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Conference paper

Egid B. Mubofu*

From cashew nut shell wastes to high value chemicals

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Abstract: The amount of waste generated in cashew nut processing factories has caused serious problems for a long time. However, this situation is about to change because they are being turned into an opportunity by a variety of bio-based chemicals. Todate, cashew nut shells (CNS) have proven to be among the most versatile renewable resource as they produce cashew nut shell liquid (CNSL). CNSL which is a dark reddish brown viscous liquid (*ca*. 30–35 wt%) is extracted from the soft honeycomb of the CNS. The shells have been regarded as a by-product of the cashew industry though now it is a cheaper source of natural unsaturated phenols. CNSL offers a multitude of interesting possibilities for the synthesis of speciality chemicals, high value products and polymers. Our recent research efforts have demonstrated that its constituents can be transformed into diverse functional chemicals. This paper reports some key results on how cashew nut shells (an agro waste from cashew nut processing factories) have been employed to produce several functional materials and chemicals. The materials that are highlighted include the synthesis of 3-propylphenol from cardanol and anacardic acid, some polymers prepared from CNSL components, heterogeneous catalysts prepared using CNSL as a templating agent and anacardic acid capped chalcogenide nanoparticles.

Keywords: anacardic acid; cardanol; cashew nut shell liquid (CNSL); cashew nut shells (CNS); Green Chemistry V; heterogeneous catalysis; hydrogenation; polymers; 3-propylphenol.

Introduction

Green chemistry, renewable energy and waste management have recently become a recurring trifactor in the forefronts of innovative research. Due to this, derivatives of by-products or wastes prepared from environmentally-friendly protocols, intended for use in various applications such as renewable energy, are increasingly receiving a lot of attention since they not only provide an alternative source of chemicals but also provide an alternative waste disposal approach. In cashew nut processing factories, cashew nut shells (CNS) which are about 25 % [1] of the cashew weight are normally released to the environment and discarded as waste. However, inside the soft honeycomb (Fig. 1) of these shells, there is a valuable viscous liquid called cashew nut shell liquid (CNSL). This reddish-brown liquid can be extracted from the soft honeycomb structure located inside the cashew nut shell by solvent, thermal or by mechanical means. Depending on the mode of extraction, CNSL is classified into natural and technical CNSL where natural CNSL is obtained by cold solvent extraction while thermally extracted is classified as technical CNSL. Cashew nutshell liquid (CNSL) constitutes up to about 30–35 wt% of the nut shell depending on the method of extraction [2, 3].

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***Corresponding author: Egid B. Mubofu,** Chemistry Department, University of Dar es Salaam, P.O. Box 35061, Dar es Salaam, Tanzania, Phone: +255-784-538-344, Phone/Fax: +255-22-2410038, E-mail: ebmubofu@gmail.com; ebmubofu@udsm.ac.tz

Fig. 1: A cross-section of a cashew nut showing the honeycomb part of the shell.

The worldwide annual production of raw cashew nuts stand at approximately 2.1 million tons; the top five producers being Vietnam (1.1 million tons), Nigeria (0.95 million tons), India (0.75 million tons), Coted'Ivoire (0.45 million tons%) and Brazil (0.11 million tons) [4]. CNSL has many industrial applications such as the manufacturing of: (a) Friction modifying materials for brake lining, clutch facing and industrial belting, (b) Various types of coatings (e.g., industrial and marine coatings, varnishes, lacquers, and enamels), (c) Rubber products of improved performance, (d) Adhesives used in the manufacturing of ply-wood and particle boards, and (e) Laminating materials for reducing brittleness and improving the flexibility of the laminates [5–7]. Furthermore, it has been reported [8] that chlorinated and copper derivatives of CNSL have pesticidal effects while components of CNSL have medicinal potential as anticancer, antioxidant and antibacterial agents [9]. The presence of a benzene ring and the side chain ($C_{15}H_{31-n}$), of varying degrees of unsaturation located at a *meta* position relative to the phenolic group of CNSL components has made them excellent renewable starting materials in the synthesis of benzene ring-containing chemicals. Furthermore, the presence of double bond(s) in the side chain presents additional advantage for generating useful bio-based chemicals. For instance, the synthesis of cardanol-based porphyrins have been possible by taking the advantage of double bonds present in the side chain of cardanol through ruthenium-catalyzed self and cross-metathesis reactions via olefin metathesis [10, 11]. The olefin metathesis reaction on cardanol has also afforded the synthesis of new olefins that are sometimes impossible to prepare via other methods and approaches [11].

