 (De Lima *et al.*, 2008).

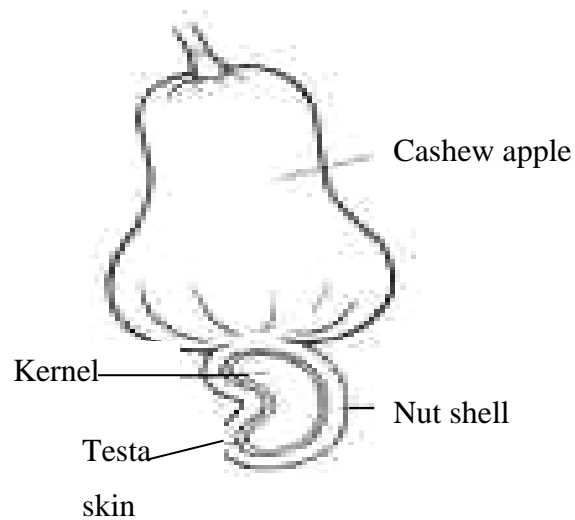


Figure 1.1: Cross section of cashew fruit and cashew nut

The cashew nut shell has a thickness of about 0.3 cm inside which is a honey comb structure containing the CNSL. The shell of the nut comprises of about 50% of the weight of the raw nut, the kernel represents 25% and the remaining 25% consists of the natural CNSL, a dark reddish brown viscous liquid which is the pericap fluid of the cashew nut (Maria *et al.*, 1999). What appears to be the fruit of the cashew tree is an oval or pear shaped accessory fruit or false fruit that develops from the receptacle of the cashew flower, called the cashew apple. It ripens into a yellow or red structure about 5 - 11 cm long as shown in Plate 1.1. It is edible and has a strong sweet smell and a sweet taste. In cashew-producing countries, the nut is only one of the products enjoyed by the local populations. The cashew "apple" or false fruit is an edible food rich in vitamin C. It can be dried, canned as a preserve or eaten fresh from the tree. It can also be squeezed for fresh juice, which can then be fermented into cashew wine, which is a very popular drink in West Africa. In parts of India, it is customary to distil cashew liquor to an alcoholic drink referred to as *feni*. In some parts of South America, local inhabitants regard the apple, rather than the nut kernel, as a delicacy. In Brazil, the apple is used to manufacture jams and soft alcoholic drinks (De Lima *et al.*, 2008).



Plate 1.1: Cashew nut and cashew apple

1.1.2 Processing of Cashew Nuts

The processing of cashew nuts is shown in the flow diagram in Fig.1.2. The nuts are first cleaned to remove foreign matter such as sand, stones and dried apples. The next stage involves soaking the nuts in water to avoid scorching them during roasting. After soaking, the nuts are roasted by either open pan, drum roasting or the hot oil method (Bambang, 2000). In the open pan method, the nuts are placed on the pan at one time while stirring constantly. The CNSL starts to exude and then ignites producing a long flame and a black smoke. After 2 min, the pan is doused and the charred, swollen and brittle nuts are thrown out of the pan. The drum roasting method involves continuously feeding the nuts into a rotating drum over a fire. This method is developed from the open pan method. A slight horizontal slope in the mounting ensures the movement of the nuts through the drum. The drum is pierced so that the flame touches the nuts and the smoke is controlled by a hood and chimney (Kristin, 1999). For the hot oil method, the principle employed is that the shells containing the CNSL when immersed in the oil in a tank at high temperatures of 185 - 190°C will lose their oil thus increasing the oil in the bath (Subbarao *et al.*, 2011; Bharat *et al.*, 2012). A wire basket is used to hold the nuts for immersion into the bath. About 50% of the CNSL is extracted from the nuts. Draining trays are needed at the end of the bath for the roasted nut to dry and the residue oil is returned to the oil bath.

Shelling of the nuts is done either manually or mechanically. In the manual shelling process, the nuts are placed on a flat stone and cracked with a wooden mallet. Due to the residual CNSL, gloves are required while using this method (Atul *et al.*, 2010; Patil, 2011). The first mechanized shelling system, Oltremare, is based on a pair of knives each shaped in the contour of half a nut. The nuts are brought to the knives on a chain, each nut in the same position to fit between the knives. The nuts are pushed between the knives and cut. Other methods have been developed based on this method, whereby they are semi-mechanized by addition of a foot-operated lever to operate the knives. After shelling, shell pieces and kernels are separated and the unshelled nuts are returned to the shelling operation. Pre-grading followed by drying is then done. The kernels are then graded and finally packaged (Atul *et al.*, 2011).

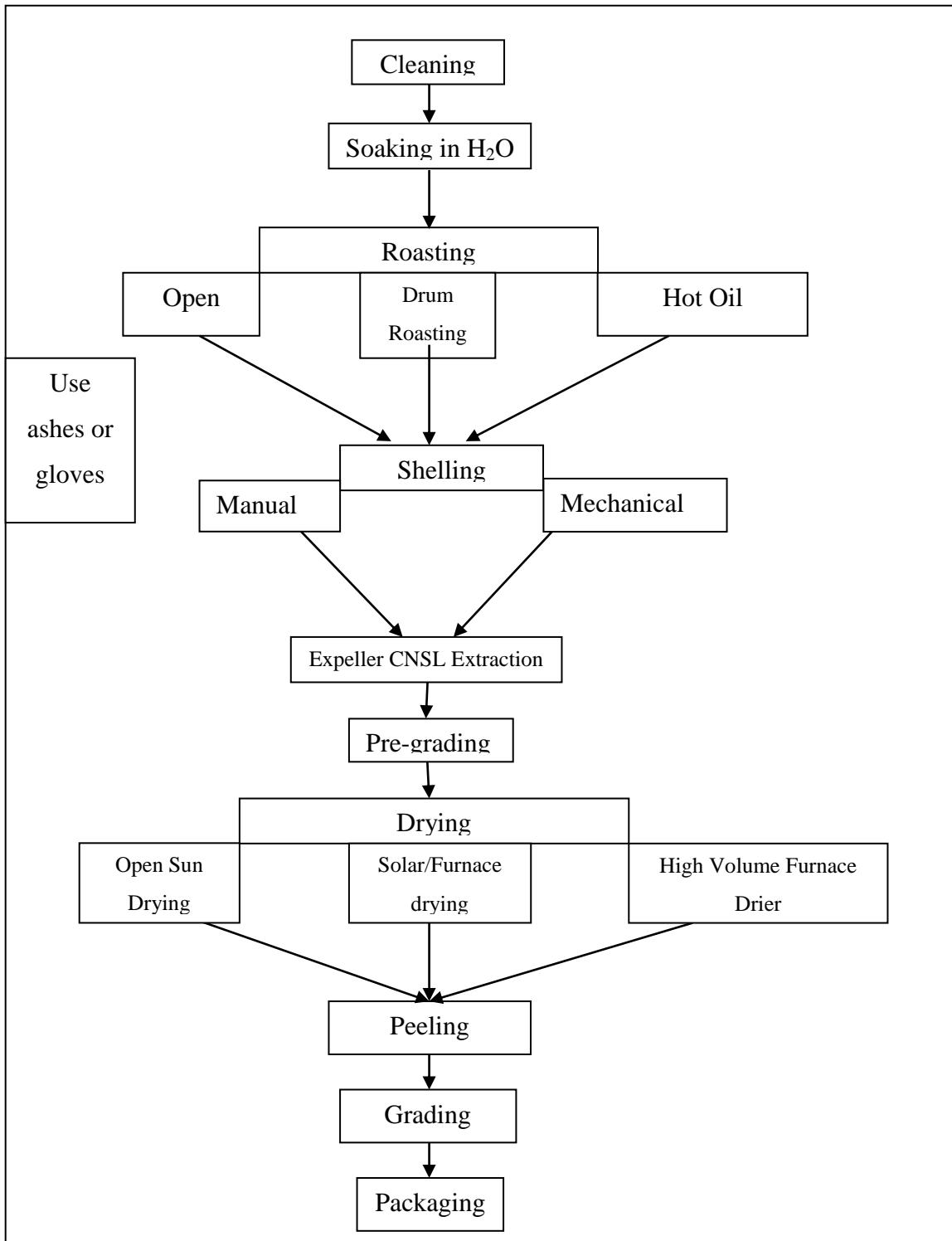


Figure 1.2: Flow diagram for cashew nut processing

1.1.3 Cashew Nut Production in Kenya

Cashew nut production in Kenya is a small holder activity and accounts for one percent of the total Kenyan agricultural production in value. There are no large plantations of cashew trees in the country. Individual holdings vary from a few trees to a few acres per farmer. According to a recent survey, cashew nut production is confined to the Coast Province (Muturi *et al.*, 2013). A few farmers in Meru also produce cashew nuts although not in substantial amounts. The Memorandum of Understanding signed in 2012 between African Cashew Alliance (ACA) and Nut Processor Association of Kenya (NUTPAK) which brought together Kenya, Tanzania and Mozambique created a platform for farmers to exchange ideas on improving the quality of cashew nuts in their member countries.

Currently, the set price per kg of unprocessed cashew nuts stands at Sh 45 but with the partnership, the future is promising for farmers. There has also been an improvement in the yield of unprocessed cashews from 9000 metric tons in 2010 to the current 13,000 metric tons in 2012 (Anon, 2014). There are five to six companies that process cashew nuts in Kenya and a few examples include the Kenya Nut Company Limited in Thika and Equitorial Nuts Processors in the coast. Through USAID assistance, the Kenya Horticulture Development Centre (HDC) initiated its collaborative cashew productivity program in Kenya's coastal region. In response to the farmer's productivity challenges, HDC developed a Cashew IPM Protocol that can be tailored to train farmers on how to cost effectively raise productivity through better agronomic practices such as pruning and biological control of pests and disease. Seeking to utilize practices made in the Cashew IPM Protocol, HDC is supporting the National Cashew Technical Committee through the MOA and KARI Mtwapa to implement the Coast Province Cashew Productivity Enhancement Program.

1.2 Cashew Nut Shell Liquid

Cashew Nut Shell Liquid (CNSL) is a viscous liquid found in the honeycomb structure of the cashew nuts shell having a bitter taste and it is dark brown in color (Fereidoon, 2005). It is essentially a mixture of 4 phenolic compounds namely

anacardic acid, cardanol, cardol and 2-methyl cardol (Francisco *et al.*, 2006). Different authors have reported differently regarding the percentages of the constituents of natural CNSL. Generally it is stated that it contains about 80 – 90% by weight anacardic acid, a derivative of O-carboxyphenol that readily decarboxylates on heating and converts to cardanol (Tyman, 1973; Paramashivappa *et al.*, 2001; Adetogun, 2011; Muturi *et al.*, 2013). The remaining 8 - 10% of CNSL consists of cardol, a resorcinol that is mainly responsible for the vesicative activity of the CNSL (Cornelius, 1966). De Lima *et al.* (2008) further stated that the actual composition of CNSL, color and stability depend to some extent on the duration and condition of storage as well as on the method of its production and the nature of heat applied. The structures of these fractions are shown in Fig. 1.3.

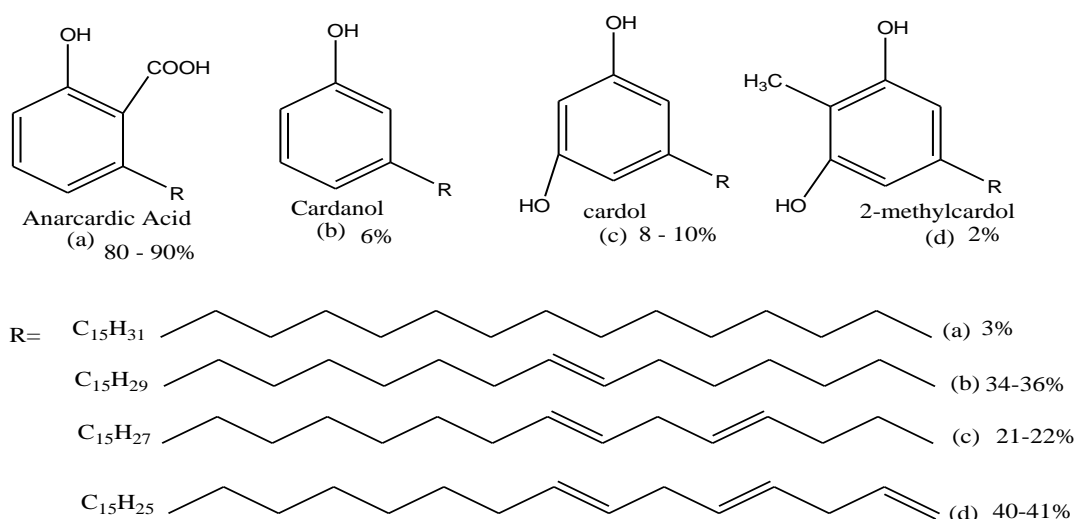


Figure 1.3: Fractions of CNSL

1.2.1 Common Applications of CNSL

Cashew Nut Shell Liquid (CNSL) is used in manufacturing cardanol based resins and varnishes, cardanol, foundry resins, brake linings, clutch facing, acid resistant paints, insecticides and fungicides, rubber compounding resins, lacquers and enamels (Kumar *et al.*, 2002). CNSL based resin possess an outstanding high resistance to acids and alkalis (Knop and scheib, 1979). A number of products based on CNSL are used as anti-oxidants, stabilizers and demulsifiers for petroleum products (Menon *et*

al., 1985). Soluble metal derivatives of CNSL are used to improve the resistance to oxidation and sludge formation of lubricating oils.

