

Chapter 2

Cashew Nutshell Liquid (CNSL): From an Agro-industrial Waste to a Sustainable Alternative to Petrochemical Resources

Diego Lomonaco, Giuseppe Mele and Selma E. Mazzetto

Abstract The global concern about the problems caused by the growing consumption of petrochemical compounds, such as global warming and the diminishing of fossil fuels reserves, has given rise to the green chemistry field—based on the design of products and processes that minimize the use and generation of hazardous substances—in both academy and industry. In face of the increasing demand for chemicals, sustainable and innovative technologies are necessary in order to overcome current difficulties and also avoid the evolution of new ones. The advent of agro-industry waste as a resource of raw materials has attracted the attention of researchers and opened a window of opportunity for the breakthrough of alternative products to the oil industry. In this sense, cashew nutshell liquid (CNSL), a by-product from cashew industrial processing and one of the richest natural sources of phenolic compounds, emerges as a promising and renewable feedstock for the development of a wide range of functional products. This chapter is focused on the discussion of the origin and chemical composition of the different types of CNSL, and also on the challenges involved in the methods of isolation and main applications of its major component, cardanol, in the context of a sustainable development.

2.1 Introduction

The cashew tree, scientifically named as *Anacardium occidentale* L., a member of the Anacardiaceae family, is considered an indigenous element from the tropical region of South America. Appointed by Lindley in 1830, this family includes

D. Lomonaco (✉) · S.E. Mazzetto

Department of Organic and Inorganic Chemistry, Federal University of Ceará, Campus Pici, Fortaleza 60440-900, Brazil
e-mail: lomonaco@ufc.br

G. Mele

Department of Engineering for Innovation, University of Salento, Via Arnesano, 73100 Lecce, Italy

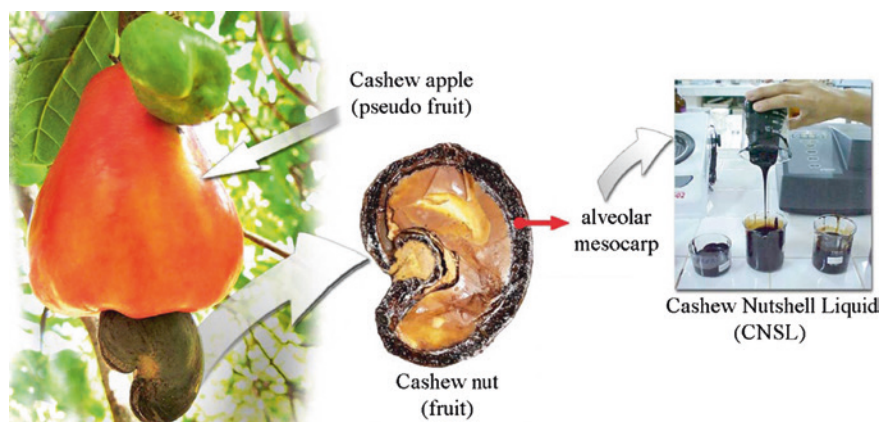


Fig. 2.1 Cashew pedicel, fruit, and mesocarp filled with CNSL

more than 700 species, distributed in 82 genera that are majorly found in tropical zones, although few of them extend to temperate zones. Members of this family are cultivated all around the world due to its edible fruits, medicinal compounds, wood properties, and scenic effects. Besides cashew, other agricultural products from Anacardiaceae are: mangos (*Mangifera indica* L.), pistachios (*Pistacia vera* L.), and marula (*Sclerocarya birrea* (A. Rich.) Hochst.) [35, 40].

The colorful cashew apple (Fig. 2.1), an overdeveloped pedicel, is edible and commonly mistaken as the fruit of the cashew tree, but it is in fact a pseudocarp (accessory fruit), scientifically known as flower stack, which is used in the production of sweet beverages and foods. On the other hand, the true fruit is a reniform (kidney-shaped) seed (also considered a nut) that grows in one of the ends of the apple, and is covered by a hard shell (pericarp). The cashew nut (kernel) is the primary commercial product of cashew plantation as it is very appreciated as a snack and is also used in the Asiatic cuisines, especially Thai and Chinese.

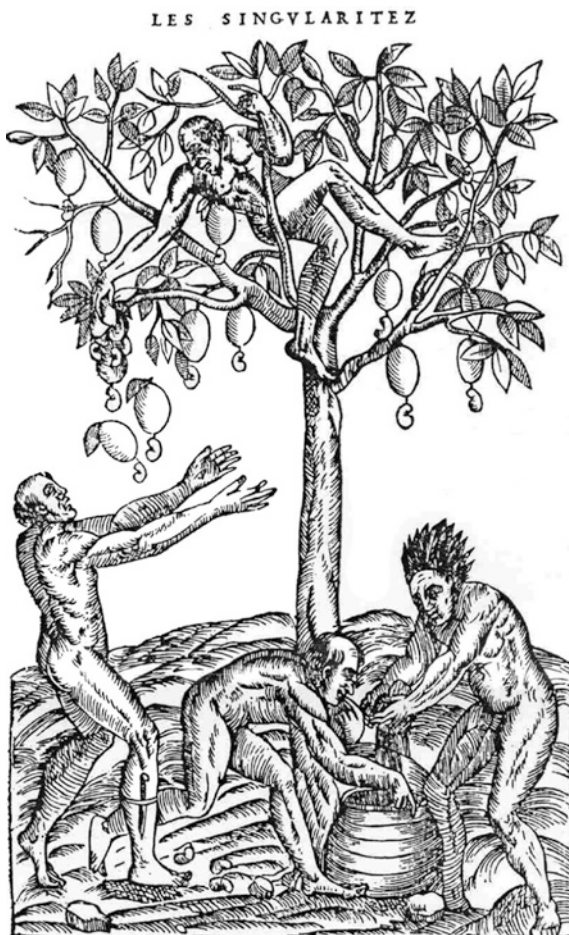
The pericarp that involves the nut, the cashew nutshell, which has an alveolar mesocarp, is filled with a dark and caustic oily substance called cashew nutshell liquid (CNSL), obtained as a by-product during the industrial processing of the cashew nut.

This oil is composed mainly by phenolic lipids and, for this particular reason, has drawn the attention of scientist and researchers all over the globe, since it has been considered as a viable alternative to petroleum products [16, 24].

2.2 Origin and Production

The origin of cashew is based on evidences that strongly indicate Brazil, or at least tropical South America, as the center of origination of the species currently known as *Anacardium occidentale*. The warm and moist climate conditions found

Fig. 2.2 An illustration made by André Thévet in his book “The singularities of Antarctic France” (Reproduced from ref. [55])



especially in the coastal regions of Northeast Brazil, with air humidity about 70 %, are ideal for cashew growing. The name cashew is in fact derived from the indigenous dialect word “*acaju*” (pronounced [kə'ʒu]) [16].