Although there are many reviews on CNSL-related topics, very few have focused on the derivatisation and/or transformation of CNSL components into fine chemicals and new hybrid materials [12]. In this contribution, the use of CNSL components as key renewable starting material(s) in the synthesis of fine chemicals and some hybrid functional materials prepared via catalytic reactions such as metathesis, isomerisation, hydrogenation, epoxidation and polymerization is reported.

Fine chemicals and functional materials synthesized from CNSL

Extraction and composition of CNSL

Natural CNSL is comprised of four major phenolic constituents, namely, anacardic acid, cardanol, cardol and 2-methyl cardol (Fig. 2) [13, 14]. The percentage composition of these phenolics vary depending on the mode of extraction where a solvent-extracted CNSL contains anacardic acid (60–65 %), cardol (15–20 %), cardanol (10 %) and traces of methylcardol. When a technical extraction mode is employed, the amount of cardanol increases to 60–65 % due to decarboxylation of anacardic acid, while the contents of cardol and methylcardol remain unchanged [15].

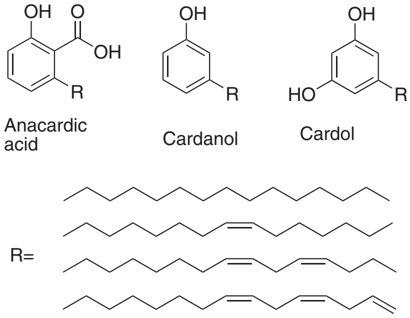


Fig. 2: Major components of cashew nut shell liquid.

Synthesis of 3-propylphenol from CNSL components

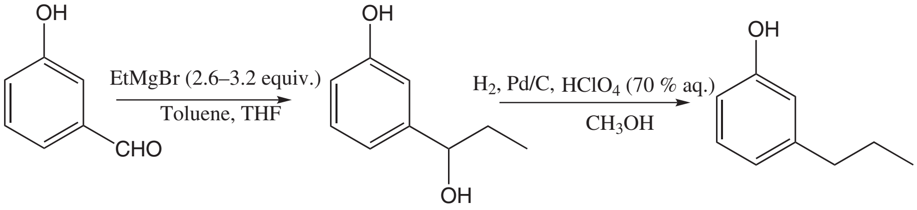
Cardanol and anacardic acid, the major components of technical-grade and solvent-extracted CNSL, respectively, are potential starting materials for the synthesis of 3-propylphenol. 3-propylphenol is among several phenolic components of cattle and buffalo urine attractive to tsetse flies, glossina spp (*diptera, glossinidae*) that are responsible for African trypanasomiasis disease [16]. Other phenolic components present in the urine, having similar characteristics are: 4-methylphenol, 3-methylphenol, 4-ethylphenol, 3-ethylphenol, 4-*n*-propylphenol, and 2-methoxyphenol. The synthesis protocols of these kairomones which are ingredients in tsetse fly attractants are undoubtedly very expensive because they are made from expensive and non-renewable environmentally unfriendly petroleum based starting materials [17]. In addition, their synthesis steps involve the use of environmentally unfriendly chemistries such as the use of Grignard reagents resulting into a lot of salt wastes (Scheme 1).

Compared to other compounds used as artificial odor bait in an effort to eradicate trypanosomiasis by eliminating the tsetse flies, it is mainly 3-propylphenol kairomone that has been extensively used [17]. This calls for a search for an alternative, relatively green, low-cost and readily-available feedstock from waste and natural sources such as cashew nut shells (CNS).