1.2.2 Cardanol

Cardanol is obtained from anacardic acid through heating process. Each of the fractions of cardanol includes four compounds because the composition of the side chain varies with its degree of unsaturation (Giuseppe *et al.*, 2011). The unique molecular structure of cardanol, especially unsaturation of long hydrocarbon side chain, makes the cross linking easy on polymerization (Ranjana and Deepak, 2008). Structural changes can be effected at the hydroxyl group, on the aromatic ring and on the side chain to make tailor made products of high value (Mythili *et al.*, 2004; Unnikrishnan, 2006). In terms of physical properties, cardanol is comparable to nonylphenol. Cardanol is hydrophobic and remains flexible. Its freezing point is below -20°C, it has a density of 0.930 g/ml and boils at 225°C under reduced pressure (10 mm Hg). Cardanol finds use in the chemical industry in resins, coatings, frictional materials and surfactants used as pigment dispersants for water-based inks. It is used to make phenalkamines, which are used as curing agents for the durable epoxy coatings used on concrete floors. Cardanol based resins possess an outstanding resistance to softening action of mineral oils and high resistance to acids, alkalis, termite and insects (Risfaheri *et al.*, 2009).

1.3 Reactive Diluents

Reactive diluents are compounds or mixture of compounds that reduce viscosity of the base resin. They have a relatively high boiling point and remain as part of the coating system (Zabel *et al.*, 1999). Reactive diluents can copolymerize with a base resin thereby reducing losses of the solvent to atmosphere on drying of the coating. They improve handling and ease of processing in various applications. They are used to optimize performance properties such as impact strength, adhesion, flexibility filler-loading and solvent resistance of a coating system. Reactive diluents are classified into groups which include aliphatic, aromatic and cycloaliphatic. A reactive diluent should have low viscosity, good compatibility with alkyd resin, low volatility

(BP > 300 °C), no-toxicity, low color, economic replacement of solvent and the ability to participate in oxidative cure (Ursula *et al.*, 2009).

1.3.1 Reactive Diluents for Alkyd Coatings

A number of approaches to identification of a suitable reactive-diluent have been described. The chemistry of the vinyl cyclic acetals and their air-drying reactions has been studied (Hochberg, 1965). Dicyclopentyl methacrylate as a reactive diluent for high-solid alkyd coatings has been studied (Larson and Emmons, 1983). The properties of vernonia oil, a naturally occurring epoxidized vegetable oil has been studied (Fig. 1.4), and compared with that of the industrially-produced epoxidized soybean (Fig. 1.5) and linseed oils with different degree of epoxidation. The viscosity of the oils was found to increase gradually with increase in the degree of epoxidation. The fully epoxidized soybean and linseed oils, which were heterogeneous semi-solids at room temperature with higher viscosities and higher melting points than vernonia oil, were found to be less suitable as reactive diluents for coatings formulations (Muturi *et al.*, 1994).

The partially epoxidized soybean and linseed oils, were found to have molecular structure and properties similar to that of vernonia oil and are potentially available at lower price. They were homogeneous liquids at room temperature with lower viscosities, lower melting points and appeared to be attractive reactive diluents for low volatile organic compound alkyd formulations. Literature search reveals studies for design and incorporation of reactive diluents for air-drying high-solid alkyd paints (Zabel *et al.*, 1999). They described some requirement and design aspects for reactive diluents and also introduced a new class of reactive diluents based on fumarates and succinates of octadienol and reported the cure and performance of octadienol/Fumarate/Succinate diluents (Fig. 1.6).

The crosslink mechanisms of high-solids alkyd resins in the presence of reactive diluents has been studied via NMR and Mass Spectroscopy employing model compounds and it was found that allyl ether groups appeared to react fast whereas

allyl esters generally showed little reactivity (Muizebelt *et al.*, 2000). Esters of Calendula oil has been synthesized and tested as reactive diluents (Scheme 1.1). A new reactive diluent, tetra (2, 7-octadienyl) titanate, has been synthesized through ether exchange reaction between tetraethyl titanate and 2, 7-octadienol for air-drying, high-solid alkyd paints (Scheme 1.2). The resulting alkyd-reactive diluent formulations exhibited low viscosities and extremely low dry times in comparison to neat alkyd resins. Their films yielded superior hardness and fast oxidative curing (Alp *et al.*, 2011).

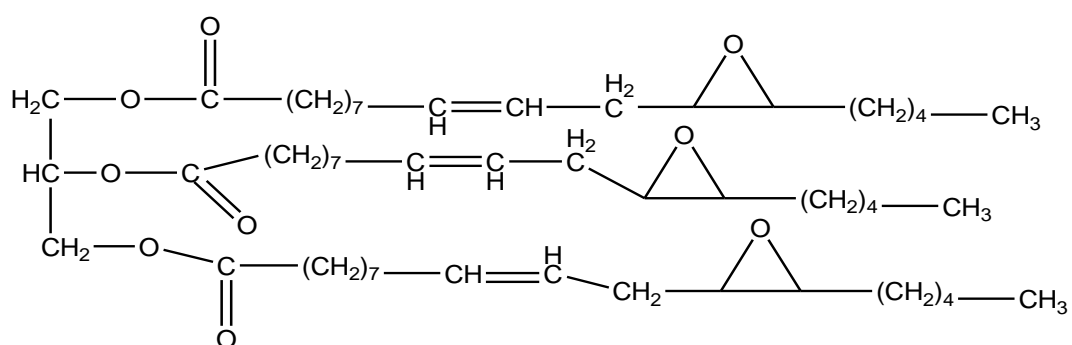


Figure 1.4: Structure of vernonia oil

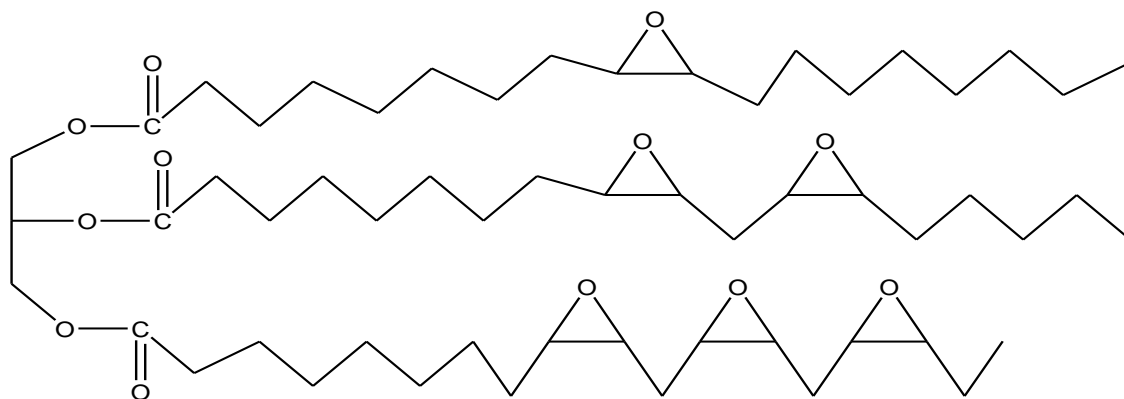


Figure 1.5: Structure of epoxidised soy bean oil/linseed oil

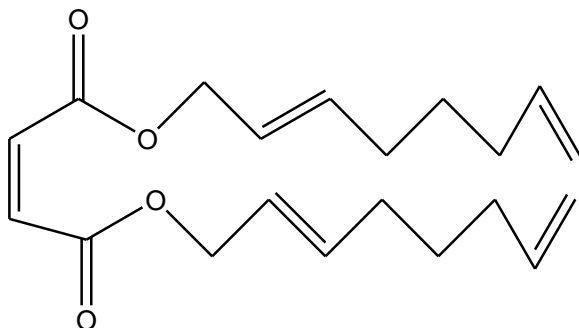
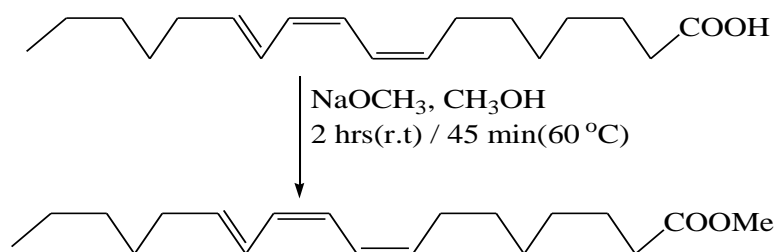
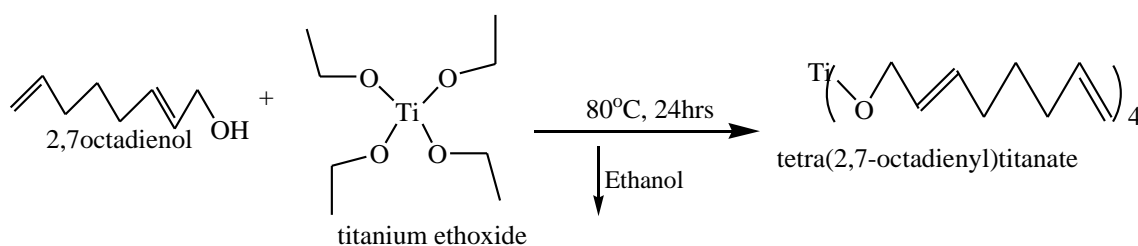


Figure 1.6: Di-octadienyl maleate



Scheme 1.1: Synthesis of methyl calendulate from calendula oil



Scheme 1.2: Synthesis of tetra (2, 7-octadienyl) titanate

1.4 Alkyd Coatings

Alkyd resins are produced by the condensation of polybasic carboxylic acids with polyhydric alcohols (Wicks *et al.*, 1992). At least one of the alcohols must be trihydric or higher. The most commonly used alkyd polyester are those produced from

phthalic anhydride and glycerol and are modified with unsaturated oils or fatty acids such as oleic or linoleic acids to achieve air drying properties (Fig. 2.7). Alkyd resins are also modified with acrylic, epoxy or silicone compounds (James, 2003).

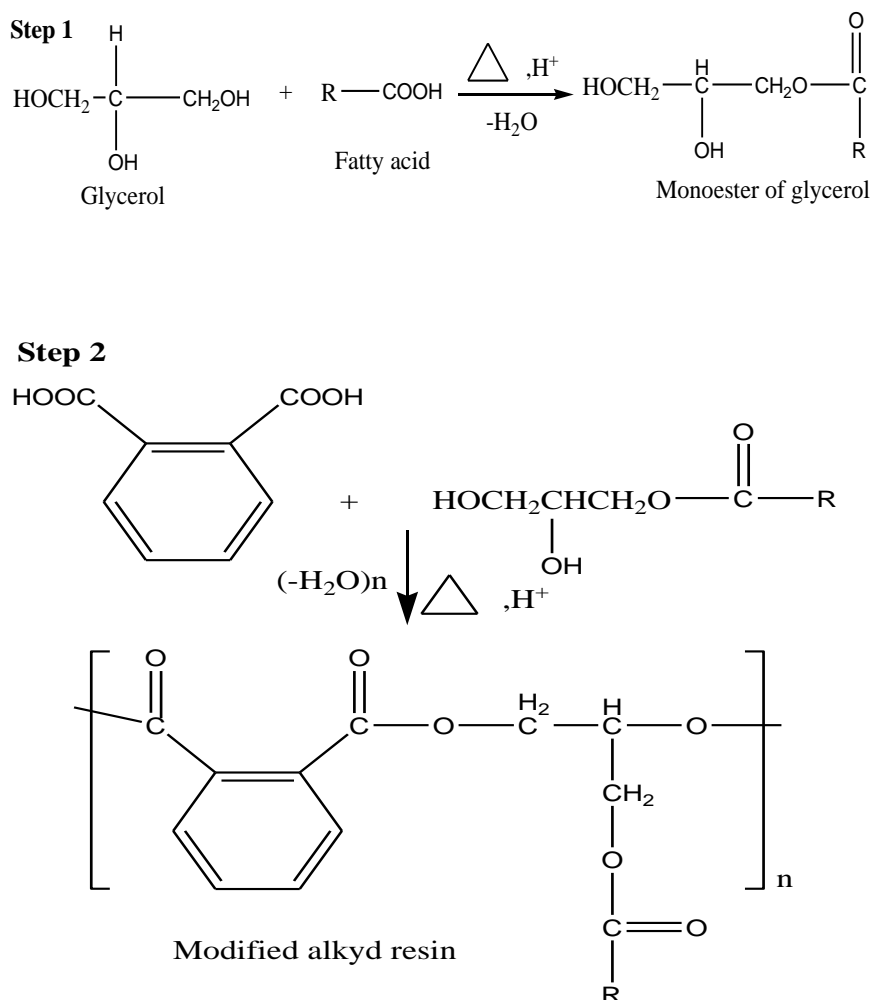


Figure 1.7: Process showing the synthesis of alkyd resin

Paints based on alkyd resin binders are usually solvent-borne paints, common solvents being white spirit, a mixture of saturated aliphatic and alicyclic C7 - C12 hydrocarbons with a content of 15 - 20% by weight of aromatic C7 - C12 hydrocarbons, or xylene (Arthur, 2006). Further important components of alkyd paints are pigments and extenders. The pigment is the substance that gives the paint color. Pigments are derived from natural or synthetic materials that have been ground into fine powders. Extenders are inert pigments used to extend or increase the bulk of

a paint (Isaac and Luvia, 2010). Extenders are also used to adjust the consistency of a paint and to let down colored pigments of great tinting strength. Another important category of additive to alkyd coating comprises the catalyst or driers (Johansson and Johansson, 2008). Driers are metal soaps or coordination compounds which accelerate paint drying, thus shortening the total drying time. Without driers, the drying time of alkyd paint would be over 24 hrs.