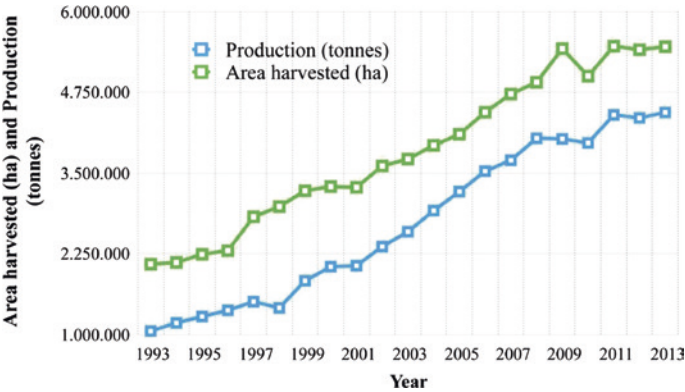
A substantial indication about the Brazilian origin of cashew can be found in an old reference about this plant made by the French naturalist monk André Thévet (1502–1590). An illustration, describing few natives harvesting what seems to be a cashew tree (Fig. 2.2), found in his book entitled “The singularities of Antarctic France,” written in 1557 during the French expeditions to south of the equator regions of Brazil between 1555 and 1567 [56].

Although native from Brazil, the plant is already disseminated in many countries around the world, especially in India, Nigeria, Viet Nam, Cote d’Ivoire, Tanzania, Philippines, Indonesia, and Guinea-Bissau. This widespread of cashew is because the Portuguese colonization of Brazil, who, in late the 1500, introduced the cashew in India, then in the African colonies, and Asia, where it quickly adapted due to the similar climate conditions.

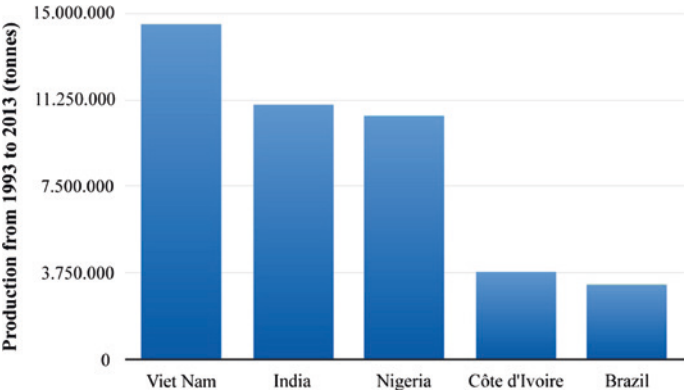
From a commercial perspective, the worldwide production of cashew is growing every year, along with the total area of plantation.

According to the Food and Agriculture Organization of the United Nations [17], considering the period of 20 years, from 1993 to 2013, the global annual production of cashew nut (with shell) increased more than 400 %, rising from 1.053.232 tonnes to 4.439.960 tonnes per year. In its turn, considering the same period, the total area harvested increased from 2.089.710 ha to 5.457.009 ha per year, a growing around 260 % (Graphic 2.1).

The top 5 producers of cashews, in this interval, were, in decreasing order, Viet Nam, Nigeria, India, Côte D'Ivoire, and Brazil, responsible for the production of 43.099.972 tonnes, around 75 % of the global production of 57.297.951 tonnes [17] (Graphic 2.2).



Graphic 2.1 Global production and area harvested of cashew nut



Graphic 2.2 Total cashew nut production (1993–2013) of the top 5 world producers

Taking into consideration the numbers presented above and the fact that CNSL comprises around 25 % of the cashew nut total weight, one can estimate that, only in 2013, about 1.000.000 tonnes of CNSL were obtained as by-product from the cashew nut industrial processing.

As mentioned before, being composed mainly by phenolic lipids, the dispose of such a large volume of CNSL becomes a real concern in light of the ecological issues it may raise. In this way, the other alternative is to make use of this agro-industrial by-product as a raw material in the synthesis of different chemical products, which will not only prevent the disposal-related problems, but also turn CNSL into a new commodity.

According to the Green Chemistry principles, the use of renewable feedstocks is an elegant approach to overcome some of the issues that the world is facing nowadays in order to achieve a more sustainable society.

Another interesting aspect important to point out is that the utilization of CNSL as a replenishable raw material will not compete for land or agricultural resources, not even food production, since the actual purpose in the cashew plantation is the obtainment of the valuable cashew kernel [23].

2.3 CNSL: Extraction and Chemical Composition

Cashew nutshell liquid is a reddish brown dark oil, with a peculiar odor, considered as one of the main natural sources of non-isoprenoid phenolic lipids. The main chemical compounds present in CNSL are: anacardic acid (1), cardanol (2), cardol (3), and 2-methylcardol (4).

These phenolic compounds have a very peculiar chemical structure, bearing an alkyl side chain comprised of 15 carbon atoms located in *meta*-position in comparison with their hydroxyl group(s). Another interesting characteristic is that these alkyl side chains may present different degrees of unsaturations, varying from none up to 3 double bonds, with *cis* (or *Z*) configuration, located in the carbons 8, 11, and/or 14 [35] (Fig. 2.3).

Depending on the method of obtainment, CNSL may present different chemical composition and, therefore, be classified into two main types: solvent-extracted CNSL (natural CNSL) and technical CNSL (tCNSL).

Natural CNSL is obtained by the utilization of some solvent extraction technique (commonly Soxhlet, supercritical carbon dioxide, or subcritical water) in order to obtain its constituents under mild conditions, without promoting any chemical modification. In this way, natural CNSL represents the original composition found in nature, which is basically composed by anacardic acids (60–70 %), cardols (10–20 %), cardanols (3–10 %), 2-methylcardols (2–5 %), and other minor constituents [19, 44].

On the other hand, technical CNSL is the by-product of the cashew nut industrial processing. Since the primary goal in the cashew industry is the obtainment of the valuable kernel, CNSL comes as a secondary product.

