CHAPTER I

INTRODUCTION

1.1 Cashew tree

The cashew tree, *Anacadium occidentale* L. is a small genus of trees, shrubs, and subshrubs indigenous to the neotropics (Figure 1.1). It ranks second only to the almond among the nine tree nuts of importance in world trade. Native to Brazil, the tree grows in the coastal areas of Asia and Africa. The tree which is now widely cultivated in Asia for its nuts and other products grows as tall as twelve metres, with a thick and tortuous trunk and branches so winding that they frequently reach the ground. The branches are adorned with leathery, oval leaves. The fragrant, reddish flowers grow in clusters, and the pear shaped fruits, called cashew 'apples', are reddish or yellowish. The cashew 'fruit' is very peculiar and is really not a fruit at all (Figures 1.2) : it is actually a swollen peduncle that grows behind the real fruit which yields the cashew nut. This large pulpy and juicy part is a pseudofruit with a fine sweet flavour and aroma and the cashew nut grows externally in its own kidney shaped hard shell at the end of the pseudofruit or peduncle. It is this peduncle, however, which is commonly referred to as the cashew fruit or apple. At the end of each fruit is a kidney shaped ovary, the nut, with a hard double shell. The cashew nut itself is grey in colour and 2.5 - 4 cm long (Figures 1.3, 1.4). The shell is 2 - 3 mm thick, with a leathery outer case and a thinner, harder inner case, between which is a honeycomb structure containing the phenolic cashew nut shell liquid (CNSL). The kernel is protected from the latter both by the testa skin and the inner case, and is a rich source of protein, carbohydrate, and the triglyceride cashew oil. The kernel and the shell liquid each comprise 20 to 25% of the nut, the remainder consisting of the testa and the shell structure[1,2].

Figure 1.1 Cashew tree.

Figure 1.2 The mighty cashew.

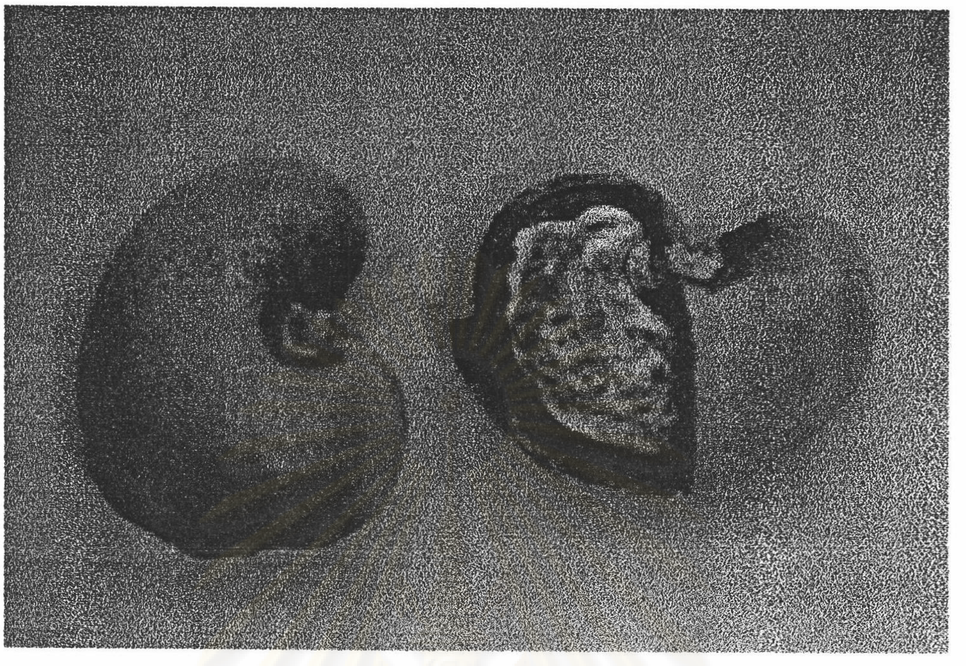

Figure 1.3 Detail of cashew nut.