Alkyds can be classified by various criteria. One classification is by oil length based on the ratio of monobasic fatty acid to dibasic acid utilized during synthesis. The amount of oil is defined as the triglyceride equivalent to the amount of fatty acids in the alkyd. Alkyds with oil lengths greater than 60 are long oil alkyds; those with oil length from 40 to 60, medium oil alkyds, and those with oil lengths less than 40, short oil alkyds (Dieter and Werner, 1998). Another classification of alkyd resins is based on whether they are oxidizing or non-oxidizing type alkyds. Oxidizing alkyds are comprised of one or more polyols, one or more dibasic acids, and fatty acid derived from one or more drying or semi-drying oils. Non-oxidizing alkyds are used as polymeric plasticizers or as hydroxy-functional resins and are crosslinked with melamine-formaldehyde (MF) resins or urea-formaldehyde (UF) resins. The last classification is modified or unmodified alkyds. Modified alkyds contain other monomers in addition to polyols, polybasic acids, and fatty acids, such as styrenated alkyds and silicone alkyds (Zeno *et al.*, 2007).

1.4.1 Solvents Used in Coatings

A solvent is defined as a substance, usually a liquid that will dissolve and change a solid to a liquid state (Candries, 2000). In the coating industry, solvents are considered as any volatile liquid formulated into a paint, even though it may not have solvency power (Koleske, 1995). Some liquids are diluents and even though the diluent may not have solvency power, it may enhance the solvency of other solvents in the paint. Water is the universal solvent, except for its use as a dispersant in emulsion coatings; it is not used as a paint solvent in durable coatings. Water-soluble resins are susceptible to softening and swelling by water (Bieleman, 2000). Organic

solvents impart low water sensitivity and are the solvents of choice when dissolving solid resins. The purpose of any solvent is to dissolve solid paint constituents, reduce viscosity, and render the paint fluid enough that it can be satisfactorily applied. The solvent is undesirable after application and must evaporate from the drying coating film (Tunga and Erick, 2009).

In addition to enabling application of the coating material, solvents must be able to wet the substrate being coated and penetrate into and help the coating seal any crevices, voids or depressed irregularities. Also, the solvent must volatilize fast enough to prevent runs and sags in the drying coating film. However, a solvent that is too volatile can cause solvent pops, loss of gloss, dry spray, poor surface wetting and penetration, and poor film flow and inhibit cure. Virtually all coating formulations use a blend of solvents to achieve optimum properties. Some solvents within the blend will evaporate fast, enabling the drying paint to set quickly. Other solvents may dry slower and provide wettability and penetrability (Marion, 2004). Ultimately, all solvents should evaporate to allow the coating to achieve hardness, cure and adhesion. Solvents can be categorized according to their chemical composition. The most commonly used categorization subdivides solvents into classes called turpentine, hydrocarbons, ketones, esters, alcohols, and glycol ethers (Thomas *et al.*, 2000).

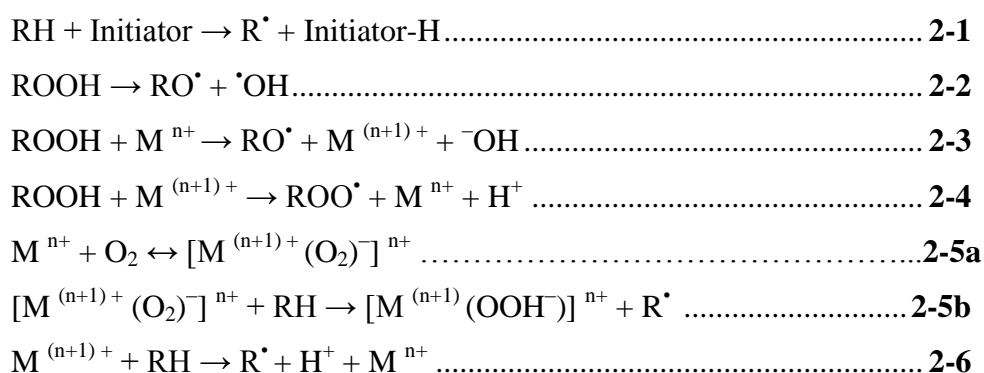
1.4.2 Curing of Alkyd Coatings in the Presence of a Reactive Diluent

The drying of alkyd coatings involves the auto oxidation of unsaturated fatty acid such as linoleic acid and requires a metal catalyst as the initiator (Gorkum and Bouwman, 2007). Reactions **2-1** to **2-13** show how the curing occurs. The role of the metal ion in a metal-catalysed autoxidation is to create new radical chains. Common transition metals capable of hydro peroxide decomposition are Fe, Cu, Co, Mn, Ti, V and Ce. A metal compound has to be able to perform both reactions **2-3** and **2-4**, or **2-3** and **2-6** so that each change of its oxidation state starts a new radical chain.

The cross linking of alkyd starts by abstraction of a bis allylic hydrogen atom from the fatty acid (RH) to form a radical as shown in reaction **2-1** (Gorkum and

Bouwman, 2005). The resulting radical (R[•]) reacts with oxygen to form a hydro peroxide (ROOH) as shown in reaction 2-2. The hydro peroxide is degraded by cobalt or manganese into radicals (reaction 2-3). The radical formed then undergoes addition into the reactive diluents which is conjugated. The reaction proceeds by a free-radical chain mechanism and can be described in terms of initiation, propagation and termination. Step 2-1 is the reaction of some arbitrary initiating species with the substrate, directly forming a carbon-centered radical (Lambourne and Strivens, 1999). Reaction 2-1 is the thermal homolytic decomposition of hydro peroxide, which only plays a significant role at elevated temperatures. In metal-mediated initiation, the initiation of radical chains predominantly occurs through steps 2-3 to 2-6. Reactions 2-3 and 2-4 are called Haber Weiss reactions, originally proposed for the decomposition of H₂O₂ by iron in aqueous media. This set of reactions is the generally accepted mechanism by which hydro peroxides are decomposed in polar media by a metal with two stable oxidation states differing one electron (Mallegol *et al.*, 2002). The situation is different in apolar media. Reaction 2-4 generally is slower than reaction 2-3. Initiation reaction 2-5b involves the activation of molecular oxygen by the metal in the lower oxidation state, forming a metal-superoxide complex. This complex can then abstract a hydrogen atom from the substrate to form a hydro peroxide complex and a carbon radical (2-5b). This initiation pathway operates predominately in apolar media. In the last initiation reaction in reaction 2-6, a carbon radical is formed by direct reaction of the higher-valent metal ion with the substrate. The most important propagation reactions are reactions 2-7 and 2-8 (Stenberg *et al.*, 2005).

Initiation



Propagation



Termination



One initiation event can set off the cycle between reactions 2-7 and 2-8, which is why these reactions are responsible for a large increase in hydro peroxide concentration during the first stages of autoxidation (Johansson and Johansson, 2006). Hydro peroxide formation will eventually be balanced by hydro peroxide decomposition, however, resulting in a steady state concentration of hydro peroxides in polar media. This is the main reason for autoxidation to attain a limiting rate. Alkoxide radicals can only be formed through metal-catalysed autoxidation, via reaction 2-3. These alkoxide radicals can also propagate radical chains via reaction 2-9 or various other reactions. Polymerization occurs through radical termination reaction forming cross-links causing gelling of the film, which is followed by drying and hardening of the film (Muizebelt *et al.*, 2000). The number of cross linked sites that are formed determines the film hardness.

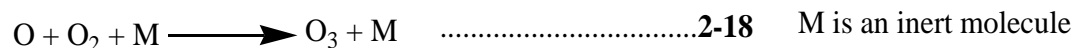
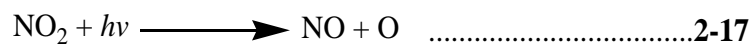
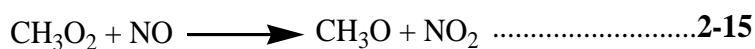
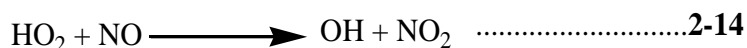
Termination reaction 2-10 is not a dominant reaction. Alkoxide radicals are much too reactive and hence their concentration is rather low. Under most autoxidation conditions, the only significant termination reaction is the reaction of two peroxy radicals with each other (reactions 2-11a and 2-11b). Reaction 2-11a proceeds according to the Russell-mechanism, where a tetraoxide intermediate is formed which decomposes to yield non-radical products, an alcohol, ketone and singlet oxygen. The other bimolecular peroxy radical termination reaction, reaction 2-11b, leads to a

peroxide cross-link. This reaction is proposed to proceed also via a tetraoxide intermediate.

1.5 Volatile Organic Compounds

Volatile Organic Compounds (VOCs³) are in most protective coatings (Nicholas, 2003; Ursula *et al.*, 2009). Common paint solvents such as aromatic hydrocarbons, aliphatic hydrocarbons, ketones, acetates and alcohols are photo chemically reactive. On evaporation into the atmosphere, these paint solvents react with nitrous oxides (combustion compounds from automotive emissions and burning of fuels) and sunlight to form tropospheric ozone and air pollutants (Collins *et al.*, 1997). Stratospheric ozone absorbs UV light in the range of 200 – 300 nm, and it has a maximum concentration of about 10 ppm in the atmosphere at about 35 km height in the stratosphere (Ronald, 2007). Thus, stratospheric ozone acts as the Earth's UV shield or sunscreen preventing UV radiation damage to the biosphere (Anon, 2008).

In effect, stratospheric ozone prevents light of wavelengths less than 300 nm from reaching the Earth's surface. Loss of stratospheric ozone sunscreen, would lead to an increase in skin cancer, eye cataracts and a decrease in photosynthesis. On the other hand, tropospheric ozone is a secondary pollutant produced during the photochemical oxidation of methane (CH₄), carbon monoxide (CO) and non-methane volatile organic compounds in the presence of nitrogen oxides (NO_x) as shown in reaction **2-14** to **2-18** (Stevenson *et al.*, 2013). Ozone is a major constituent of photochemical smog. It is a powerful oxidant that damages human health and natural ecosystems, and reduces crop yields. It is also an important greenhouse gas, with a radiative forcing since 1750 third only to carbon dioxide (CO₂) and methane (CH₄).



The net result is the formation of tropospheric ozone (reaction **2-18**).

1.6 Statement of the Problem

Alkyd resins are viscous and tacky materials that are often dissolved in organic solvents to reduce their viscosity. These organic solvents often evaporate into the atmosphere developing tropospheric ozone on reaction with nitrous oxides. Tropospheric ozone is harmful to plants, animals and humans since it is a greenhouse gas. Also pollution generated from the cashew nut processing plants in Kenya has brought concern over their health and environmental implications. This is because cashew nuts are processed by the steaming method which leaves the shells with most or all of the CNSL. These shells are subsequently burned to provide energy for processing of the nuts. The burning of the shells containing CNSL produces fumes and dark smoke with particulate matter thus polluting the environment and also is harmful to the workers since it can cause respiratory diseases. Further, current use of cashew nut shells containing CNSL for fuel is a waste of an important raw material. Thus Cashew Nut Shell liquid should always be extracted from the shells before being used as fuel.

1.7 Justification of the Study

Commercially manufactured coatings have brought concern in many parts of the world due to their environmental implications because they are formulated with mixtures of organic solvents that are essentially VOCs' which are non-reactive in the coating and thus evaporate into the atmosphere causing air pollution. Although most of the VOCs' originate from petroleum products and internal combustion engine exhausts and plants, a significant amount is derived from solvent based coatings. Photochemical reactions in the atmosphere are complex and dependent on many variables in addition to the amount and structure of VOCs', especially the concentrations of various nitrogen oxides. Replacement of commercially produced solvents with modified CNSL products will minimize VOCs' emission to the environment, reduce the viscosity of the coatings thus increasing ease in handling, processing and even accelerate drying in various applications. This will also reduce solvent expenses and optimize performance properties such as adhesion and solvent resistance of alkyd coatings.

1.8 Hypothesis

Reactive diluents from modified CNSL products are compatible with alkyd coatings, have low viscosity and are nonvolatile.

1.9 Objectives

1.9.1 Main Objective

To develop reactive diluents based on modified CNSL products and evaluate their suitability for alkyd coatings.

1.9.2 Specific Objectives

- i) To extract raw CNSL from cashew nut shells by solvent extraction method, isolate cardanol and determine some selected physical and chemical characteristics.

- ii) To prepare cardanyl acetate and cardanyl methyl ether and test their compatibility with alkyd coatings.
- iii) To formulate coating from cardanol, cardanyl acetate and cardanyl methyl ether with alkyd resin and characterize the coating formulation.
- iv) To test the coatings formed for physical – mechanical properties such as pencil hardness and adhesion.