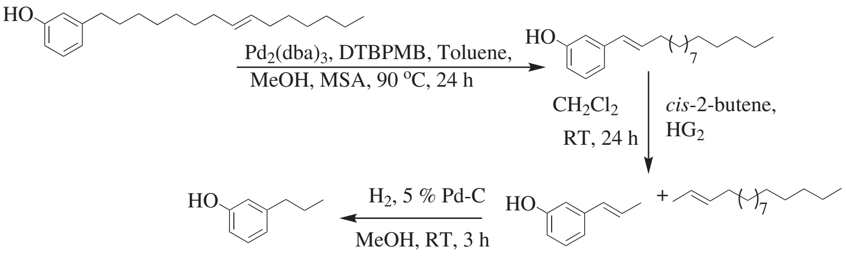
Synthesis of 3-propylphenol from cardanol

The synthesis protocol of 3-propylphenol using cardanol as a starting material [18] involves three steps (Scheme 2): i) Isomerisation of the carbon-carbon double bond from its natural position (C8) to the benzylic position (C1) thus forming isocardanol, ii) Cross-metathesis of isocardanol with *cis*-2-butene to form *trans*-3-(prop-2-enyl)phenol, and iii) Hydrogenation of *trans*-3-(prop-2-enyl)phenol to form 3-propylphenol.

The isomerisation of cardanol is known to be accomplished by employing a catalytic system of Pd_2 $(dba)_3$, methane sulfonic acid and DTBPMB [19]. During this reaction step, the uncontrolled migration of the double bond across the long alkyl chain of cardanol occurs and results into a mixture of isomers where the desired isomer (double bond at C1) accounts for about 40 % [18–20]. The cross-metathesis of the isomeric mixture with



Scheme 1: Synthesis of 3-propylphenol from petroleum-based starting materials.



Scheme 2: Synthesis of 3-propylphenol from cardanol.

cis-2-butene uses the Hoveyda-Grubs second generation catalyst (HG$_2$) to successfully yield the desired products. The hydrogenation of *trans*-3-(prop-2-enyl)phenol obtained from the cross-metathesis is the last step and produces the desired product, 3-propylphenol in a yield of 4.4 % relative to the amount of cardanol used [18].

Synthesis of 3-propylphenol from anacardic acid

The kairomone, 3-propylphenol can also be obtained when monoene anacardic acid is employed as an alternative starting material where the yields are improved to 18 % from 4.4 % when the starting material is cardanol [21]. Consistent with the available literature [22], pure monoene anacardic acid can be obtained by refluxing anacardic acids (a mixture of triene, diene and monoene) in a mixture of propan-2-ol as a reducing agent and ruthenium(III) chloride catalyst in acetone. Under these conditions, triene and diene anacardic acids are selectively hydrogenated to form monoene anacardic acid. At any catalyst proportion, the monoene anacardic acid remains unaffected by this transfer hydrogenation [22]. At this high refluxing temperatures (105–110 °C) one would expect anacardic acid to decarboxylate to cardanol but surprisingly it remains unaffected.