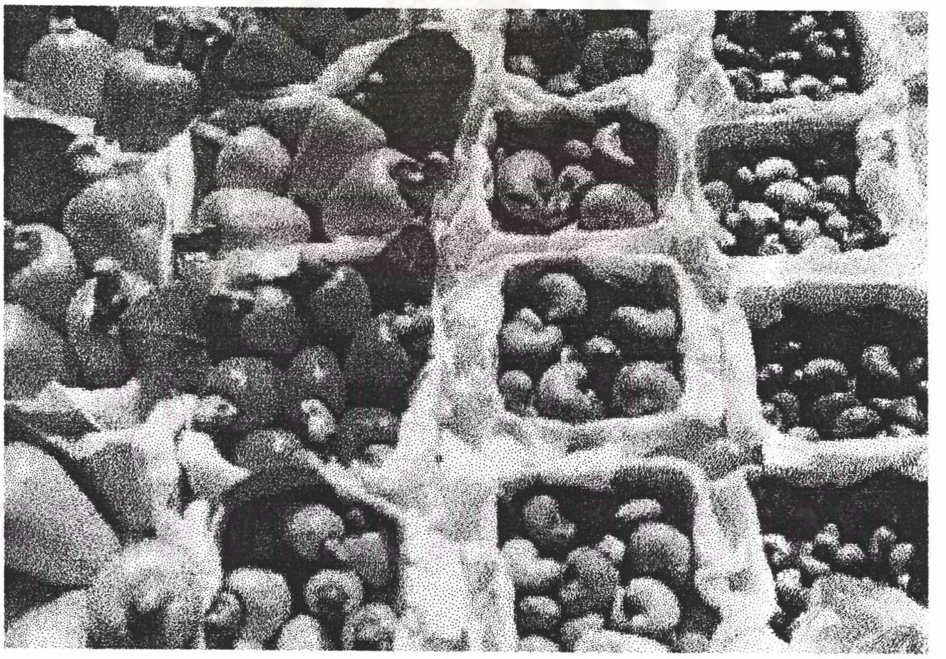

Figure 1.4 Cashew fruit and nuts.

However, of the various natural products of the cashew, it is the caustic, black phenolic oil known as ***cashew nut shell liquid (CNSL)***, until recently routinely discarded as a waste product, which has been found to be of most interest, as it can be used in numerous industrial and engineering applications. CNSL is essentially a mixture of phenolics and is a good natural alternative to petrochemically derived phenol. Furthermore CNSL has been used in areas as diverse as paints, corrosion resistant varnishes, and natural composite materials. The fact that CNSL is also a low cost renewable resource which until recently was thought of as a waste product only added to its appeal and suggests that an exciting future awaits this fascinating material.

1. 2 Cashew nut shell liquid (CNSL)

From the fruit to the nut to the shell, cashew is basically edible and useful. However of the various natural products of the cashew, it is the caustic, black phenolic oil (known as cashew nut shell liquid or CNSL) that has to be removed by a roasting process which has been found to be of most interest, as it can be used in the plastics and varnish industries.

CNSL occurs as a reddish brown viscous liquid in the soft honeycomb structure of the shell of cashewnut. Cashewnut attached to cashew apple is grey coloured, kidney shaped and 2.5 - 4 cm long.

The shell is about 0.3 cm thick, having a soft leathery outer skin and a thin hard inner skin. Between these skins is the honeycomb structure containing the phenolic material popularly called CNSL. Inside the shell is the kernel wrapped in a thin brown skin, known as the testa.

The nut thus consists of the kernel (20 - 25%), the shell liquid (20 - 25%), and the testa (2%), the rest being the shell [2].

1.2.1 Extracting Process of CNSL

Traditionally, Indian processors of cashewnuts roast them in an open perforated drum. CNSL either leaks away or is burnt in the fire. With increase in the price of CNSL, many refined extraction techniques have come into vogue.

Hot oil bath method

This is the most common method of commercial extraction. The raw nuts are passed through a bath of hot CNSL (180-200 ^{O}C) itself, when the outer part of the shell bursts open and releases CNSL (50% recovery). Another 20% could be extracted by passing the spent shells through an expeller and the rest by solvent extraction techniques. The expeller oil, however, does not satisfy IS specifications (Table 3) and needs upgrading. This can be done by acid washing followed by centrifugation and heating.