CHAPTER TWO

MATERIALS AND METHODS

2.1 Materials and Equipment

Methyl Iodide (analar grade) was obtained from the Loba Chemie PVT limited Mumbai, India and acetic anhydride (analar grade) from Sigma Aldrich, Germany. Wijs solution analar grade (Sigma-Aldrich) and *n*-hexane general purpose reagent (Sigma-Aldrich) were used without further purification. Long oil alkyd resin (70%) and metal driers (32% lead naphthenate and 10% cobalt octoate) which were used for formulation with reactive diluents were obtained from Worlee-Chemie India Private Limited. Fourier Transform Infrared (FT - IR) spectroscopy was performed on Shimadzu 8400 FT-IR spectrometer located in Science Complex Chemistry Laboratory, JKUAT. Gas Chromatography-Mass Spectrometer analysis was carried out using a Finnigan GC 8000 series and interfaced with a Voyager Electron Impact-Mass Selective Detector, on an RTX-5MS column located in the Institute of Energy and Environmental Technology, JKUAT. Viscosity measurement was accomplished by NDJ-5S Digital Viscometer at room temperature (23°C) located in Chemistry Product Centre, JKUAT. Drying time study was evaluated using a Quadracycle Electronic Drying Time Recorder DT 5040 located at the New Science Complex, JKUAT.

2.2 Sample Collection and Preparation of the Cashew Nut Shells

Cashew nut shells were obtained from Kenya Nut Company in Thika, Kenya. Cashew nut shells were milled using screw press mills at the Biomechanical and Environmental Engineering Workshop in JKUAT. Cashew nut shell which formed part of the oil rich component was weighed and CNSL extracted using *n*-hexane solvent.

2.3 Extraction of Cashew Nut Shell Liquid

2.3.1 Cold Solvent Extraction Method

Milled cashew nut shell (200 g), and *n*-hexane solvent (600 g) were stirred together in a 2 L conical flask and allowed to stand overnight. CNSL was extracted twice with *n*-hexane using a two stage batch extraction process. Fresh solvent was employed per stage and stirred together to ensure maximum extraction. After settling of the tiny particle, the clear liquid was decanted while the solvent that remained in the cake was recovered using a simple distillation apparatus. The CNSL rich solvent was covered using aluminium foils to prevent loss of solvent. The CNSL was subsequently concentrated using a Rotary Evaporator, Buchi Rotavapor R 200 series in GK laboratory, JKUAT. and the solvent recovered for reuse. This procedure was done in triplicate and an average value taken as the yield of CNSL.

2.3.2 Decarboxylation of CNSL

Decarboxylation of raw CNSL was done to convert anarcadic acid into cardanol which would then be easy to isolate. Raw CNSL (305.2 g) was weighed into a beaker and allowed to undergo decarboxylation at 140°C for 2 hrs or until all effervescence was over (Risfaheri *et al.*, 2009). The decarboxylated CNSL was then weighed. This procedure was done in triplicate and an average value taken as the amount of decarboxylated CNSL obtained.

2.4 Isolation of Cardanol from CNSL

Decarboxylated CNSL (100 g) was dissolved in methanol (320 mL), and ammonium hydroxide (25%, 200 mL) was added and stirred for 15 min. This solution was then extracted with *n*-hexane (4 × 200 mL). The organic layer was washed with 5% HCl (100 mL) followed by distilled water (100 mL). Activated charcoal (10 g) was added to the organic layer, stirred for 10 min, and filtered through a filter paper. The filtrate was dried over anhydrous sodium sulfate and concentrated to get pure cardanol (Kumar *et al.*, 2002). The percentage yield of cardanol obtained was then determined in triplicate and an average value taken.

2.5 Synthesis of Cardanyl Acetate

The method described by Saeid and Somayeh (2010) was adopted. Cardanol (31.6 g), acetic anhydride (15.8 g), concentrated sulphuric acid (0.4 g) and acetonitrile (10 mL) were mixed together. The reaction mixture was refluxed at 80°C in an oil bath for 4.5 hrs. After completion of the reaction, the mixture was filtered off. The product was extracted with ethyl acetate (60 mL) and washed with water and finally dried over anhydrous sodium sulphate (20 g) to obtain pure product.

2.6 Synthesis of Cardanyl Methyl Ether

Cardanol (23.5 g), methyl iodide (30.3 g), anhydrous potassium carbonate (34.6 g) and acetone (100 mL) were mixed together. The mixture was refluxed in a hot plate for 8 hrs. After completion of the reaction, the mixture was poured into 500 mL of water in a beaker. The organic layer was separated using a separating funnel and extracted with (3 × 20 mL) diethyl ether. The combined organic layer and diethyl ether extract was washed with 2 M sodium hydroxide solution (60 mL) and dried over anhydrous sodium sulphate (20 g). The diethyl ether was removed in a rotary evaporator under reduced pressure to obtain pure product (Brian *et al.*, 1989).

2.7 Characterization of CNSL, Decarboxylated CNSL, Cardanol, Cardanyl Acetate and Cardanyl Methyl Ether.

2.7.1 Determination of Specific Gravity

A dry pycnometer (25 mL capacity) was weighed and its weight recorded. The pycnometer was filled with distilled water, dried on the outer side and the weight recorded. This was repeated using two other values and the corresponding weights obtained recorded. The pycnometer was then oven dried, cooled to room temperature, filled with CNSL and the weight measured. This procedure was also repeated for decarboxylated CNSL, cardanol, cardanyl acetate and cardanyl methyl ether in triplicates and an average value of the samples taken as the result for the samples.

2.7.2 Determination of Iodine Value

Raw CNSL (0.51 g), decarboxylated CNSL (0.51 g) and cardanol (0.51 g) were weighed into separate 250 mL conical flasks and dissolved using 10 mL of chloroform each. Chloroform (10 mL) was added into a conical flask containing no sample. Wij's solution (25 mL) was added into each conical flask containing sample and an equal volume to the blank. Each flask was shaken vigorously and allowed to stand in the dark for 30 mins. The solutions in each flask were diluted with 70 mL of water and 25 mL of 10% KI solution. Four drops of starch indicator solution was added to each flask and the sample and blank titrated using 0.1N sodium thiosulphate solution to the end point (Kailas *et al.*, 2013). This procedure was repeated in triplicate for each sample and an average value of the samples taken as the result for the samples.

2.7.3 Determination of Acid Value

Raw CNSL (1.3 g) was weighed accurately into a 250 mL conical flask. Diethyl ether (25 mL) and ethanol (25 mL) were mixed and introduced into the conical flask and three drops of phenolphthalein indicator added. The solution was shaken until the fatty acids present in the oil dissolved. This solution was titrated with 0.1N aqueous KOH while shaking. This procedure was repeated in triplicates for raw CNSL, decarboxylated CNSL, cardanol, cardanyl acetate and cardanyl methyl ether and an average value of the samples taken as the result for the samples.

2.7.4 Determination of pH

Measurement of pH was done using a pH meter from Hanna Instruments Model 211 Microprocessor. The pH meter was calibrated using buffer 4 and 7 and readings were obtained by inserting the probe of the pH meter into raw CNSL and three values were taken. This procedure was repeated for decarboxylated CNSL, cardanol, cardanyl acetate and cardanyl methyl ether in triplicates and an average result taken for the samples (Ahmad *et al.*, 2013).

2.7.5 Determination of Moisture Content

Moisture content was determined using a Dean and Stark apparatus (Robert *et al.*, 2006). CNSL (10 g) was weighed and transferred into a 500 mL round bottomed flask and toluene (75 mL) was added to the test sample. The receiving tube was filled with toluene by pouring it through the top of the condenser until it began to overflow into the distillation flask. A loose cotton wool was inserted on top of the condenser to prevent condensation of atmospheric moisture in the tube. The mixture was brought to boil and refluxed slowly at the rate of two drops per second until most of the water distilled over. The rate of distillation was increased to four drops per second and continued until two consecutive readings fifteen minutes apart showed no change. Any water held up in the condenser was dislodged. The distillation was continued for five minutes and the receiver cooled to room temperature by allowing it to stand in air. Solvent and water layers were seen clearly and the reading obtained. This procedure was repeated in triplicates for decarboxylated CNSL, cardanol, cardanyl acetate and cardanyl methyl ether and an average value taken as the result for the samples. Moisture content was calculated according to the formula below.

$$\text{Moisture content (\% by weight)} = 100 \times V/M$$

Where V = Volume in ml of water collected

M = Weight of sample

2.7.6 Determination of Viscosity

Capillary viscometer number 3 was mounted on a water bath that had stabilized at 40°C. Distilled water (10 mL) was measured and put into the viscometer using a pipette. The time taken for water to move from the upper mark to the lower mark was recorded. This procedure was repeated in triplicates for raw CNSL, decarboxylated CNSL, cardanol, cardanyl acetate and cardanyl methyl ether and an average value taken as the result for each of the samples (John, 2003).

2.7.7 Fourier Transform Infrared Analysis

Fourier Transform Infrared (FT - IR) spectra were obtained using a Shimadzu Model 8400 Spectrometer located in Science Complex Chemistry Laboratory, JKUAT (Appendix I). Samples (1 g) dissolved in carbon tetra chloride (10 mL) were prepared. Thin liquid samples were then casted on a KBr plates and ran in FTIR machine and the various peaks recorded (John, 2000).

2.7.8 Gas Chromatography - Mass Spectrometer

Gas Chromatography - Mass Spectrometer (GC - MS) analysis was carried out using a Finnigan GC 8000 series and interfaced with a Voyager Electron Impact-Mass Selective Detector, on an RTX-5MS column located in the Institute of Energy and Environmental Technology, JKUAT (Appendix II). Sample (1 mg) was dissolved in 10 mL of dichloromethane and 1 μ L of this solution was injected into the GC - MS. The temperature was programmed from 50 to 250°C at 10°C/ min and maintained at 250°C for 30 min (Kumar *et al.*, 2002).

2.8 Formulation of Alkyd Resin Coating with Reactive Diluent

The formulation described by Muturi (1984) was adopted. The alkyd resin (70% wt; 143 g) was diluted with cardanol, cardanyl acetate and cardanyl methyl ether at weight percentages of 0, 5, 10, 15, 20, and 25%. Metal driers were added at levels of 1 and 0.6% for lead naphthenate and cobalt octoate respectively (Appendix III). In addition, white spirit was incorporated at weight percentages of 50, 45, 40, 35, 30 and 25%.

2.8.1 Preparation of Metal Surfaces

Clean mild steel panels were applied with coatings containing alkyd resin (70% wt solution in white spirit) and reactive diluents using a Bird Film Applicator (2 mils wet film). The wet films were cured at room temperature for 10 days before any tests were

performed to ensure a through cure was achieved. All experiments were performed in triplicate for each formulation and controls.

2.8.2 Test for Volatile Organic Compounds

Testing of volatile organic compounds (VOCs') was done in a dry oven Model Advantec KL-420 Electric Muffle Furnace from Toyo Seisakusho Company limited. It was operated by adopting the ASTM standard D 2369 (2004). The oven was preheated to 110 °C for approximately 30 min. A crucible was weighed using a Denver Instrument XL-1810 Scale. This weight was recorded. While the crucible was still on the scale, the scale was tared and approximately 1 g of the sample swirled onto the crucible. After the samples had been prepared, they were placed into the preheated oven for 60 min. At the conclusion of 60 min, the samples were immediately removed from the oven, allowed to cool on the bench and weighed. The percent volatile was calculated according to the formula below. An average value of the samples was taken as the result for each of the samples.

$$\text{Volatile content, (\%)} = \frac{w_2 - w_3}{w_2 - w_1} \times 100$$

Where, w_1 = weight of crucible, g

w_2 = weight of crucible + sample, g

w_3 = weight of crucible + sample, after heating, g

2.8.3 Test for Viscosity

The viscosity was measured by NDJ-5S Digital Viscometer at room temperature (23°C) located in Chemistry Product Centre, JKUAT (Appendix IV). Rotor number one was used at 60 rotations per min rotating speed (shear rate of 100 mPa.s). Approximately 200 g of samples was put in a 250 mL beaker and mixed for 30 min (John, 2003).

2.8.4 Test for Drying Time

Drying time study was evaluated by adopting ASTM standard D 5895-03 (2008) method using a Quadracycle Electronic Drying Time Recorder DT 5040 (Appendix VI) from Gardco Company, USA. The coating (2 mils) wet film formulation was applied to clean glass panels using a Bird Film Applicator (Appendix V) and a circular dry time recorder was immediately placed on the wet film and switched on. The drying time was observed and recorded.

2.8.5 Test for Adhesion of Coating Film to the Metal Surface

Adhesion test study was evaluated by adopting ASTM standard D 3359-09e2 (2009). Cross-cut tape test was undertaken to assess the adhesion of coatings on the metal. After curing the coating by air-drying for 10 days, the panels were held firmly and then six cross-cuts, 1 mm apart, were made manually on the coated surface. The detached flakes or ribbons of coating were removed from the surface with a soft brush. A strip of fiber-reinforced cellulose acetate pressure-sensitive tape was then applied over the surface of the metal panel. The tape was manually smoothed, and pressure was applied using a rubber eraser to ensure good contact between the tape and the coating film. After 1 min of application, the tape was removed from the coated surface by rapidly pulling it off, back upon itself, at an angle as close to 180° as possible. The grid area was inspected for removal of coating from the panel surface using an illuminated magnifier. The rate of adhesion was averaged for six panels of each group based on the code given in the standard for classification.

2.8.6 Test for Pencil Hardness

This test was carried out by adopting the ASTM D 3363 (2011) method using a HA - 3401 Gardco/Wolff Wilborn mechanical pencil scratch hardness kit. Pencils of increasing hardness values were moved over the substrate surface in a precisely defined way using a Mechanical Pencil Lead Holder by applying sufficient pressure so that the coating film was damaged by the lead or the pencil point were crushed. In this experiment, if the pencil cut through the coating film then the pencil was harder

than the coating. On the other hand if the pencil was not able to cut through, the coating was considered harder than the pencil. Surface hardness was defined by the hardest pencil grade which failed to damage the surface.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Yield of Raw Cashew Nut Shell Liquid, Decarboxylated CNSL, Cardanol, Cardanyl Acetate and Cardanyl Methyl Ether

3.1.1 Yield of Raw CNSL and the Amount of Solvent Recovered

The yields of raw CNSL and percentage recovery of the solvents are presented in Table 3.1.