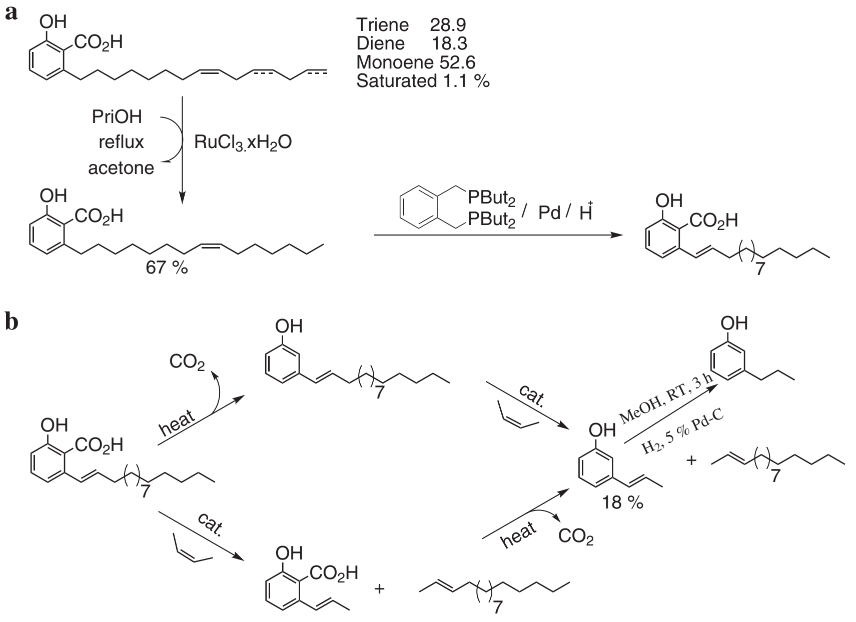
As it is for cardanol, the first step towards the synthesis of 3-propylphenol from monoene anacardic acid is also the isomerisation reaction. This isomerisation reaction also results into a mixture of isomers in which the desired isomer, isoanacardic acid, constitutes about 67 % [21] (Scheme 3). The notable difference between isocardanol (from the isomerisation of cardanol) and isoanacardic acid (from the isomerisation of monoene anacardic acid) is that the former product is an oily compound while the latter product is a crystalline solid whose crystal structure could be obtained readily [21]. Moreover, isoanacardic acid is produced in high yields compared to isocardanol. The metathesis of isoanacardic with *cis*-2-butene produces (*E*)-3-(prop-1-enyl)phenol in 18 % yields whose subsequent hydrogenation yields 3-propylphenol. This yield is an encouraging improvement compared to the yield of 4.4 % propylphenol previously obtained from the isomerisation of cardanol [18].

The yield of 3-propylphenol have recently been improved further by other workers [23] via the isomerisation metathesis of 3-(non-8-enyl)phenol (Scheme 4). The reaction protocols involve the one pot conversion of either cardanol or anacardic acid mixture (triene, diene and monoene), to 3-(non-8-enyl)phenol (98 % purity) via ethenolysis and distillation. The resulting phenol is then subjected to isomerising cross-metathesis with short-chain olefins in the presence of [Pd(μ-Br)(tBu3P)]$_2$ isomerisation catalyst assisted by a second-generation Hoveyda–Grubbs catalyst, to shorten the olefinic side chain [23]. The synthesis is then followed by the hydrogenation step to afford 3-propylphenol up to 78 % yield.

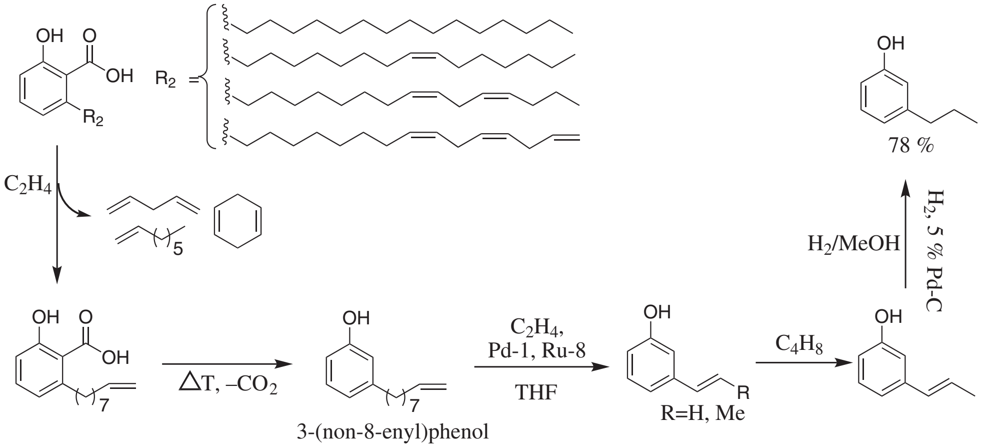
Based on these developments, it is clear that cashew nut shells are not wastes but rather potential renewable agro-waste resource capable of replacing the non-renewable resources in the synthesis of 3-propylpheno kairomone.