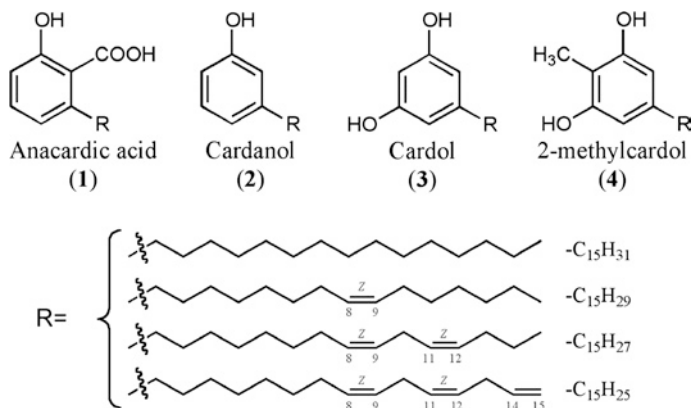
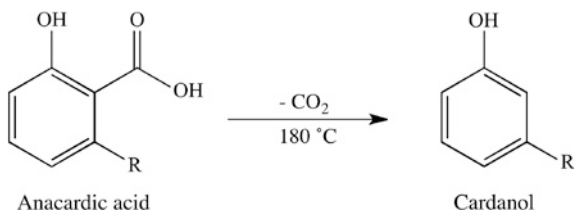


Fig. 2.3 Chemical structures of the main components of CNSL

Fig. 2.4 Decarboxylation of anacardic acid into cardanol



Initially, technical CNSL was employed as a source of phenolic compounds for the synthesis of phenol/formaldehyde polymers. Nowadays, with the advances in the chemistry of these phenolic lipids, tCNSL appears as an economically feasible source of phenolic components. In the industry, CNSL is extracted by an automated process that employs high temperatures in order to open the shell and recover the cashew kernel. In this process, named “hot-oil process,” cashew nutshells are immersed in the CNSL and heated to 180–190 °C.

Under these temperatures, anacardic acid present in natural CNSL suffers a decarboxylation reaction converting itself into cardanol, generating technical CNSL, which is chemically differently from natural CNSL, composed mainly by cardanol (60–70 %), cardol (10–20 %), 2-methylcardol (2–5 %), polymeric materials (5–10 %), and other minor constituents (Fig. 2.4).

In Table 2.1 are described different compositions of natural and technical CNSL reported in the literature.

At first, these differences can be attributed to the fact that CNSL is a natural product, and therefore, its composition may vary according to the geographical coordinates, climate, and soil conditions.

Other important factors that may contribute for the differences in composition are the extraction techniques and the methods of analysis. On the basis of the extraction mode (solvent used, temperature, time, etc.) chemical compounds will

Table 2.1 Chemical composition of natural and technical CNSL

Compound	Natural CNSL			Technical CNSL		
	Tyman [57] (%)	Oliveira et al. [42] (%)	Paramashivappa et al. [43] (%)	Tyman [57] (%)	Andrade et al. [2] (%)	Kumar et al. [26] (%)
Anacardic acid (1)	71.65	62.90	63.00	–	–	–
Cardanol (2)	5.10	6.99	10.50	67.80	40.26	67.00
Cardol (3)	22.30	23.98	22.50	18.20	29.95	22.00
2-Methylcardol (4)	1.10	–	–	3.30	–	–

present distinct affinities for the mobile phase, thereby altering their concentration in the final product [63]. Although gas chromatography (GC) is an useful method for the study of phenolic compounds, HPLC is a much more efficient and sensitive technique [59].

Another interesting difference between the chemical composition of natural and technical CNSL is the existence of oligomeric and polymeric materials.

Tyman et al. [59], by using HPLC analysis under gradient elution with THF and acetonitrile, estimated quantitatively the presence of polymeric material in three diverse tCNSL samples.

They have found that the concentration and complexity of polymeric materials raise with the age of the sample, increasing from 7.38 %, in the case of a fresh sample, to as far as 21.63 %, for a five-year-old sample.

The eluted polymeric material was recovered and evaluated by TLC, which indicated an increase in complexity and polarity with the level of polymerization.

The authors also suggested that the majority of these materials is composed by dimeric and trimeric oligomers with a relatively saturated alkyl side chain.

Since the recovery of the almond (kernel) in perfect conditions as an edible product is the main purpose in the industrial environment, the continuous heating of this process leads to the degradation of the CNSL obtained as a by-product, promoting the polymerization of its unsaturated compounds as well.

The mechanism of the polymerization reaction through the double bonds in the alkenyl side chain of cardanol has been studied in different conditions.

Manjula et al. [34] investigated the kinetics and mechanism of the oligomerization of cardanol using acid catalysts, while Rodrigues et al. [49] studied the influence of the temperature on the oligomerization of cardanol.

Since the harsh conditions in which cashew nutshells are submitted during industrial processing involve temperatures as high as 190 °C, and that in this condition the oxidation of organic compounds may lower the pH, these two situations may present a synergistic effect and therefore can be considered as the main factors that initiate the oligomerization of the double bonds present in the alkenyl side chain of the phenolic compounds of CNSL.

Upon consideration of data obtained by rheological analyses, ¹H nuclear magnetic resonance (NMR), and infrared spectroscopy (FT-IR), it was suggested that, in thermal oligomerization, the dimeric structure is the main oligomer that was

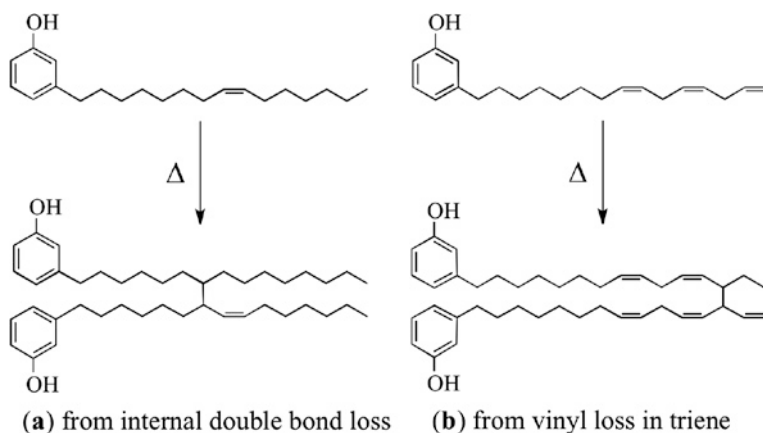


Fig. 2.5 Possible oligomerization reactions of cardanol under high temperatures

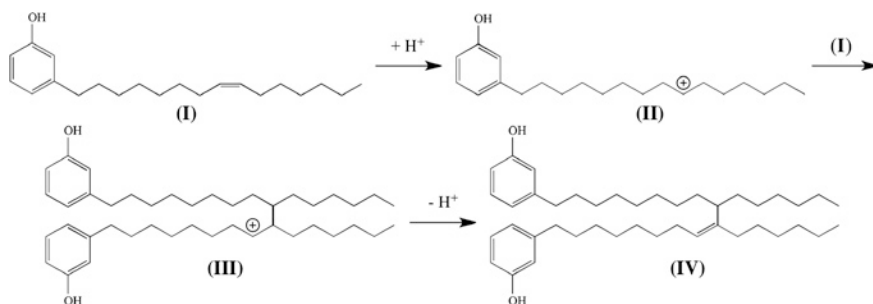


Fig. 2.6 Possible oligomerization reactions of cardanol under acidic conditions

formed by two possible reactions: (a) from internal double bond loss and (b) from vinyl loss in triene, as described in Fig. 2.5 [49].