Table 3.1: Yield of raw CNSL and the amount of solvent recovered

Amount of ground cashew nut shell used (g)	200
Amount of raw CNSL obtained (g)	62.77
Average % yield (w/w)	30.9 ± 0.2
Solvent used (g)	600
Solvent recovered (g)	432
Average % recovered solvent (w/w)	72

Cold solvent extraction of ground cashew nut shells with *n*-hexane gave an average percentage yield of $30.9 \pm 0.2\%$ g/g in the two stage recovery process of CNSL. The amount of solvent recovered was 72% g/g implying that about 28% of the solvent was lost during the extraction process and pre-concentration process.

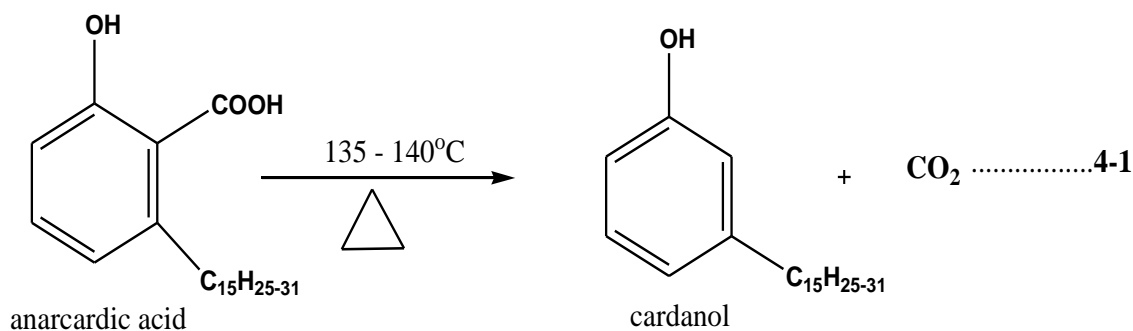
3.1.2 Yields of Decarboxylated CNSL, Cardanol and the Amount of Solvent Recovered

The percentage yields of decarboxylated CNSL, cardanol and the amount of solvent recovered are presented in Table 3.2.

Table 3.2: Percentage yield of decarboxylated CNSL, cardanol and the amount of solvent recovered.

Weight of raw CNSL (g)	305.2
Weight of decarboxylated CNSL (g)	260.46
Percentage yield of decarboxylated CNSL (w/w)	85.34 ± 0.02
Amount of decarboxylated CNSL used (g)	30
Amount of cardanol obtained (g)	19.54
Average % yield (w/w)	63.93 ± 0.20
Solvent recovered (g)	94
Average % recovered solvent (w/w)	78.01

Decarboxylation of CNSL was done at 135 - 140°C for 2 hrs (reaction **4-1**) and gave an average percentage yield of 85.34 ± 0.02% g/g. During decarboxylation there was the loss of carbon dioxide as a gas, moisture content and possibly small residues of solvent. The average percentage yield of isolated cardanol was found to be 63.93 ± 0.2% compared to 70% from literature (Bharat *et al.*, 2012). The yield of isolated cardanol was high implying that the chemical method of extraction is very efficient. The solvent recovered for extraction of cardanol was 78% implying that about 22% of the solvent was lost to the environment.



3.1.3 Yield of Cardanyl Acetate and Cardanyl Methyl Ether

The results for synthesized cardanyl acetate and cardanyl methyl ether are presented on Table 3.3

Table 3.3: Percentage yield of cardanyl acetate and cardanyl methyl ether

Cardanol (31.6 g) + acetic anhydride (15.8 g)	47.4
Cardanyl acetate obtained (g)	27.93
Average percentage yield obtained (% w/w)	$58.94 \pm 0.01\%$
Cardanol (23.5 g) + methyl iodide (30.3 g)	53.8
Cardanyl methyl ether obtained (g)	28.19
Average percentage yield obtained (% w/w)	$52.39 \pm 0.01\%$

Mean \pm Standard Deviation, n = 3

The Cardanyl acetate synthesized had an average percentage yield of $58.94 \pm 0.01\%$ and hence the yield was good as compared to $52.39 \pm 0.01\%$ of cardanyl methyl ether which was a bit low.

3.2 Characteristics of Raw CNSL, Decarboxylated CNSL and Cardanol

Results for characteristics tests as presented on Table 3.4.

Table 3.4: Characteristics of raw CNSL, decarboxylated CNSL and cardanol

Parameter	Raw CNSL	Decarboxylated CNSL	Cardanol
Specific gravity at 25 °C, g/ cm ³	0.988 ± 0.001	0.957 ± 0.001	0.947 ± 0.001
pH at 25 °C	3.07 ± 0.01	6.02 ± 0.01	6.16 ± 0.01
Iodine value, g/100 g	231.5	231.2	232.0
Acid value, g/100 g KOH	12.643 ± 0.001	1.732 ± 0.001	1.176 ± 0.001
Viscosity at 40 °C, mPa.s	52.36 ± 0.10	46.56 ± 0.10	45.31 ± 0.10
Moisture content (%)	0.55	< 0.01	< 0.01

Mean ± Standard Deviation, n = 3

There was a significant variation in the specific gravity of the three samples. Raw CNSL had a high relative density because it has anarcadic acid as the major fraction; there are intermolecular and intramolecular hydrogen bonds which contribute to attraction between the electronegative oxygen atom and the partially positive hydrogen atom within the molecule and between the molecules as a result the molecules are closely packed together. Decrease in specific gravity in decarboxylated CNSL was due to the release of CO₂ gas, which decreased the effect of intermolecular and intramolecular hydrogen bonding (Morrison and Boyd, 2002). There was a significant variation in the pH values of the three samples. The high pH value in raw CNSL was attributed to the presence of the carboxylic acid functional group. There was no significant variation in the iodine values of the three samples. This is because

iodine value is a measure of the amount of unsaturation in given oil and unsaturation of the samples due to the side chain was the same for the three samples. The iodine values of more than 140 in the samples showed that they are drying oils. From Table 3.4 it is clear that the acid value of the three samples showed a significant variation. Raw CNSL indicated a high acid value as compared to decarboxylated CNSL and cardanol because of the presence of the carboxylic acid group. There was a significant variation in the viscosity values of the three samples. Raw CNSL has a combination of intermolecular and intramolecular hydrogen bonding which results in the molecule being held together (Table 3.4). There was a significant difference in the moisture content of the three samples. Raw CNSL had high moisture content because during processing of cashew nut the nuts are soaked in water which then imbibes some water. During the decarboxylation process, the moisture was lost since high temperatures are involved.

3.3 Comparison of the Characteristics of Cardanol, Cardanyl Acetate and Cardanyl Methyl Ether

The characteristics of cardanyl methyl ether, cardanyl acetate and cardanol are presented in Table 3.5.

Table 3.5: Characteristics of cardanyl methyl ether, cardanyl acetate and cardanol

Parameter	Cardanyl methyl ether	Cardanyl acetate	Cardanol
Specific gravity at 25 °C, g/cm ³	0.926± 0.001	0.963± 0.001	0.947 ± 0.001
Viscosity at 40 °C, mPa.s	36.10 ± 0.10	42.06 ± 0.10	45.31± 0.10
Iodine value, g/100 g	232.6	232.4	232.0
Moisture content (%)	< 0.01	< 0.01	< 0.01
pH at 25 °C	7.01 ± 0.01	6.23 ± 0.01	6.16 ± 0.01

Mean ± Standard Deviation, n = 3

There was a significance difference in the viscosity values of neat cardanol, cardanyl acetate and cardanyl methyl ether. Cardanyl methyl ether had the lowest viscosity due to its molecular structure. The substituent in the phenyl core arranged themselves in such a way that they did not interact as the molecule flew down the capillary tube. In neat cardanol, there was molecular interaction (intermolecular hydrogen bonding) which resulted in the entanglement of the long aliphatic chain and the viscosity was increased. There was no significance difference in the iodine values of neat cardanol, cardanyl acetate and cardanyl methyl ether. This showed that methylation and acetylation of cardanol with methyl Iodide and acetic anhydride respectively did not affect the unsaturation of the side chain. There was no significance difference in the moisture content of the three products.

3.4 Identification of Decarboxylated CNSL, Cardanol, Cardanyl Acetate and Cardanyl Methyl Ether Using Fourier Transform Infra-Red (FT - IR) Spectroscopy

The Fourier Transform Infra-Red Spectras for decarboxylated CNSL, cardanol, cardanyl acetate and cardanyl methyl ether are presented in Figs. 3.1, 3.2, 3.3, and 3.4, respectively.