Polymers derived from cardanol

Generally, phenols are used as good monomers for the preparation of phenolic resins. They are mainly prepared by reacting a (un)substituted phenol with formaldehyde. The properties of these resins vary with the nature of the phenols, the stochiometric ratio of phenol to formaldehyde, and the pH of the reaction.



Scheme 3: Preparation of a) isoanacardic acid from anacardic acids, and b) 3-propylphenol from isoanacardic acid.

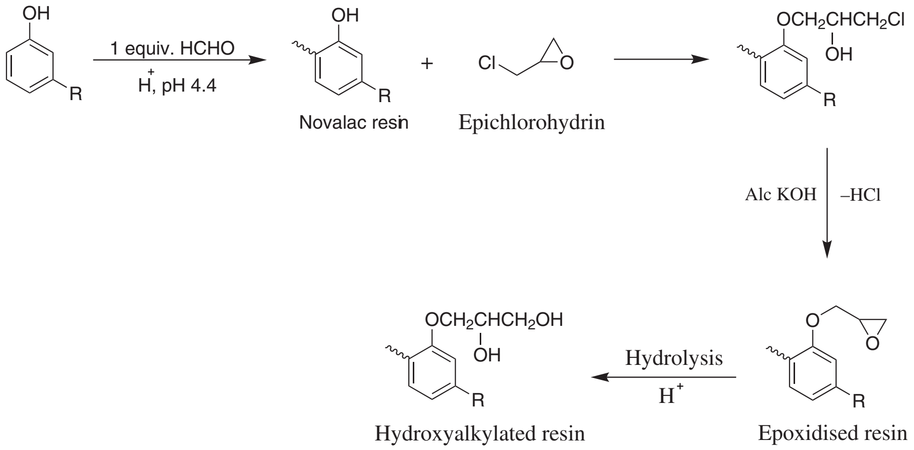


Scheme 4: Synthesis of 3-propylphenol via isomerising-metathesis of 3-(non-8-enyl)phenol.

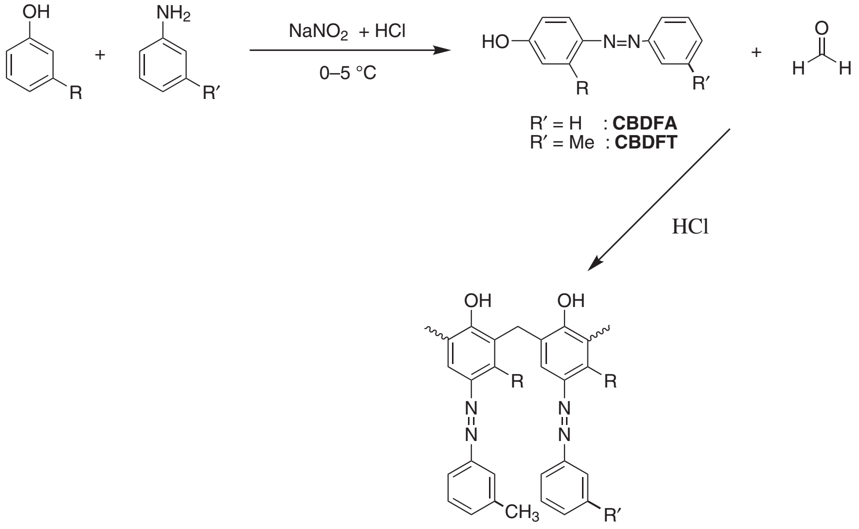
The phenolic nature of cardanol enables it to react with formaldehyde and other aldehydes to produce numerous phenolic resins used in industrial coatings and high-gloss films for indoor use, among other applications. A proper example of this is the condensation of cardanol with formaldehyde (1:1 mole ratio) using sebacic acid as a catalyst leading to a novalac-type phenolic resin (Scheme 5). Upon epoxidation and hydrolysis of this resin, a polyol is formed. The polyol can be condensed with other commercially available polyol such as polypropylene glycol-1200 (PPG-1200) and hexamethylene diisocyanate to produce a robust polyurethanes [24].

