A Process for Selective Extraction of Cardanol from Cashew Nut Shell Liquid (CNSL) and its Useful applications

Dr.Kathir.Viswalingam* and Dr.F.Emerson Solomon[1]

Abstract— Cashew Nut Shell Liquid (CNSL) is an useful product of cashew Industries. The cashew plantation and productions are high in the countries such as Africa, Australia and India etc. Cardanol is an important and very useful product of cashes nut shell liquid. This paper deals the extraction process of Cardanol and its industrial applications .

Index Terms— CNSL. Cardanol. Cardol. Industrial

1 INTRODUCTION

Extracting Process of CNSL and its byproducts

A process for extracting **cashew nut shell** oil has been developed at Laurenco Marques, Portuguese Africa by Sociedade Imperial De Caju E Oleos LDA, a Portuguese body corporate and has been patented in India in September 1961 (Indian Patent 78612, September 25, 1961)15. The invention disclosed in the above patent relates to an improved unitary continuous industrial method for extraction of shell oil from cashew nuts which is valuable from industrial and therapeutic point of view and for separation of cashew kernels having exquisite flavour and vitamin content without any contamination by the oil (which is acrid and produces painful inflammation of the skin) and untarnished by treatment. This method is have greater advantages in respect of producing quality products at cheaper rates and higher production levels than the primitive extraction methods which entailed more labor, higher costs and lower output.

The CNSL process sequence in basic steps:

i. Wetting of the cashew nuts by dipping in a hot water vat at 20-25°C to strike a moisture balance between the shell and kernel of the cashew nut and removal of superficial moisture from the nuts and then steaming of the nuts to open up the pores of the shells,

ii. Subjecting the conditioned nuts dipping in a vat containing cashew nut shell oil where temperature is kept at 170°C to 185°C or preferably at 180°C, for a predetermined period when most of the oil issues out of the shells,

iii. Vibrating the nuts discharged from the oil bath and subsequent centrifugation in order to remove the adhered oil,

iv. Incision of the shell walls of the nuts and centrifugation of the seed against a breaking wall,

v. Separation of the kernel from the cracked cashew shells and peeling of the skin by heating with hot air and mechanical rubbing of the kernel and effecting the removal of the peel under the action of an air stream; and

vi. Classifying the peeled nuts and subsequent packing under inert gas in tightly closed containers.

Extraction of Cardanol and Cardol from CNSL

It is known that CNSL mostly contains two important constituents ***anacardic acid*** -an acidic substance; and ***Cardol*** - a non-acidic material. The main objectives of extraction of Cardanol from CNSL are

- to provide a simple and economical method for isolating the so called cardol complex from anacardic acid,
- to provide an improved method of extraction of the decarboxy lated product 'Anacardol' or otherwise known as 'Cardanol' from cashew nut shell liquid,
- to provide a method of forming and extracting cardanol from CNSL by direct treatment of the oil and not by the indirect route of separation of anacardic acid and then treating the same,
- to provide a simple laboratory apparatus for the extraction of the above materials, Which may ulti mately be practised on a commercial scale and
- to indicate the commercial application of anacardol.

According to the invention CNSL is subjected to fractional distillation at 200° to 240°C under reduced pressure not exceeding 5mm. mercury in the shortest possible time which gives a distllate containing cardol and the residual tarry mat-

*Dean- Research, BIST, Bharath University,
[1]Professor, Department of Bio Medical Engineering,
173, Agharam Road, Selaiyur- 600073,
Tamil Nadu, India.

ter, for example, in the case of a small quantity of oil, say 200 ml/ the distillation period is about 10 to 15 minutes. A semi-commercial or commercial scale distillation of CNSL may however take longer times. It has been found that there are certain difficulties of operation with regard to single-stage fractional distillation method, i.e. frothing of the oil which renders difficult the fractionation of cardol and also formation of polymerised resin. These difficulties can be over come in the two-stage distillation, if care is taken not to prolong the heating; this is to avoid the undue formation of polymerised resins and possible destruction partially or completely of the cardol or anacardol. When CNSL is distilled at a reduced pressure of about 2 to 2.5 mm. mercury, the distillate containing anacardol and cardol distils firstly at about 200°C to 240°C. This first distillate is then subjected to a second distillation under the same identical conditions of temperature and pressure when the anacardol distils over at a temperature of 205°C to 210°C and the cardol distils over at a temperature of 230°C to 235°C. In practice it has been found that the preliminary decarboxylation of the oil is essential, since there will be excessive frothing, which renders the distillation procedure unproductive and uneconomical. A specific feature of this invention is that both cardol and anacardol may be obtained by a three-step process. The first step of the process is to get the decarboxylated oil by heating the oil to a temperature of 170°C to 175°C under reduced pressure of 30-40 mm. mercury. The next two steps are the same as above for the production of both cardol and anacardol. This invention is significant in the sense that it can be applied not only to the cashew nut oil but also to cashew nuts themselves or nut shells.

Chemical Composition of CNSL

CNSL is a mixture of four components: all are substituted phenols - ***anacardic acid, cardanol, cardol and 2-methyl cardol.*** The first two are *monohydric phenols* whereas the other two are *dihydric phenols*. In the nut, CNSL occurs mainly as anacardic acid(~90%) and cardol around slightly lower than 10%. During the hot-oil bath process for extraction of CNSL, anacardic acid gets decarboxylated to cardanol. So in the technical grade CNSL, the main components will be cardanol and cardol and of course, some polymerised CNSL.