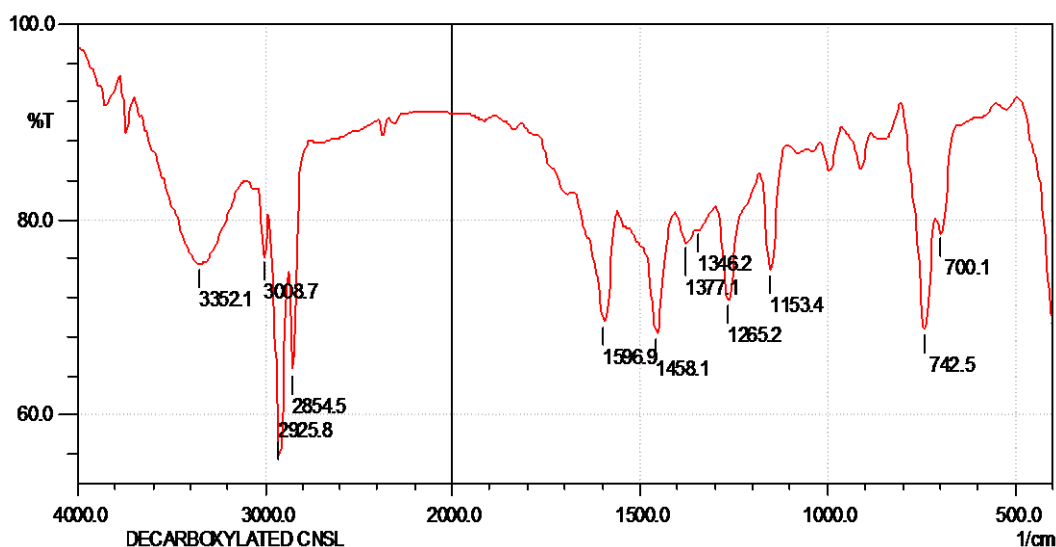


Figure 3.1: FT - IR spectrum for decarboxylated CNSL

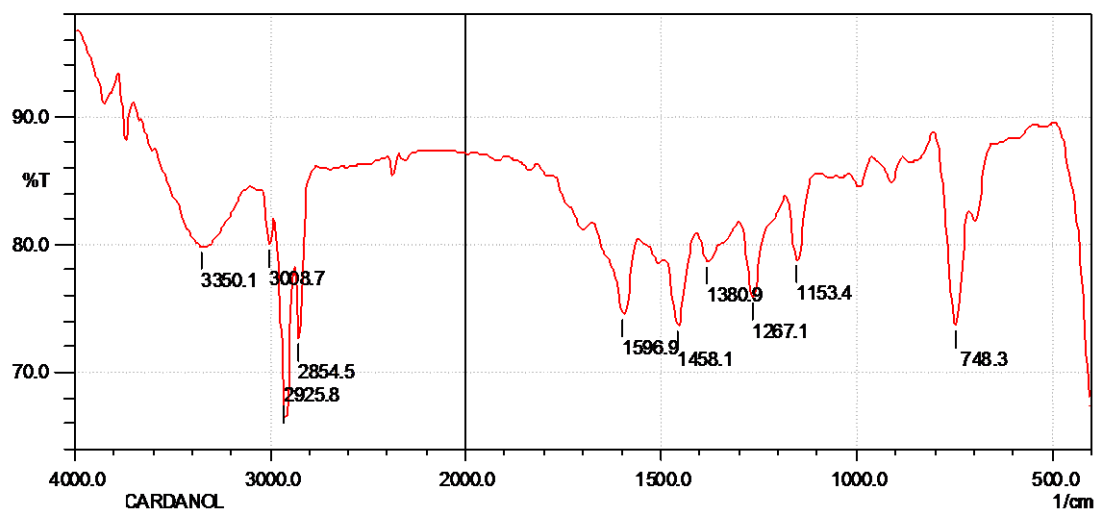


Figure 3.2: FT - IR Spectrum for cardanol

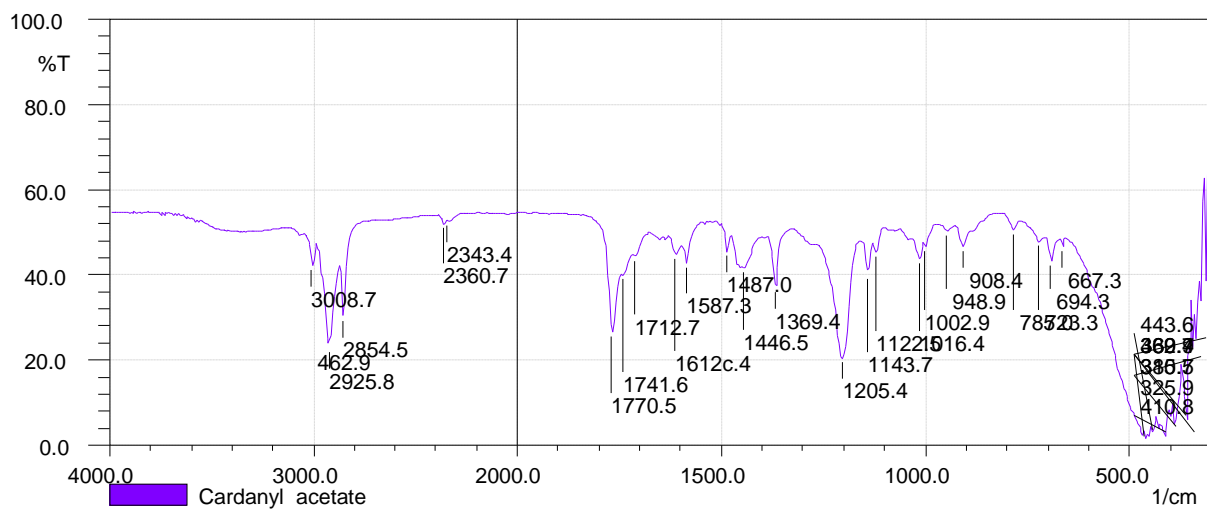


Figure 3.3: FT - IR Spectrum for cardanyl acetate

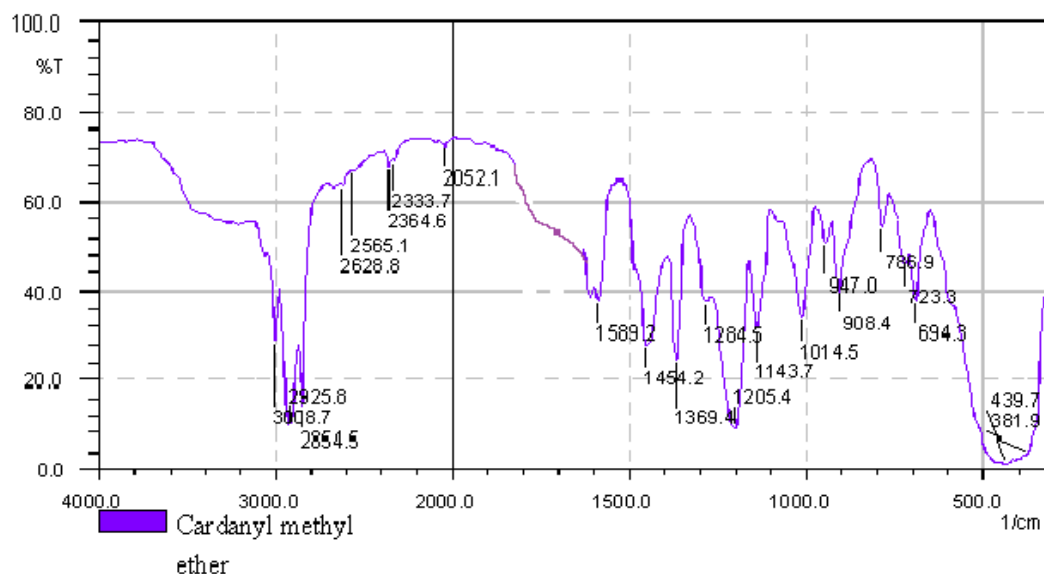


Figure 3.4: FT - IR Spectrum for cardanyl methyl ether

The peaks at frequency of 3352.1 and 3350.1 cm^{-1} indicated the presence of OH group of phenolic compounds (Fig. 3.1 and 3.2, respectively). The peaks that appeared at frequency of 3008.7 cm^{-1} indicated the presence of C-H symmetrical stretch of the aromatic compounds as shown in Figs. 3.1, 3.2, 3.3 and 3.4. The peaks that appeared at frequency 2925.8 cm^{-1} indicated the presence of methylene C-H symmetrical stretch of the long aliphatic chain (Figs. 3.1, 3.2, 3.3 and 3.4). The peak that appeared at 1265.2 cm^{-1} indicated C-O symmetrical stretch of the phenolic compounds. The absorption peak that appeared at the 1596.9 cm^{-1} frequency indicated C=C bonds of the long aliphatic chain (Figs. 3.1 and 3.2), while the peak that appeared in the 1458.1 cm^{-1} frequency indicated the C=C symmetrical stretch of the aromatic chains. The peak that appeared at frequency 1770.5 cm^{-1} (Fig. 3.3) indicated the presence of C=O symmetrical stretch for an ester. The peak at frequency 1205.4 cm^{-1} area indicated C-O symmetrical stretch characteristic of an ether (Fig. 3.4) while that at frequency 1143.7 cm^{-1} indicated C-O-C symmetrical stretch characteristic of an ether.

3.5 Interpretation of GC-MS Spectra for Raw CNSL, Decarboxylated CNSL, Cardanol, Cardanyl Acetate and Cardanyl Methyl Ether

Figs. 3.5, 3.6, 3.7, 3.8 and 3.9 represent the GC-MS profile for raw CNSL, decarboxylated CNSL, cardanol, cardanyl acetate and cardanyl methyl ether, respectively.