Another possible route is described under acidic conditions. A suggested mechanism involves protonation of the side chain of cardanol, followed by a cationic chain growth reaction, as depicted in Fig. 2.6 [34].

2.4 Cardanol as a Sustainable Feedstock

With the continuous exploration for new renewable and biodegradable chemical resources, the large quantities of cashew nutshell liquid, especially technical CNSL, which possess elevated percentual of cardanol, have need for the development of purification/isolation processes of its main constituents in expectation to a authentic acceptance by the industrial market structure.

This should represent the first step into the promotion of a sustainable development, supported by a technological autonomy, due to the potential achievement of new high added value products derived from CNSL.

Based on the above assumptions, cardanol turns into one of the most important and promising chemical constituents of CNSL.

Once isolated in high purity, this green start material could be employed in many different industrial sectors, with emphasis in those that the prices of the final products are substantially elevated, like fine chemicals and pharmaceuticals.

Although cardanol is a phenol, compared to the main commercial mono-hydroxyl phenolic compounds used as starting materials, e.g., *p*-cresol, it presents some peculiarities in its physicochemical properties, due mainly by the long aliphatic side chain containing up to three double bonds (*Z* configuration), which enables a great number of functionalizations and hydrophobicity, low volatilization, no aggressive odor, and a higher boiling point, important characteristics for safe operations.

Furthermore, are also available the traditional reactive sites of phenolic chemical structures: the nucleophilic aromatic carbon atoms located at the *ortho*- and *para*-positions and the hydroxyl group (Fig. 2.7).

In an academic point of view, cardanol is a compound already known by many groups but, considering its potential, it still has a lot of space to grow. Many useful applications are found every year as it begins to substitute traditional phenolic raw materials in the synthesis of different classes of products, or new one is developed taking advantage of its unique properties.

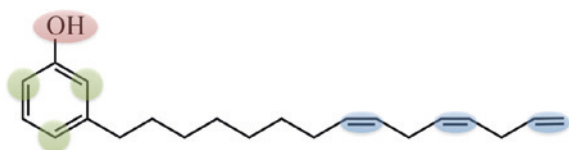
Considering a bibliographic research involving the period of the last 30 years (1985–2015), made by a simple search using Scopus and SciFinder, the term “cardanol” exhibited 575 and 848 articles as results, respectively.

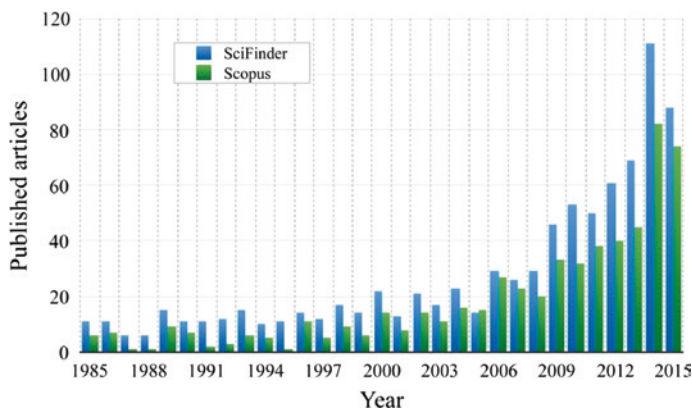
A more careful look at these results (Graphic 2.3) shows a progressive accession in the number of published articles, which indicates an increasing interest in this chemical compound and its applications more recently. Nevertheless, these numbers can be considered very inexpressive in view of the true potential that cardanol has as feedstock.

Taking into account all these particularities, it is not difficult to understand that the isolation of the constituents of cashew nutshell liquid is one of the fundamental drawbacks to reach its summit as an attractive starting material in a industrial sector searching for more sustainable alternatives.

In spite of the few different methods reported in the literature dealing with the obtainment of cardanol (and other constituents) from CNSL, they continue to collide into many adversities, e.g., the elevated price of reagents and solvents

Fig. 2.7 Main reactive sites of cardanol molecule





Graphic 2.3 Number of published articles, according to Scopus and SciFinder

involved in the process, low yields, contamination of the final product, and the cost-effectiveness of energy employed, invalidating remarkably its fulfillment in large scales.

Historically, the distillation process under reduced pressure was the first method to isolate cardanol from technical CNSL.

A patent by M. T. Harvey in 1937 [21] described that at a pressure of about 10 mmHg cardanol could be obtained in a temperature at about 225 °C, with very little amount of other compounds.

An interesting fact about this document is that there is made the first mention of the name “cardanol” to indicate the chemical compound originated by the decarboxylation of anacardic acid from natural CNSL under high temperatures, once previous publications used mistakenly the term “anacardol” [62], which identified a different mono-phenol isolated from the kernel of *Semecarpus anacardium*, to make reference to cardanol.

Currently, many articles still mention the use of distillation process in order to collect cardanol from commercially available or decarboxylated natural CNSL. Recently, the utilization of distilled cardanol as an additive for biofuels was reported. In that paper, the authors obtained cardanol at 230 °C at 0.2 mmHg and added in concentrations up to 20 % in diesel [50].

In another work, the synthesis of new oximes based on cardanol described a one-pot procedure for decarboxylation followed by a distillation process of natural CNSL. The flask containing CNSL was heated slowly to 180 °C, under 5 mm Hg, and after 20 min of the evolution of a carbon dioxide mist, the system was heated to 220–230 °C, temperatures at which a light yellow liquid was collected (70 % v/v) and posteriorly characterized by FT-IR and ¹H NMR as high-purity cardanol [22].

The isolation of cardanol, with elevated purity, is only achieved through the use of column chromatography, which, in a industrial perspective, is inviable, due not

only to the costs involved (silica gel, or other adsorbent) and amounts of solvent employed, but especially for being a time-consuming methodology.

Laboratory-scale processes for obtainment of pure cardanol are still based on chromatographic methods.

One of the first mentions of this process was made by Murthy et al. [41]. In this work, the authors described a procedure for the purification of 1.0 g of cardanol from fresh distilled CNSL (containing approximately 5 % cardol) using a 200-cm long glass column, filled with 50 g of silica gel (100–200 mesh). Different solvents were used (petroleum ether, benzene, ethyl acetate) as the polarity of eluent was increased. The authors also described the process of argentation of silica gel to separate the three different olefinic constituents of cardanol (mono-, di- and tri-unsaturated).

In 1986, Sood et al. [52] improved significantly the chromatographic technique to separate CNSL constituents. Prior to the advent of flash chromatography, the authors detailed the use of TLC type silica gel (much thinner than that used for tradition column chromatography) and pressurized air, in order to enhance the efficiency of the process.