Expeller method

Some factories introduced manually operated cutting machines in which shells of lightly roasted nuts are cut, keeping the kernel intact. The shells are then fed to an expeller to recover 90% of the oil.

Kiln method

In this method, the nuts are shelled after sun drying or after drum roasting. The liquid obtained is, however, crude and contaminated.

1.2.2 Chemistry and Composition of Cashew nut shell liquid

Typically, CNSL is a mixture of four components: all are substituted phenols anacardic acid, cardanol, cardol and 2-methyl cardol (Figure 1.5). 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 of unsaturation. Thus, cardanol is a mixture of a four components: saturated (~5%), monoene (~49%), diene (16.8%) 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 [3].

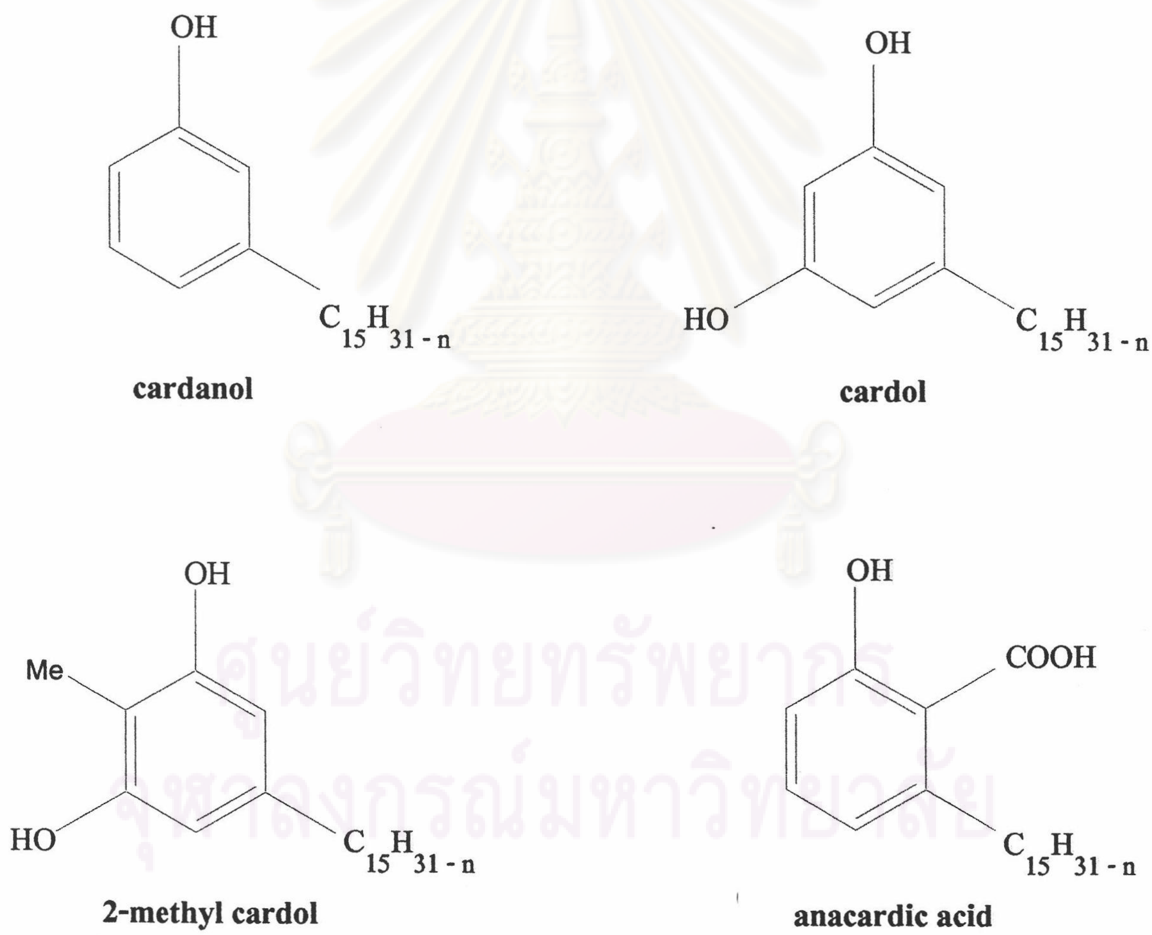

Figure 1.5 Composition of Cashew nut shell liquid : when n = 0, 2, 4, 6

In the roasting process, some polymerization as well as decarboxylation occurs, because of the highly unsaturated nature of CNSL. Since anacardic acid is easily decarboxylated to give cardanol, the cardanol is obtained more from the CNSL in commercial use by heating at a high temperature and using calcium hydroxide as an activated catalyst [4]. Thus, a typical product could contain polymer (20-25%), cardanol (60-65%), cardol (10-12%) and other minor components. Several workers have reported the composition of CNSL. The phenolic composition of natural and technical CNSL, characteristics of cardanol and IS specification for CNSL are given in Tables 1.1, 1.2 and 1.3 respectively [2].

Table1.1 Phenolic Composition of Natural and Technical CNSL (Mozambique Origin) (Values are in %) [2]

Component or other material	'Natural' CNSL*	Technical CNSL†
Cardanol	1.20	62.86
Cardol	11.31	11.25
2-Methylcardol	2.04	2.08
Anacardic acid	64.93	- ‡
Polymer (and minor materials) by difference‡	20.3	23.8

*Results expressed on the basis of hydrogenated methylated materials.

†Approximately up to 1% anacardic acid is present in technical CNSL.

‡The minor materials are mainly homologus phenols (or hydrogenated methyl ethers)

Source: Tyman J H P, *Chem Soc Rev,* **8** (4) (1979) 522.

Table1.2 Characteristics of Cardanol [2]

Boiling point, ^{O}C	228 - 235 (3.4 mmHg)
Colour (Lovibond, 1 cm cell) (freshly distilled)	Red (1.0 - 3.0) Yellow (1.5 - 3.5)
Viscosity, 30 ^{O}C (cP)	45 - 52
Acid value	1.9 - 2.0
Iodine value (Wij's)	210 - 235
Hydroxyl value	180 - 200