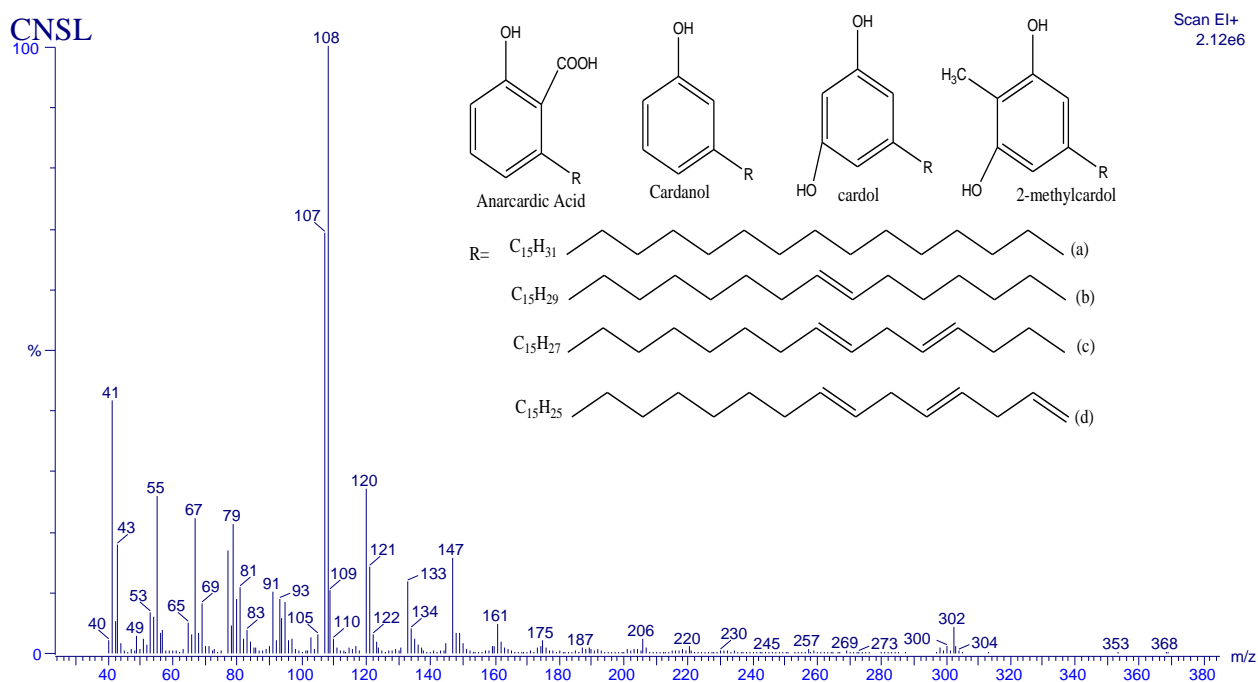


Figure 3.5: GC-MS profile of raw CNSL

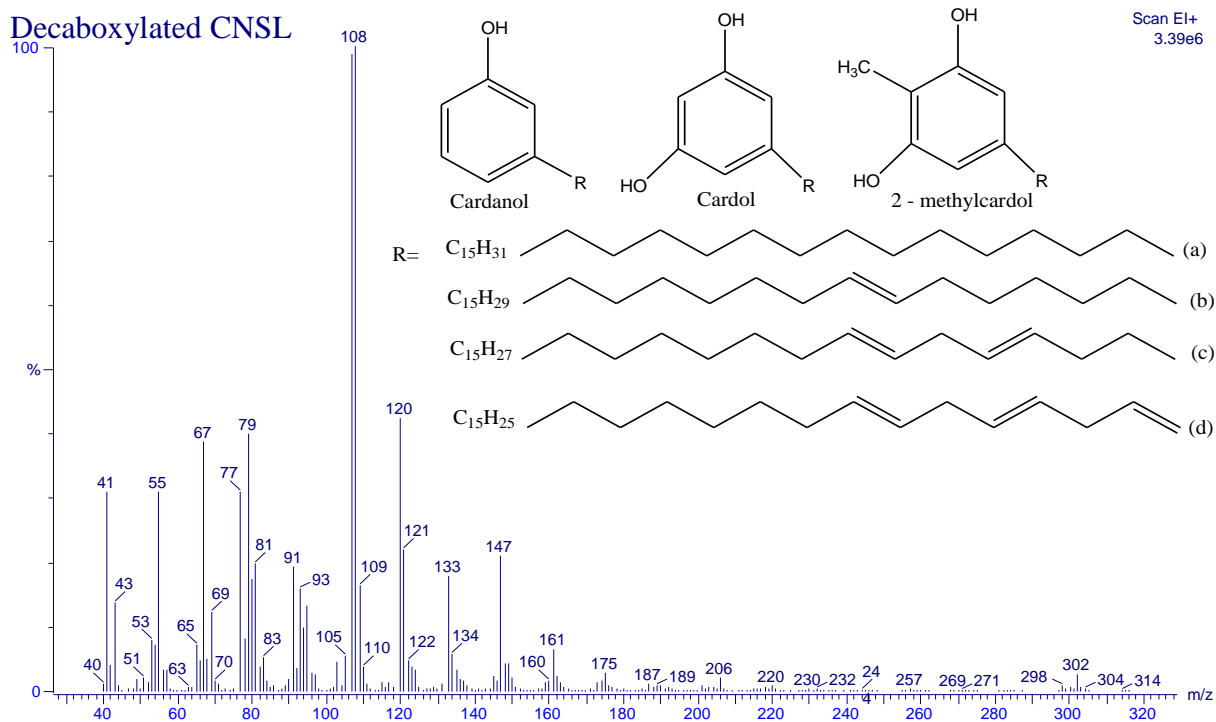


Figure 3.6: GC-MS profile of decarboxylated CNSL

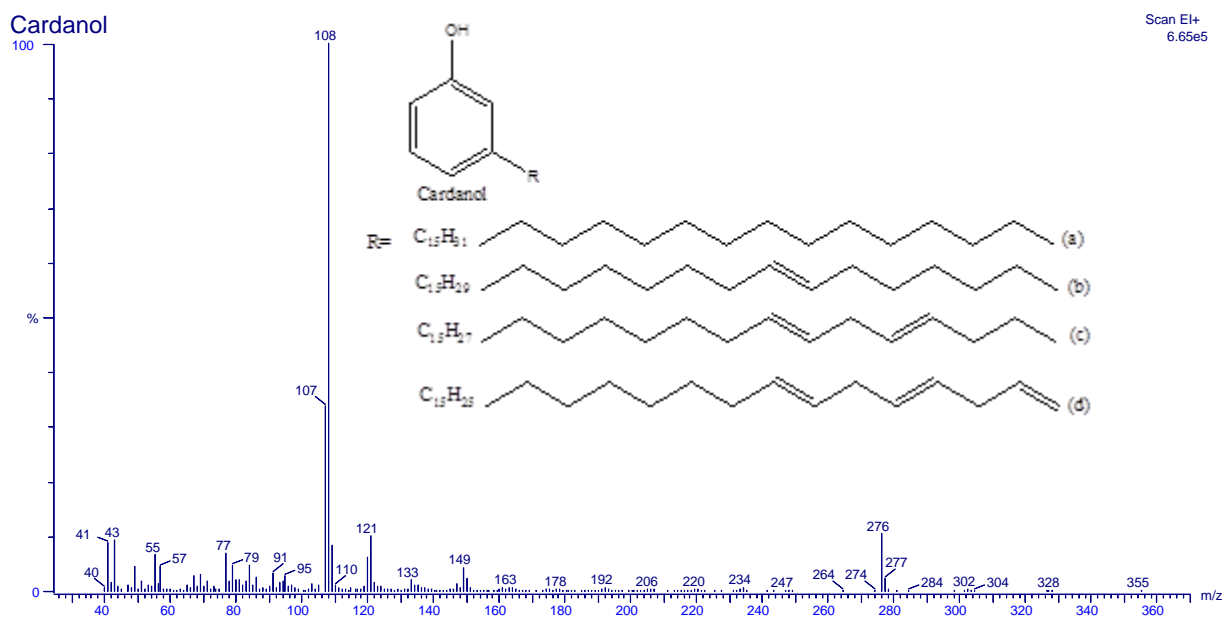


Figure 3.7: GC-MS profile of cardanol

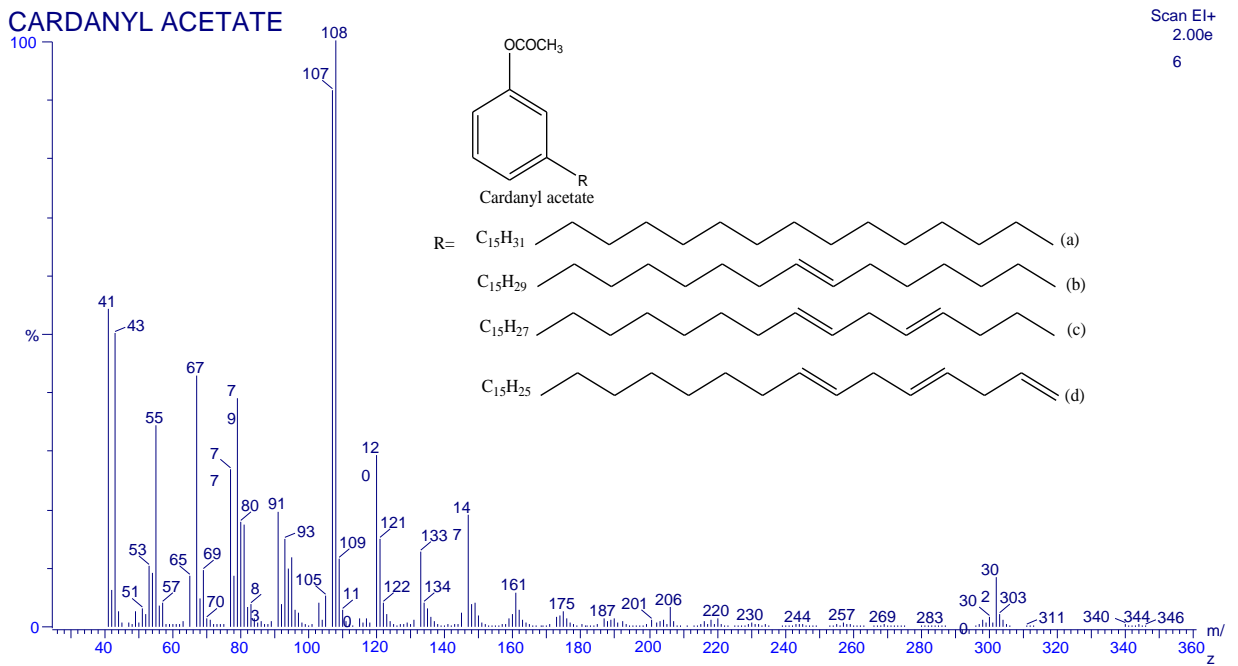


Figure 3.8: GC-MS profile of cardanyl acetate

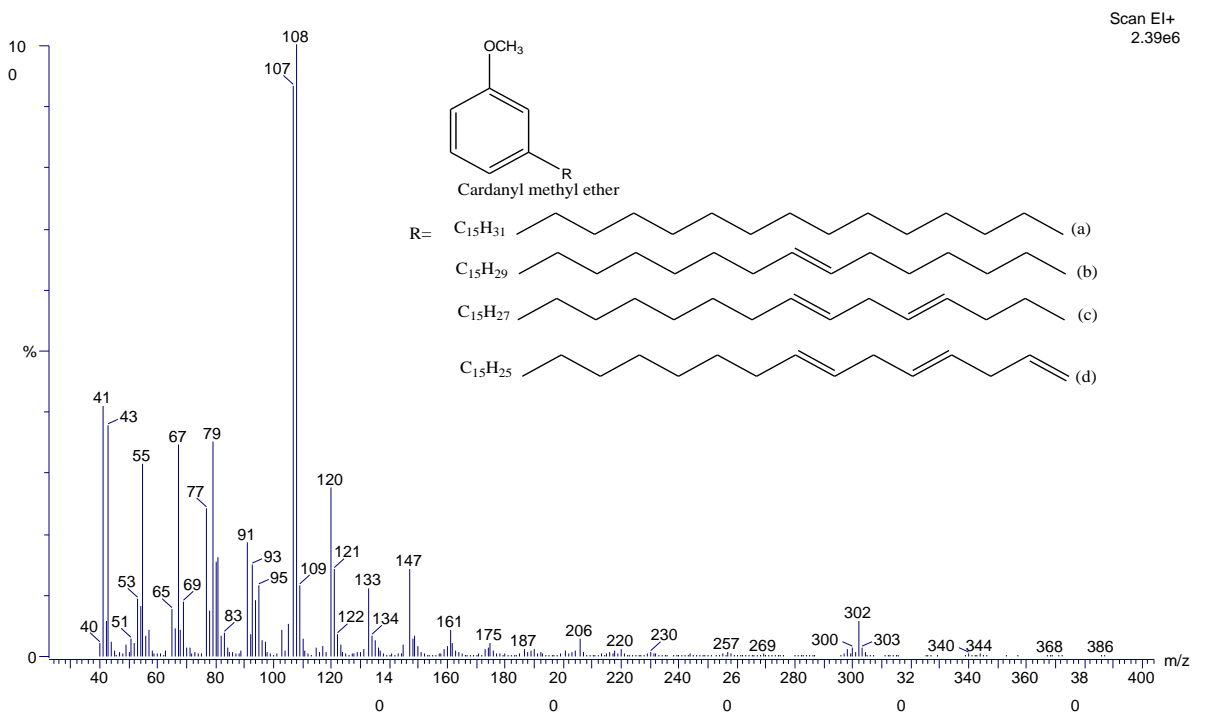
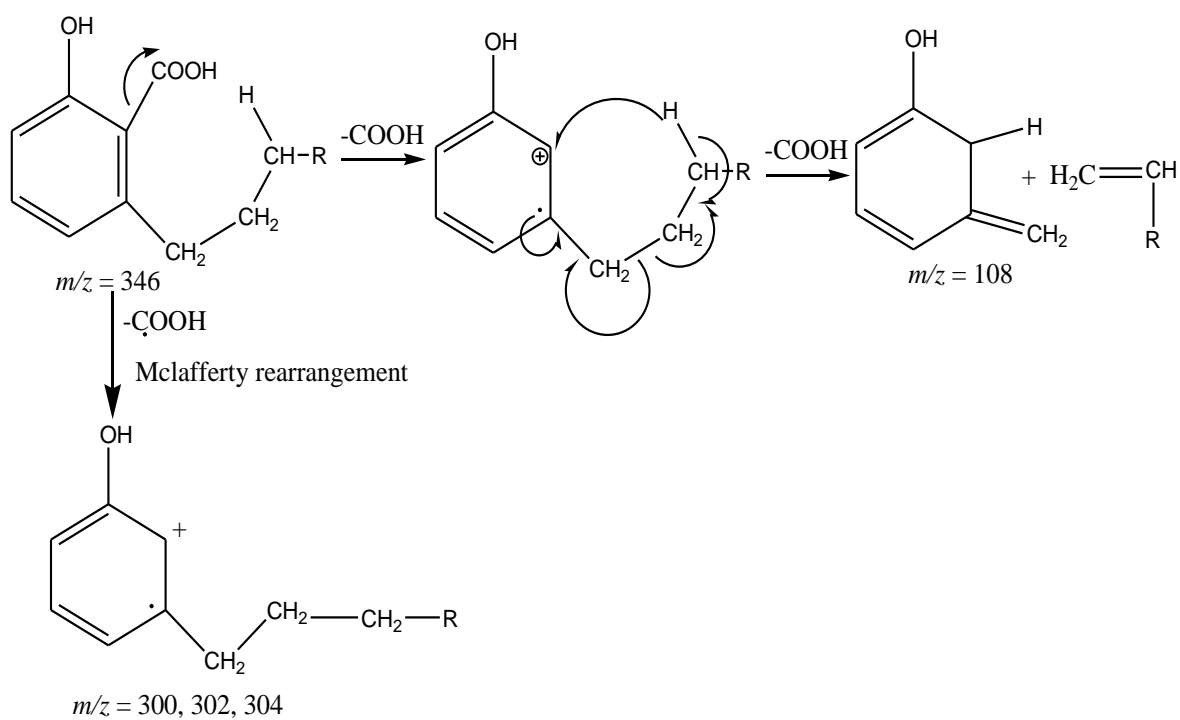
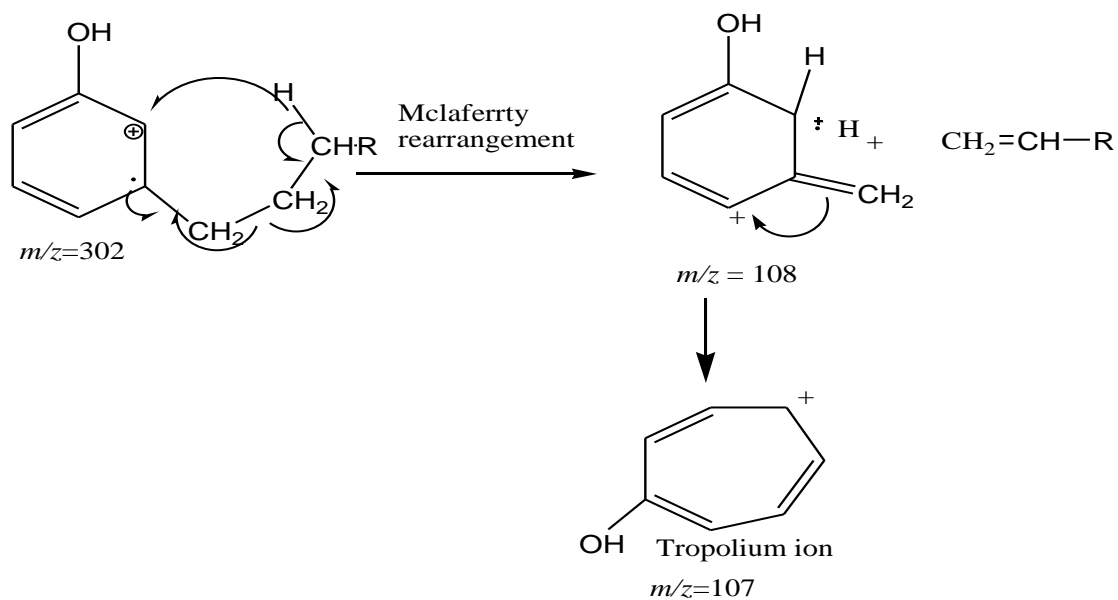


Figure 3.9: GC-MS profile for cardanyl methyl ether

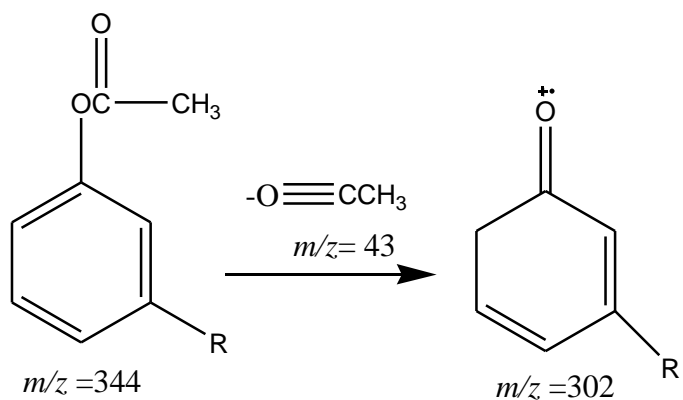
A phenolic compound consisting of an aliphatic chain will experience fragmentation in the β position of the alkyl chain to form tropylium ions which are more stable (Fred and Frantisek, 1993). This position gave a base of $m/z = 108$ as shown in Fig. 3.5, 3.6, 3.7, 3.8 and 3.9. Scheme 3.2 shows the fragmentation of cardanol to give tropylium ions. The peaks at $m/z = 300, 302$ and 304 correspond to the molecular ion of 3(-8Z,11Z pentadecadienyl) -phenol, 3(-8Z-pentadecenyl)- phenol, 3(-pentadecyl) phenol respectively and are as a result of fragmentation of the COOH group of anarcadic acid to form cardanol (Fig. 3.1) since the identification was done at a high temperature of $100 - 250^\circ\text{C}$. These peaks are also present in decaboxylated CNSL and cardanol (Figs. 3.6 and 3.7, respectively). The peak at $m/z = 302$ in Fig. 3.8 is attributed to the cleavage of $^+\text{COCH}_3$ $m/z = 43$ group from molecular ion as shown in the fragmentation pattern in scheme 3.3. The Peaks at $m/z = 340, 344$ and 346 correspond to the molecular ions of the three fractions of cardanyl acetate Fig. 3.8. Cardanyl methyl ether fragments by first cleavage of the long aliphatic chain $m/z = 306$ to form a radical center in the molecular ion. The molecular ion then undergoes McLafferty rearrangement whereby a radical center in the molecular ion derived from a lone pair or a pi-bond, abstracts a hydrogen from the alpha (α) position of the ether (Scheme 3.4) (Fred and Frantisek, 1993).