Another progress made was the proportion of CNSL/adsorbent used, in the range of 1:5–1:6, in a column measuring 50 cm long. The experiments reported the use of 25.6 g of technical CNSL for 125 g of silica gel and a total volume of around 5.2 L of different solvents (light petroleum, diethyl ether and methanol), resulting in the separation of pure cardanol (17.68 g) and cardol (2.84 g), besides other fractions with lower efficiency.

By employing a two-step reversed-phase (RP) column chromatography, Yuliana et al. [63] successfully isolated isomers of the three major constituents of solvent-extracted CNSL in high purity. Using a mass ratio of CNSL to silica gel of 1:20 and methanol as mobile phase, the authors reported 81.8 % recovery of 3-*n*-pentadecylphenol (saturated cardanol) with 99.2 % purity, verified by HPLC analysis.

Tyman et al. [58] proposed a different methodology in order to isolate cardanol from technical CNSL.

In a work from 1992, a solvent extraction purification system was described as an improvement on the previous methods available in the scientific literature. A non-aqueous immiscible bi-phase solvent system composed of a solution of technical CNSL in light petroleum and one of many diols (ethane, propane, butane and pentane) was used to separate cardanol, which was recovered from the petroleum phase in yields above 90 % and purity, analyzed by HPLC, over 99 % [58].

Later, also through a phase extraction process, Kumar et al. [26] presented a methodology based on the acidity difference between cardanol and cardol.

Basically, a methanolic solution of technical CNSL mixed with ammonium hydroxide was extracted with portions of hexane, from which pure cardanol was recovered with great efficiency. An important point here, the authors mention, is that the scale used (up to 1 kg of tCNSL is reported) makes this an industrially feasible process for the obtainment of large quantities of cardanol.

Innumerable advances have been made in order to isolate cardanol from CNSL with great yields and high purity. Indeed, the need for improvements in the technical and economical performances of this agro-business demands a new and

adequate development of practical techniques for the isolation of cardanol and, overall, its adequate chemical employment in the sense to aggregate value to a versatile by-product that continues to be overlooked inside and outside the academic field.

2.5 Synthetic and Technological Advances in the Cardanol Chemistry

In the last decade, our group has been dedicate its research activities to the development of new products and processes based on CNSL chemistry that justify its uses as ecofriendly technological materials, guided by a policy of aggregate value to its constituents, working in consonance with the green chemistry principles and the existing environmental legislation, in search of a sustainable industrial development.

The utilization of CNSL and its constituents has been reviewed in the literature in the last 20 years [19, 35, 39, 60, 53, 6, 7, 61] .

Although the main applications of cardanol were based on the production of resins and polymers [61], it did not take long for the appearance of new advanced materials, taking advantage of the peculiar chemical structure of cardanol [35, 39, 60, 6].

As presented in the beginning of this chapter, Brazil, Vietnam, Nigeria, Cote d'Ivoire, and India are the largest producers and exporters of cashew kernel in the world.

At the same time, Africa, Asia, and South America are endemic regions for the globally known dengue fever. It is estimated that, globally, each year up to 50 million dengue cases occur, from which 500,000 cases are diagnosed as the more seriously related illness, dengue hemorrhagic fever (DHF) [13].

The main vector for dissemination of dengue is a mosquito, also responsible for the spreading of yellow fever and malaria, called *Aedes aegypti*.

Despite the number of cases and the efforts of many countries to control infestations, dengue is considered a neglected disease, which has no effective drug or vaccine.

The method for controlling mosquito proliferation continues to be prevention of the mosquito breeding through the use of larvicides, since in larval stage is easier, compared to adult stage, to control *Aedes aegypti* reproduction.

The main problems associated with the commonly used larvicides are the emergence of insect species showing resistance and the toxicity associated with nontarget organisms.

In face of these arguments, the utilization of CNSL and its components for controlling mosquito infestation could be of great interest and economically feasible in developing countries that cultivate cashew and are also endemic areas.

The biological assays of cardol and cardanol against *Aedes aegypti* larvae presented interesting values of LC₅₀ (the concentration of compound to kill half of

the sample population) of 14.20 ± 0.62 and 32.90 ± 0.25 mg/mL, which are considered promising results once substances with LC_{50} lower than 100 mg/mL are potential larvicidal candidates [30].

Exploring the biocomposites field, many studies involving the interaction of cardanol–formaldehyde thermoset resins reinforced with different types of natural fibers were made.

Fibers of jute (*Corchorus capsularis*) [8], green-dwarf coir (*Cocos nucifera* L.) [9], and sisal (*Agave sisalana*) [10] were used in their natural form and chemically modified by alkaline treatment, to increase the thermal and mechanical properties of these biocomposites. In other works, the utilization of bamboo fibers (*Bambusa vulgaris*) [25] and sponge gourd fibers (*Luffa cylindrica*) [51] was also evaluated as reinforcements for cardanol resol-type resins. In all these studies, the chemical modification of fibers surface was important to improve the adhesion between fiber and matrix in the biocomposites and resulted in materials more homogeneous, resistant to thermal decomposition and with increased mechanical resistance.

Polybenzoxazines, a polymer originated by a ring-opening polymerization (ROP) of benzoxazine monomers, are bicyclic benzoheterocycles containing at least one oxazine ring, which are generated by the Mannich-like reaction of a phenol, formaldehyde, and an amine. This class of phenolic resin has attracted much attention due to its enhanced properties in comparison with traditional phenol formaldehyde resins, e.g., molecular design flexibility, no need of catalysts, excellent dimensional stability, low water absorption, and flammability.

Since the most used phenolic raw material for the synthesis of polybenzoxazines is still bisphenol-A (BPA), a pioneer work from Calò et al. [14] reported the utilization of cardanol as a renewable feedstock for the preparation of this type of resin and its application as a polymeric matrix in the production of bio-based composites.

Later on, another paper evaluated the synthetic feasibility of cardanol and other main constituents of technical CNSL as precursors of new mono- and

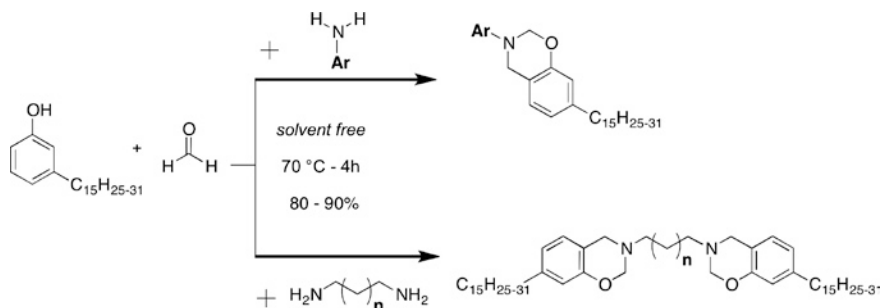


Fig. 2.8 Cardanol-based mono- and bis-benzoxazine synthetic scheme

bis-benzoxazines structures via cyclization reactions with formaldehyde and different aromatic amine derivatives under ecofriendly conditions (Fig. 2.8) [3].