Table1.3 IS Specifications* for Cashewnut Shell Liquid [2]

Characteristic	Requirement
Specific gravity, 30/30 ^{O}C	0.950 - 0.970
Viscosity at 30 ^{O}C, cP (max)	550
Moisture, % by wt (max)	1.0
Matter insoluble in toluene, % by wt (max)	1.0
Loss in wt on heating, % by wt (max)	2.0
Ash, % by wt (max)	1.0
Iodine value (max) (a) Wij's method (b) Catalytic method	 250 375
Polymerization (a) Time, min (max) (b) Viscosity at 30 ^{O}C, cP (min) (c) Viscosity after acid washing at 30 ^{O}C, cP (min)	 4 30 200

*IS 840: 1964

1.3 Use and application of cashew nut shell liquid

Cashew nut shell liquid is essentially a mixture of phenolics extracted from the shells of the cashew nut and is good natural alternatives to petrochemically derived phenol, a product whose price is inherently linked to the fickle oil price and availability of fossil fuels. The major components of CNSL, which depend slightly on the geographical location of the tree, are anacardic acid and cardol. During the heat treatment applied to deshell the nut most of the anacardic acid breaks down to give cardanol, which is essentially a phenol. The interesting molecular structure of cardanol gives some interesting properties such as quick drying after baking, high electrical insulation, and good thermal stability. Additionally, cardanol based resins possess outstanding resistance to the softening action of mineral oils, as well as high resistance to acids and alkalis, antimicrobial properties, and termite and insect resistance.

On the basis of these properties cardanol excels over petroleum based phenol products and can easily substitute for it, often at significantly reduced cost. Typical applications that exploit these properties include brake linings, paints and varnishes, foundry core oil, and distilled cardanol for epoxy resins and laminates. Numerous other minor uses, such as in chemically resistant cements, oil tempered hardboard, and waterproofing compounds and resins [1,2,3].

Today's chemical industries, anionic surfactants like sodium dodecylbenzene sulfonate are used extensively. The structure of CNSL is similar to dodecylbenzene in aromatic and the side chain of hydrocarbon, cardanol which is recovered from CNSL possesses a typical lipid structure with a hydrocarbon hydrophobic group and a hydrophilic phenolic end group. Therefore it is presumed that the chemical reaction is attached to aromatic ring, an agent, the product has the same properties as dodecylbenzene sulfonate.