Cardanol can also be used as a scaffold to prepare heterolepetic phenols such as the CBDFA and CBDFT dyes, using aniline and *m*-toluidine as reactants, respectively (Scheme 6).

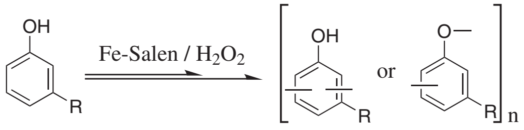
These dyes are good monomers when subjected to acid-catalyzed condensation reactions with formaldehyde in the presence of azo groups which enhance the thermal stability of the resulting resins to temperatures as high as 400 °C [25].



Scheme 5: Formation of the hydroxyalkylated resin using a cardanol monomer.



Scheme 6: Preparation and condensation of cardanol-based a) CBDFA, and b) CBDFT dyes.



Scheme 7: Oxidative polymerization of cardanol.

Cardanol-based polymers can also be prepared using formaldehyde-free protocols such as the oxidative polymerization of cardanol using iron-*N,N′*-ethylenebis(salicylideneamine) (Fe-salen) as a catalyst (Scheme 7) [26].

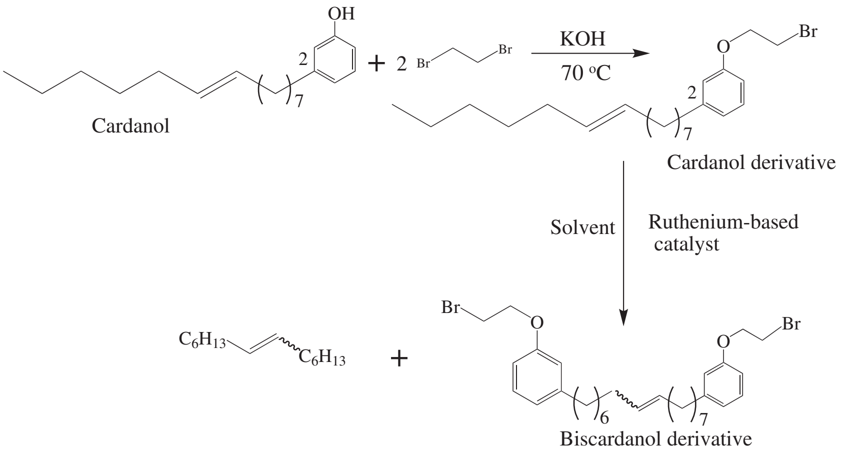
In addition, cardanol can be used to modify resole-type resins to form copolymers. The copolymer is prepared by standard reaction protocols for resoles, the difference being the presence of the additional phenolic reactant, cardanol. The maximum cardanol content in the reaction mixture can be as high as 40 % and it has been noted that the higher the cardanol content, the more viscous is the resin [27]. The modification of the resole-type resin with cardanol, results to a proportional increase in the flexibility and fracture toughness, as well as the decrease in the flexural modulus of the cured resins due to a decrease in the crosslink density and the brittleness of the resins [27].

Furthermore at 70 °C in the presence of KOH, cardanol is capable of reacting with 1,2-bromoethane to yield a cardanol derivative (Scheme 8) which upon self-metathesis of cardanol derivative using ruthenium catalyst yields a biscardanol that has a potential use in resins, surface coatings and friction lining materials [10].