Hindered phenolic compounds are well known for their antioxidant activity.

The mechanism responsible for this activity is based on the donation of a proton (an H atom, from the hydroxyl group) that reduces the free-radical oxidation reaction of organic molecules, promoted by peroxy species ($\text{ROO}\cdot$).

This antioxidant effect can be enhanced by the presence of bulky groups linked to the aromatic ring of the phenolic structure. Butylated hydroxytoluene, commonly called BHT, is the most widely used phenolic antioxidant in the world and is synthesized by the alkylation of p-cresol.

As cardanol already has a 15 carbon atoms long side chain, which is considered a large group although located in *meta*-position, the investigation of its antioxidant capacity was evaluated by computational methods and electrochemical analyses (square wave voltammetry and cyclic voltammetry) and compared to BHT [32]. The results obtained showed that saturated cardanol presented a lower oxidation potential compared to BHT.

A further analysis [33] concluded that unsaturated cardanol isomer has even lower values, and experiments of square wave voltammetry demonstrated that the unsaturated compound presented higher current values than saturated compounds indicating that a higher number of unsaturated molecules were participating in the oxidation process.

In order to increase the steric hindrance over the phenolic hydroxyl of cardanol, Rios et al. synthesized two *ortho*-substituted derivatives of cardanol, adding to the aromatic ring a *tert*-butyl group [48] and a *tert*-amyl group [47, 46].

Both compounds, when added to mineral lubricant oils, reduced the formation of oxidation products and also proved to be more thermally stable than BHT.

Another important class of antioxidants used in the industry is the “secondary type antioxidants,” which prevent oxidation by reacting with hydroperoxides formed by thermal oxidation reactions.

Organophosphates and organothiophosphates are the most common compounds in this class. They are usually combined with hindered phenols and applied as a synergetic formulation to retard the initiation of oxidative processes.

Cardanol was used as starting material in the synthesis of many useful substances that showed excellent activity as secondary type antioxidants.

In the work of Façanha et al., the antioxidant activity of a diethylphosphate derivative of hydrogenated cardanol in naphthenic mineral oils (NH10 and NH20) was investigated through thermogravimetric analysis (TGA).

The authors reported improvement in their thermal-oxidative stability by the increase in the temperature of initial degradation of the additivated samples when compared to the pure oils [18].

Another paper described the synthesis of a diethylthiophosphate derivative of cardanol and similar results of antioxidant activity [31].

Other organophosphorus compounds derived from cardanol were also synthesized and evaluated as antioxidants in mineral oils [29, 36], polymers [27], biodiesel [28], and others [45, 47, 46].

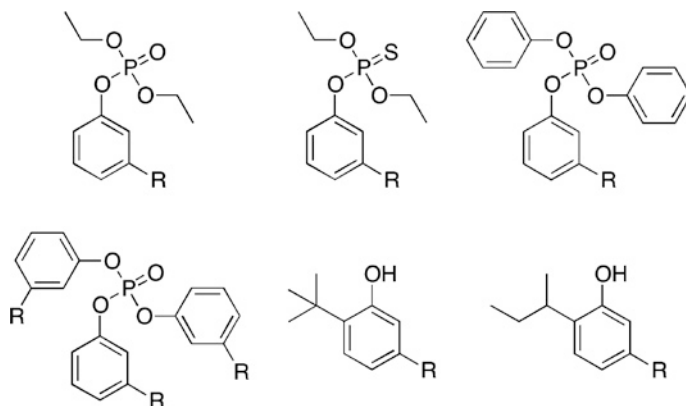


Fig. 2.9 Chemical structure of cardanol-based antioxidants

In Fig. 2.9 is described the chemical structure of some cardanol-based antioxidants.

Porphyrins and phthalocyanines are interesting classes of macrocyclic compounds. Due to their extended π -system and metal ion binding capacity, these compounds are commonly used in optical/electronic devices, as active layers for gas sensors, homogeneous/heterogeneous catalysis, organic dyes for photoinduced electron-transfer processes, liquid crystals, and OLEDs.

In homogeneous catalysis, the utilization of porphyrins and phthalocyanines is limited, since their active sites are strongly hindered due to the low solubility of these molecules in most commonly used organic solvents.

To overcome this situation, cardanol was used as raw material in the synthesis of many of these macroheterocyclic compounds. The presence of long alkyl chains of cardanol has shown a great influence in the physical properties of these derivatives, such as a low melting points and high solubility in organic solvents [4, 5] (Fig. 2.10).

A composite material obtained by impregnation of a Cu-substituted cardanol-based porphyrins onto TiO_2 (anatase phase) increased the photoactivity in the degradation of 4-nitrophenol in aqueous suspension. In this context was confirmed the importance of lipophilicity, photostability of the sensitizer, and the involvement of the Cu(II) in the process [38] (Fig. 2.10).

Cardanol-based porphyrins were also applied in the preparation of a super-paramagnetic fluorescence nanosystem composite material, by the interaction of side chains derived from cardanol with oleic acid, which was assembled onto the Fe_3O_4 surface modified [15].

Sandwich-type phthalocyanines containing a rare earth metal core (Pr, Nd, Eu–Lu) and macrocycles peripherally substituted by pentadecylphenoxy groups were synthesized using a cardanol-based phthalonitrile precursor and the respective lanthanide acetate [54] (Fig. 2.10).



As shown in Fig. 2.11, palladium-catalyzed cyclocarbonylation of allylic cardanol and cardol derivatives produced selectively heterocycles having different ring sizes [1].



Olefin metathesis reaction on cardanol is an important class of reactions that allows for the synthesis of new olefins.

The presence olefin group in the long chain attached to the *meta*-position of the phenolic ring allowed the preparation of new cardanol-based compounds via Ru-catalyzed metathesis reactions [20, 37, 60]. Cardanol was subjected to transfer hydrogenation catalyzed by RuCl_3 using isopropanol as a reductant.

Green nanocarriers based on the combination of natural renewable materials like cardanol and cholesterol have been used to encapsulate lipophilic or hydrophilic compounds such as the chlorogenic acids extracted from different rowanberries like *Sorbus Americana* and *Vaccinium* sp. [12, 11].