CNSL can be extracted by the expeller method but the oil has to be heated after extraction to convert anacardic acid to cardanol. The expelled and heated CNSL will have less amount of polymerised CNSL. However, if there is a requirement for pure monomers, the best source will be solvent extracted CNSL. Each component again is a mixture of four structurally related monomers, the difference being only in the degree ofunsaturation. Thus, cardanol is a mixture of a four components: saturated (~5%), monoene (~49%), diene(l6.8%) and triene (29.3%). (This makes the chemistry of addition polymerisation essentially complex). Thus, CNSL contains a total of 16 components, which makes it a complicated system.

Advantages of CNSL based Polymers

- Improved Flexibility and reduced brittleness.
- Solubility in Organic Solvents.
- Improved Processability.
- Low Fade Characteristics for Friction.
- Resistance to 'Cold Wear'.
- Good Electrical Resistance.
- Better Water Repellence.
- Improved alkali and acid resistance.
- Compatibility with other polymers
- Antimicrobial Property.
- Termite and Insect Resistance.
- Structural Features for Transformation into High Performance Polymers.

Polymerisation Characteristics of CNSL

CNSL can be polymerised by a variety of methods:

- Addition Polymerisation through the side chain double bonds using cationic initiators such as sulphuric acid, diethylsulphate etc..
- Condensation Polymerisation through the phenolic ring with aldehydic compounds.
- Polymerisation after Chemical Modification to introduce speciality properties.
- Oxidative Polymerisation.
- Various Combinations of the above.

Industrial Significance of CNSL

- Low Cost Phenol
- Versatility in Polymerisation and Chemical Modification
- Possibilities for Development of High Performance Polymers

Property advantage over phenolics in certain applications such as impact resistance; flexibility, faster heat dissipation etc. Reactivity CNSL undergoes all the conventional reactions of phenols.

Applications of CARDANOL:

Oil Soluble Resins

The meta substitution and the long hidrocarbon chain in its molecule makes the resins prepared with Cardinol, highly soluble in oils and imparts superior properties such as high electric insulation and resistance against chemicals to its films. It is to manufacture both solid and semi solid resol or novolac type of resins depending upon the nature of catalyst and the aldehyde compound.

Cardanol resin varnishes have good electrical insulating properties and resistance against water and chemicals. They give superior quality Stamping Varnishes. Because of their high insulation and dielectric losses, these varnishes are preffered to compositions based on usual Phenol such as Cresol or Substituted phenols.

Surface Coatings and Paints

Cardanol resin Varnishs in addition to water and Chemical resistance have good air drying and baking properties. These compositions are suitable for wood finishes, food can lacquers textile bobins and high quality paints. Stoving paints can be prepared which could be baked at 60°C. The Cardanol based resins have good compatibility with other synthetic resins such as alkydes, epoxies chlorinated rubber, Phenolic etc., and can serve as raw material for variety of paints.

Lamination Industry

By partly replacing the Phenol or Cresol in alcohol soluble resins used for Lamination one could prepare resins which imparts greater flexibility resistance to Chemical and water, and superior electrical insulation to the lamination sheets

Surface Active Agent

Sulphonated ether of Cardanol has been found to be wetting agent and finds use in Textile Industry, ethoxylated Tetrahydrocardanol Sulphonate performs better at high temperature than the detergents based on Dodoeyl benzene.

Pesticides

Chlorinated Cardanol is reported to have good insecticidal, pesticidal and germicidal properties. Cardanol Formaldehyde resin is also used as a solvent for well known pesticides such as Pyrethrin and Rotanes. Paranitro Tetrahydro Cardanol finds use as a coupling compound in sprayable pesticides such as Parathion.

Rubber Compoundings

Oil soluble Cardanol resins are used in Rubber Compounding. They impart high tear strenght and resistance against Petroleum based solvents. Pure Cardanol acts as a Deoxident and Plasticizer when incorporated in rubber. Its ethers are also used as plasticizers for synthetic rubbe to reduce the shore hardness and improve the ageing properties.

Azo dyes

Three pentadecyl phenol and sulphonated products of Cardanol are being used as intermediates for Azo Dyes.

Wax Substitutes

Waxing solids with high melting points could be prepared from Cardanol resins and suitable Amide such as Stearamide. When 3 pentadecyl phenol is reacted with 1:4 Dichlorobutane a wax with a melting point of 90/93°C is obtained. These waxes are comparatively cheaper and compatible ith other waxes such as bees wax, carnauba wax, paraffin wax etc. etc.

Mineral Oil Additives

Mineral oil additives based on Amino Cardanol ethers of hydronated Cardanol and salts of its Sulphonated ethers are found to improve the viscosity index of mineral oil, inhibit sludge formation and antioxident properties.

Food Can lacquers

Co-polymers of Cardanol with other film forming materials give good quality lacquers giving golden yellow films both of air drying and baking type. These have been found to be very effective for food can application.

Adhesives based on Cardanol Resins give superior water resistance and bonding properties to the plywood.

Adhesives

Many types of adhesives and cements can be prepared with Cardanol. When it is reacted with Epichlorohydrin and modified with Phthalic Anhydride a coating compound is obtained which has excellent film properties and adhesion. An excellent quality of Friction dust could be prepared from Cardanol which finds use brake linings and Clutch facings.

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