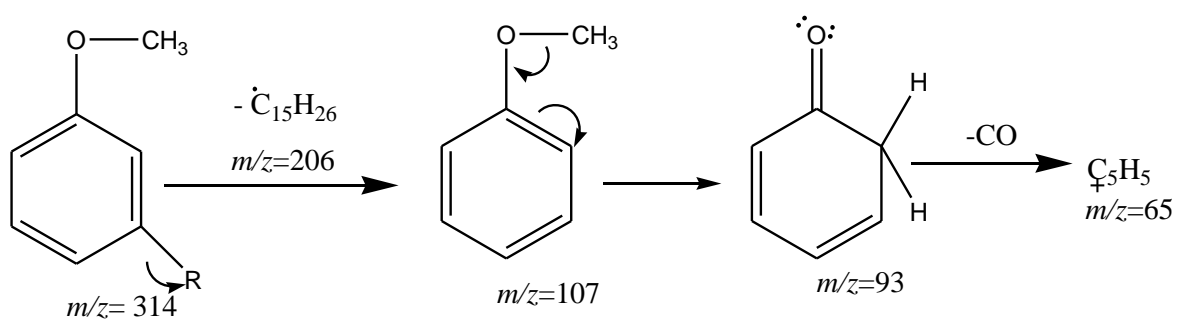
Scheme 3.1: Fragmentation of anarcadic acid



Scheme 3.2: Fragmentation of cardanol



Scheme 3.3: Fragmentation of cardanyl acetate



Scheme 3.4: Fragmentation of cardanyl methyl ether

3.6 Volatile Organic Compounds

The Volatile Organic Compounds for all the formulations studied is reported in Table 3.6. Cardanol, cardanyl acetate and cardanyl methyl ether reduce VOCs' when used as reactive diluents.

Table 3.6: Volatile Organic Compounds in alkyd resin coatings formulations with different reactive diluents

Percentage reactive diluent	VOC (% wt) Cardanol	VOC (% wt) Cardanyl acetate	VOC (% wt) Cardanyl methyl ether
0	47.24 ± 0.2	47.17 ± 0.2	47.21 ± 0.3
5	45.90 ± 0.3	45.81 ± 0.3	46.51 ± 0.2
10	44.59 ± 0.1	44.63 ± 0.2	44.71 ± 0.3
15	43.72 ± 0.2	43.83 ± 0.1	43.79 ± 0.2
20	41.20 ± 0.3	41.31 ± 0.2	41.41 ± 0.3
25	39.23 ± 0.2	39.28 ± 0.2	39.31 ± 0.2

Mean ± Standard Deviation, n = 3

The study indicates that it is possible to formulate compositions having substantially lower VOCs' and higher solids due to lower viscosities of cardanol, cardanyl acetate and cardanyl methyl ether compared to commercially prepared formulations. Cardanyl acetate, cardanyl methyl ether and cardanol had good solubility and compatibility with alkyd resin resulting in very low Volatile Organic Coating formulations.

3.7 Viscosity of the Coating Formulations

A Plot of the viscosity versus percentage of neat cardanol, cardanyl acetate and cardanyl methyl ether are presented in Fig 3.10. The viscosity of a reactive diluent is an important characteristic because it determines the flow of the liquid.

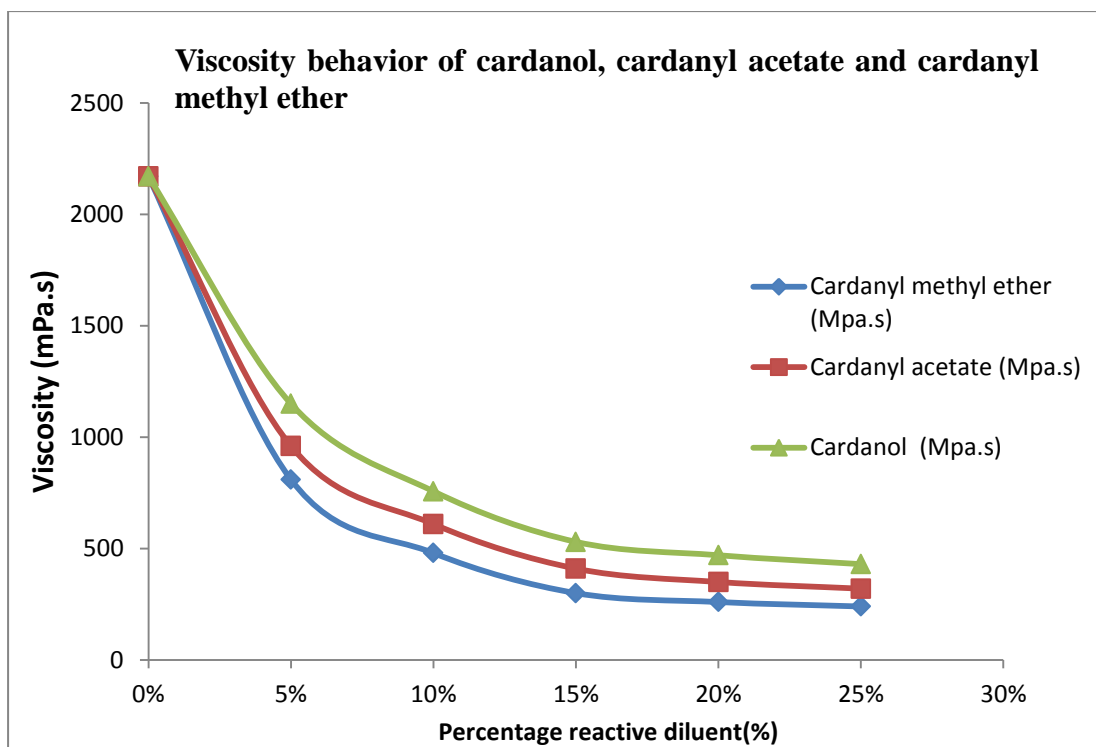


Figure 3.10: Viscosity levels of cardanol, cardanyl acetate and cardanyl methyl ether

The viscosity reducing abilities of cardanyl methyl ether, cardanyl acetate and cardanol were tested at different weight percentages in alkyd coatings. The prediction showed that there was a decrease in viscosity as the amount of reactive diluent (cardanol, cardanyl acetate and cardanyl methyl ether) was increased. It was found that cardanyl methyl ether had an inherently lower viscosity than cardanyl acetate and neat cardanol due to decreased effect of hydrogen bonding. The high viscosity in Cardanol was due to the presence of OH group that increased the hydrogen bonds with the alkyd resin. Cardanyl methyl ether, cardanyl acetate and neat cardanol all showed good compatibility with alkyd resin.

3.8 Drying Performance of Reactive Diluent–Alkyd Formulations

Drying times increased with increasing reactive diluent concentration (Table 3.7). The amount of diluent added into the system caused the drying mechanism to be slower.

Table 3.7: Drying times of alkyd coating formulations blended with different reactive diluents

Weight (%)	Alkyd/ cardanol (hrs)	Alkyd/cardanyl acetate (hrs)	Alkyd/ cardanyl methyl ether (hrs)
0	6	6	6
5	7	7	7
10	7	7	7
15	7	7	7
20	8	8	7
25	8	8	8

Drying times of alkyd coatings with cardanol, cardanyl acetate and cardanyl methyl ether were between 7 and 8 hrs. Feasibility of cure for cardanol, cardanyl acetate and cardanyl methyl ether could be explained by the higher functionality due to the double bonds and low viscosity of the system. Low viscosity provided mobility to the long aliphatic chain to react, and hence the curing time was faster.

3.9 Pencil Hardness for Neat Cardanol, Cardanyl Acetate and Cardanyl Methyl Ether –Alkyd Films

Pencil hardness results for cardanol, cardanyl acetate and cardanyl methyl ether are presented in Table 3.8.

Table 3.8: Pencil hardness test on coatings based on alkyd resin with: i) cardanol, ii) cardanyl acetate and iii) cardanyl methyl ether mixture (after 10 days of curing)

Percentage reactive diluents (%)	Cardanol (H)	Cardanyl acetate (H)	Cardanyl methyl ether (H)
0	5	5	5
5	4	4	4
10	4	4	4
15	4	4	4
20	4	4	4
25	4	4	4

ASTM 5H: Hard, 4H: Fairly Soft

The pencil hardness of the films remained fairly constant for systems containing neat cardanol, cardanyl acetate and cardanyl methyl ether. All films were relatively soft (4H), based on the pencil hardness tests (Table 3.8), and all films displayed constant hardness with reactive diluent as compared to the control which was a little bit hard (5H) which had no reactive diluent. All these reactive diluents had comparable pencil hardness because they contain a rigid aromatic structure due to the benzene ring (Ramya *et al.*, 2000).

3.10 Adhesion for Cardanol, Cardanyl Acetate and Cardanyl Methyl Ether – Alkyd Films

Results for adhesion of coatings on metal surfaces for the various percentages of reactive diluents are presented in Table 3.9.

Table 3.9: Adhesion test on alkyd resin coatings with varying percentages of cardanol, cardanyl acetate and cardanyl methyl ether allowed to cure for 10 days

Percentage reactive (%)	Cardanol (B)	Cardanyl acetate (B)	Cardanyl methyl ether (B)
0	5	5	5
5	5	5	5
10	4	4	4
15	4	4	4
20	4	4	4
25	4	4	4

ASTM 5B: Excellent, 4B: Good, 3B: Fair

Addition of reactive diluents with the metal driers resulted in films with good adhesion (**4B**) for all the three products from 10 to 25% reactive diluent added compared to 5% reactive diluent added for all the formulations and the control which had excellent (**5B**) adhesion (Table 3.9). Crosslink density versus time was improved in all reactive diluent–alkyd mixtures relative to controls. These results validate that the reactive diluents play a role in increasing chemical cross-linking between alkyds and the reactive diluent.

CHAPTER FOUR

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

A High percentage of Cashew Nut Shell Liquid (CNSL) was extracted by the cold solvent extraction method. A percentage of up to $30.9 \pm 0.2\%$ w/w was obtained implying that solvent extraction method is an efficient and effective method. Data based on the characteristics of CNSL showed that CNSL had a high specific gravity of up to 0.988 ± 0.001 . Isolation of cardanol using methanol and ammonium hydroxide gave a high yield of up to 63.93 ± 0.20 implying that the chemical method of isolation was very effective.

Moderate yields of cardanyl methyl ether and cardanyl acetate were realized. This study has shown that incorporation of cardanol, cardanyl acetate and cardanyl methyl ether acted effectively as reactive diluents since they were found to be compatible with alkyd coatings.

Characterization of the coating formulation showed that the amount of Volatile Organic Compounds (VOCs') that is added into alkyd coating was greatly reduced to the extent of 39%. The study reveals that there was significant reduction in the amount of VOCs' that are added to the atmosphere. . Use of modified CNSL products had better viscosity reducing abilities and hence the viscosity of alkyd resin was greatly reduced.

This study has shown that the use of the modified CNSL products as reactive diluents developed had better adhesion and all the films were soft based on pencil hardness test.

4.2 Recommendations

- i) It is recommended that further work be done on the cross linking mechanism of CNSL based products with alkyd coatings and how they get incorporated into alkyd systems.
- ii) It is recommended that the purity of cardanyl methyl ether and cardanyl acetate should be determined to clarify whether etherification and esterification yielded other products.
- iii) Further research in the drying mechanism of CNSL based products in the presence of alkyd resin should be done employing other percentages of the same driers to determine whether there can be an improvement in the drying times.

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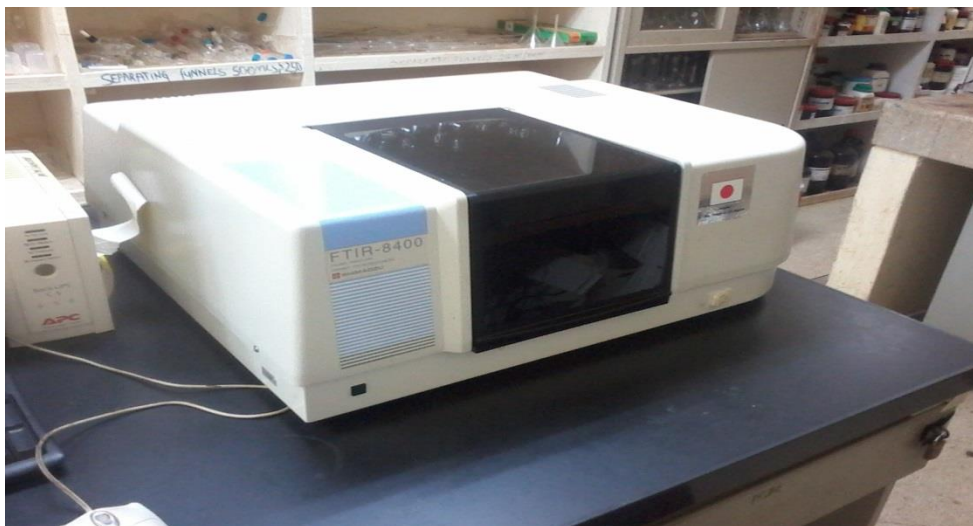
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APPENDICES

Appendix I: Shimadzu FTIR 8400 series



Appendix II: Finnigan GC 8000 series interfaced with a voyager EI-Mass Selective Detector



Appendix III: Table showing the composition of clear alkyd coating formulations based on long oil alkyd resin (70% wt solids)

Alkyd resin (70% wt solid)	White spirit (g)	Lead Naphthenate (32%)	Cobalt octoate (10%)	Reactive diluent (g)
143 g (100 g pure resin)	50	1 % (3.13 g)	0.6 % (6 g)	0
143 g (100 g pure resin)	45	1 % (3.13 g)	0.6 % (6 g)	5
143 g (100 g pure resin)	40	1 % (3.13 g)	0.6 % (6 g)	10
143 g (100 g pure resin)	35	1 % (3.13 g)	0.6 % (6 g)	15
143 g (100 g pure resin)	30	1 % (3.13 g)	0.6 % (6 g)	20
143 g (100 g pure resin)	25	1 % (3.13 g)	0.6 % (6 g)	25

Appendix IV: NDJ-5S Digital Viscometer



Appendix V: Application of coating to a glass panel using a Bird Film Applicator



Appendix VI: Quadracycle Electronic Drying Time Recorder DT 5040 with a Template Replacement