2.6 Final Considerations

Among the green chemistry concepts developed by P. Anastas and J. Warner in 1998, the 7th principle, which addresses the “use of renewable feedstock,” can be highlighted when considering the use of CNSL and its constituents as starting material in the development of new chemical compounds.

As modern society faces the continued growth demand for chemicals, sustainable and innovative technologies are necessary in order to overcome current difficulties and also avoid the evolution of new ones. The advent of agro-industry waste as a resource of raw materials has attracted the attention of researchers and opened a window of opportunity for the breakthrough of alternative products to the oil industry.

The increasing number of research papers dedicated to this theme, and also the increasing production of cashew nuts turns cardanol into a promising renewable feedstock for the development of a wide range of functional products.

However, for this forthcoming industry to develop efficiently and consistently, are mandatory the investments in innovation, especially the development of new products and processes focused on the strengths and peculiarities of these phenolic lipids, not only seeking alternatives for the commercially known products, but also envisioning the arising of new ones with breakthrough properties and applications.

In any case, it is still valid to point out challenges involved in CNSL development, in particular when it comes to the efficiently isolation of cardanol, free from impurities, in high yields and industrial scales. Another important aspect to be considered is the need of a closer relationship between universities and research centers with the industrial segment, which is the driving force for technological transformations.

Acknowledgements The authors would like to thank the Brazilian agencies CNPq (Universal 449060/2014-4, PVE 401359/2014-0 and 402566/2013-0) and Capes for the financial support.

References

1. Amorati R, Attanasi OA, El Ali B et al (2002) Synthesis of new cardanol and cardol derivatives by allylation and regioselective cyclocarbonylation reactions. *Synthesis* 18:2749–2755
2. Andrade TJAS, Araújo BQ, Citó AMGL et al (2011) Antioxidant properties and chemical composition of technical Cashew Nut Shell Liquid (tCNSL). *Food Chem* 126:1044–1048
3. Attanasi OA, Behalo MS, Favi G et al (2012) Solvent free synthesis of novel mono- and bis-benzoxazines from cashew nut shell liquid components. *Curr Org Chem* 16:2613–2621
4. Attanasi OA, Ciccarella G, Filippone P et al (2003) Novel phthalocyanines containing cardanol derivatives. *J Porphyr Phthalocyanines* 07:52–57
5. Attanasi OA, Del Sole R, Filippone P et al (2004) Synthesis of novel lipophilic porphyrin-cardanol derivatives. *J Porphyr Phthalocyanines* 08:1276–1284
6. Balachandran VS, Jadhav SR, Vemula PK et al (2013) Recent advances in cardanol chemistry in a nutshell: from a nut to nanomaterials. *Chem Soc Rev* 42:427–438
7. Balgude D, Sabnis AS (2014) CNSL: an environment friendly alternative for the modern coating industry. *J Coating Tech Res* 11:169–183
8. Barreto ACH, Esmeraldo MA, Rosa DS et al (2010) Cardanol biocomposites reinforced with jute fiber: microstructure, biodegradability, and mechanical properties. *Polym Compos* 31:1928–1937
9. Barreto ACH, Júnior AEC, Freitas JEB et al (2013) Biocomposites from dwarf-green Brazilian coconut impregnated with cashew nut shell liquid resin. *J Compos Mater* 47:459–466
10. Barreto ACH, Rosa DS, Fachine PBA et al (2011) Properties of sisal fibers treated by alkali solution and their application into cardanol-based biocomposites. *Compos Part A Appl Sci* 42:492–500
11. Bloise E, Becerra-Herrera M, Mele G et al (2014) Sustainable preparation of cardanol-based nanocarriers with embedded natural phenolic compounds. *ACS Sustain Chem Eng* 2:1299–1304
12. Bloise E, Carbone L, Colafemmina G et al (2012) First example of a lipophilic porphyrin-cardanol hybrid embedded in a cardanol-based micellar nanodispersion. *Molecules* 17:12252–12261
13. Callaway E (2007) Dengue fever climbs the social ladder. *Nature* 448:734–735
14. Calò E, Maffezzoli A, Mele G et al (2007) Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites. *Green Chem* 9:754–759
15. Clemente CS, Ribeiro VGP, Sousa JEA et al (2013) Porphyrin synthesized from cashew nut shell liquid as part of a novel superparamagnetic fluorescence nanosystem. *J Nanopart Res* 15:1–10
16. Duarte O, Paull RE (2015) Exotic fruits and nuts of the new world. CABI Publishing, Boston
17. FAOSTAT (2015) Food and Agriculture Organization of the United Nations. <http://faostat.fao.org>. Accessed 20 Dez 2015
18. Façanha MAR, Mazzetto SE, Carioca JOB et al (2007) Evaluation of antioxidant properties of a phosphorylated cardanol compound on mineral oils (NH10 and NH20). *Fuel* 86:2416–2421
19. Gedam PH, Sampathkumaran PS (1986) Cashew Nut Shell Liquid: extraction, chemistry and applications. *Prog Org Coat* 14:115–157
20. Guo Y-C, Mele G, Martina F et al (2006) An efficient route to biscardanol derivatives and cardanol-based porphyrins via olefin metathesis. *J Organomet Chem* 691:5383–5390
21. Harvey M (1937) Process of destructively distilling cashew nut shell liquid. US Patent 2,098,824, 9 Nov 1937
22. Hoang AS, Tran TH, Nguyen HN et al (2015) Synthesis of oxime from a renewable resource for metal extraction. *Korean J Chem Eng* 32:1598–1605