Figure 1.6 Structure of sodium dodecylbenzene sulfonate

Objectives

Objectives of this research are to prepare sodium cardanol sulfonate from cardanol and to compare sodium cardanol sulfonate with dodecylbenzene sulfonate.

Scope of Investigation

In this research, the preparation of surfactant from cardanol which can be purified from CNSL by using the sulfonation with sulfonating agent, that can gives the sulfonate group such as fuming sulfuric acid. After that, a base, such as sodium hydroxide can neutralizes it. Many different parameters such as reaction time and reaction temperature are determined to give desired yield. Finally, its characteristics are considered for physical properties such as solubility in hard water, surface tension, critical micelle concentration (C.M.C.) and detergency.

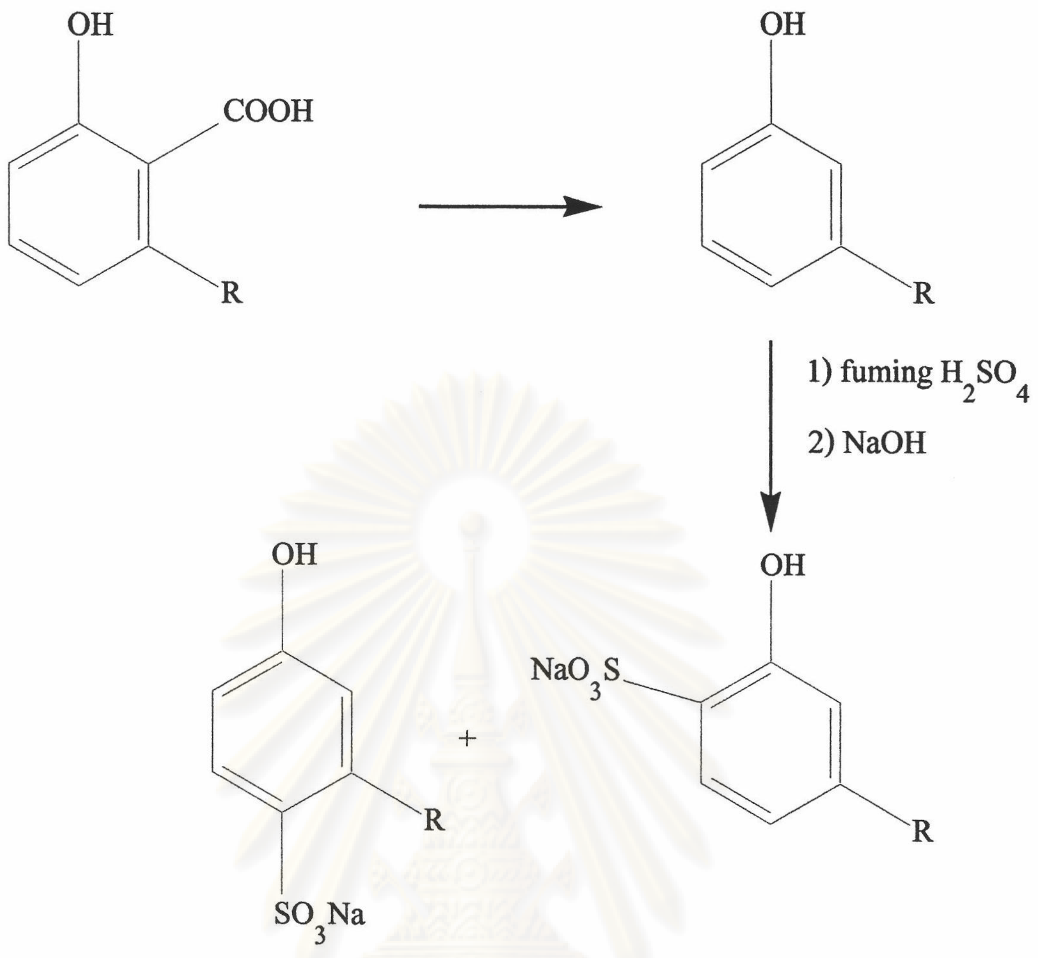

Figure 1.7 Chemical reactions used in this research.