23. Horváth IT, Anastasia PT (2007) Innovations and green chemistry. *Chem Rev* 107:2169–2173
24. Janick J, Paull RE (eds) (2008) Encyclopedia of fruit and nuts. CABI Publishing, Boston
25. Júnior AEC, Barreto ACH, Rosa DS et al (2015) Thermal and mechanical properties of bio-composites based on a cashew nut shell liquid matrix reinforced with bamboo fibers. *J Comp Mater* 49:2203–2215
26. Kumar PP, Paramashivappa R, Vithayathil PJ et al (2002) Process for isolation of cardanol from technical Cashew (*Anacardium occidentale* L.) Nut Shell Liquid. *J Agric Food Chem* 50:4705–4708
27. Lomonaco D, Cangane FY, Mazzetto SE (2011) Thiophosphate esters of cashew nutshell liquid derivatives as new antioxidants for poly(methyl methacrylate). *J Therm Anal Calorim* 104:1177–1183
28. Lomonaco D, Maia FJN, Clemente CS et al (2012) Thermal studies of new biodiesel antioxidants synthesized from a natural occurring phenolic lipid. *Fuel* 97:552–559
29. Lomonaco D, Maia FJN, Mazzetto SE (2013) Thermal evaluation of cashew nutshell liquid as new bioadditives for poly(methyl methacrylate). *J Therm Anal Calorim* 111:619–626
30. Lomonaco D, Santiago GMP, Ferreira YS et al (2009) Study of technical CNSL and its main components as new green larvicides. *Green Chem* 11:31–33
31. Lopes AAS, Carneiro EA, Rios MAS et al (2008) Study of antioxidant property of a thiosphorated compound derived from cashew nut shell liquid in hydrogenated naphthenics oils. *Braz J Chem Eng* 25:119–127
32. Maia FJN, Clemente CS, Oliveira TMBF et al (2012) Electrochemical and computational studies of phenolic antioxidants from cashew nut shell liquid. *Electrochim Acta* 79:67–73
33. Maia FJN, Ribeiro FWP, Rangel JHG et al (2015) Evaluation of antioxidant action by electrochemical and accelerated oxidation experiments of phenolic compounds derived from cashew nut shell liquid. *Ind Crop Prod* 67:281–286
34. Manjula S, Kumar VC, Pillai CKS (1992) Kinetics and mechanism of oligomerization of cardanol using acid catalysts. *J Appl Polym Sci* 45:309–315
35. Mazzetto SE, Lomonaco D, Mele G (2009) Óleo da castanha de caju: oportunidades e desafios no contexto do desenvolvimento e sustentabilidade industrial. *Quím Nova* 32:732–741
36. Mazzetto SE, Oliveira LDM, Lomonaco D et al (2012) Antiwear and antioxidant studies of cardanol phosphate ester additives. *Braz J Chem Eng* 29:519–524
37. Mele G, Li J, Vasapollo G (2008) Fine chemicals from cardanol via cross metathesis reaction. *Chim Oggi* 26:72–74
38. Mele G, Del Sole R, Vasapollo G et al (2004) Polycrystalline TiO₂ impregnated with cardanol-based porphyrins for the photocatalytic degradation of 4-nitrophenol. *Green Chem* 6:604–608
39. Mele G, Vasapollo G (2008) Fine chemicals and new hybrid materials from cardanol. *Mini-Rev Org Chem* 5:243–253
40. Mitchell JD, Mori SA (1987) The cashew and its relatives (*Anacardium*: *Anacardiaceae*). *Mem New York Bot Gard* 42:1–76
41. Murthy BG, Samban MA, Aggarwal JS (1968) Identification of some naturally occurring alkyl-substituted phenols in cashew-nut shell liquid by chromatographic techniques. *J Chromatogr* 32:519–528
42. Oliveira MSC, Morais SM, Magalhães DV (2011) Antioxidant, larvicidal and anti acetylcholinesterase activities of cashew nut shell liquid constituents. *Acta Tropica* 117:165–170
43. Paramashivappa R, Kumar PP, Vithayathil PJ (2001) Novel method for isolation of major phenolic constituents from Cashew (*Anacardium occidentale* L.) Nut Shell Liquid. *J Agric Food Chem* 49:2548–2551
44. Patel RN, Bandyopadhyay S, Ganesh A (2006) Extraction of cashew (*Anacardium occidentale*) nut shell liquid using supercritical carbon dioxide. *Bioresour Technol* 97:847–853
45. Rios MAS, Mazzetto SE (2012) Thermal behavior of phosphorus derivatives of hydrogenated cardanol. *Fuel Process Technol* 96:1–8

46. Rios MAS, Nascimento TL, Santiago SN et al (2009) Cashew Nut Shell Liquid: a versatile raw material utilized for syntheses of phosphorus compounds. *Energy Fuel* 23:5432–5437
47. Rios MAS, Sales FAM, Mazzetto SE (2009) Study of antioxidant properties of 5-n-pentadecyl-2-tert-amylphenol. *Energy Fuel* 23:2517–2522
48. Rios MAS, Santiago SN, Lopes AAS et al (2010) Antioxidative activity of 5-n-pentadecyl-2-tert-butylphenol stabilizers in mineral lubricant oil. *Energy Fuel* 24:3285–3291
49. Rodrigues FHA, Souza JRR, França FCF et al (2006) Thermal oligomerisation of cardanol. *e-Polymers* 6:1027–1040
50. Sanjeeva SK, Pinto MP, Narayanan MM et al (2014) Distilled technical cashew nut shell liquid (DT-CNSL) as an effective biofuel and additive to stabilize triglyceride biofuels in diesel. *Renew Energy* 71:81–88
51. Silva AL, Silva LRR, Camargo IA et al (2015) Cardanol-based thermoset plastic reinforced by sponge gourd fibers (*Luffa cylindrica*). *Polímeros* (in press)
52. Sood SK, Tyman JHP, Durrani A et al (1986) Practical liquid chromatographic separation of the phenols in technical cashew nutshell liquid from *Anacardium occidentale*. *Lipids* 21:241–246
53. Stasiuk M, Kozubek A (2010) Biological activity of phenolic lipids. *Cell Mol Life Sci* 67:841–860
54. Słota R, Dyrda G, Hofer M et al (2012) Novel lipophilic lanthanide bis-phthalocyanines functionalized by pentadecylphenoxy groups: synthesis, characterization and UV-photostability. *Molecules* 17:10738–10753
55. Thévet A (1558) The singularities of France Antarctica, otherwise called America, and of several Lands and Isles discovered of our times
56. Thévet A (1997) *Le Brésil d'André Thévet: Les singularités de la France antarctique (1557)*. Edition Chandeigne, Paris
57. Tyman JHP (1996) *Synthetic and natural phenols*. Elsevier, Amsterdam
58. Tyman JHP, Bruce IE, Payne P (1992) Specific isolation of phenolic lipids by phase separations. *Nat Prod Lett* 1:117–120
59. Tyman JHP, Tychopoulos V, Colenutt BA (1981) Long-chain phenols. *J Chromatogr A* 213:287–300
60. Vasapollo G, Mele G, Del Sole R (2011) Cardanol-based materials as natural precursors for olefin metathesis. *Molecules* 16:6871–6882
61. Voirin C, Caillol S, Sadavarte NV et al (2014) Functionalization of cardanol: towards biobased polymers and additives. *Polym Chem* 5:3142–3162
62. Wasserman D, Dawson C (1948) Cashew Nut Shell Liquid. III. The cardol component of Indian Cashew Nut Shell Liquid with reference to the liquid's vesicant activity. *J Am Chem Soc* 70:3675–3679
63. Yuliana M, Tran-Thi NY, Ju Y-H (2012) Effect of extraction methods on characteristic and composition of Indonesian cashew nut shell liquid. *Ind Crop Prod* 35:230–236

Cashew Nut Shell Liquid

A Goldfield for Functional Materials

Parambath, A. (Ed.)

2017, VIII, 230 p. 146 illus., 47 illus. in color., Hardcover

ISBN: 978-3-319-47454-0