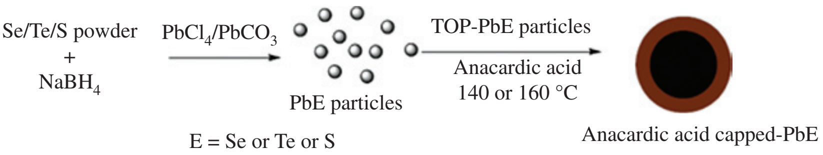
Anacardic acid capped chalcogenide nanoparticles

The naturally occurring anacardic acid which is extracted from CNS as one of the components in CNSL was isolated from CNSL using procedures described by other workers [14]. The acid is an effective capping agent for synthesis of nanomaterials at low reaction temperatures [28, 29]. In a typical synthesis of these metal chalcogenide nanoparticles, a chalcogen powder was reduced to the corresponding ion by adding 0.32 mmol of chalcogen powder to 20.0 mL of deionized water in a three neck flask at room temperature. A 0.79 mmol solution of sodium borohydride was then added to the flask contents and the flask was purged with nitrogen flow to create an inert atmosphere. The reduction reaction was carried out for 2 h with continuous stirring. A 0.32 mmol solution of the metal salt (Cd or Pb) was added to the reduced ion solution and stirred for 5 min, followed by the addition of excess methanol to form the bulk ME (M = Cd/Pb and E = S, Se, Te). The latter was isolated by centrifugation and dispersed in 6.0 mL of TOP. The resultant ME-TOP mixture was then injected into 6.0 g of anacardic acid. The reaction contents were cooled to room temperature, followed by the addition of excess methanol to flocculate the nanoparticles. The anacardic acid capped ME nanoparticles were isolated after centrifugation. This preparation procedure which enabled shape control and the stabilization of ME (M = Cd/Pb, E = S, Se and Te) nanoparticles via a simple solution-based thermolysis route at moderate reaction temperatures as summarized in Scheme 9 for PbE.

The use of anacardic acid as a capping agent confers on the route, some degree of adherence to the principles of green chemistry. The anacardic acid-capped PbS and PbSe nanoparticles displayed spherical shapes, whereas cube-like shapes were obtained for PbTe nanoparticles. These results are similar to the olive oil-capped PbS nanoparticles previously reported by other workers [29]. Recently, the synthesis and shape



Scheme 8: Synthesis of biscardanol derivative from cardanol.



Scheme 9: Reaction scheme for the synthesis of anacardic acid-capped PbE (E = Se, Te or S).

control of CdE (E = S, Se and Te) nanoparticles stabilized by anacardic acid have also been reported [30]. Both anacardic acid capped CdSe and CdTe nanoparticles showed anisotropic morphologies with CdTe particles being more oblate in shape with an average size of 15.80 ± 2.8 nm. In general, the assembly of all anacardic acid capped CdE (E = S, Se and Te) nanoparticles were well ordered in a mosaic type arrangement. An almost equal inter-particle distance of approximately 3 nm for the CdS, CdSe and CdTe particles as observed from the TEM images (Fig. 3).

The use of CNSL in the synthesis of heterogeneous catalysts

One of many methods to prepare heterogeneous catalysts is by attaching a catalyst (metal or an enzyme) to a solid support, such as micelle templated silica (MTS). The MTS and its derivatives are prepared through sol-gel reactions using micelle templates. The pores of these materials are usually greater than two nanometres, sufficient to accommodate a metal or a small enzyme catalyst. The general synthesis strategy for MTS involves the condensation of an appropriate monomer in the presence of a templating agent [31]. The removal of the templating agent from the composite material is usually achieved by a soxhlet extraction, hot filtration or calcinations, thereby exposing a material bearing a network of pores (Fig. 4). The silica surface displays different types of Si–O bonds which may either be silanols (≡Si–OH) or siloxanes (≡Si–O–Si≡), which have a significant influence on the particle properties.

In this regard, CNSL has been reported [32] to be a good templating agent for the synthesis of mesoporous materials. MTS synthesized using CNSL templates have pores with diameters of up to 25 nm and are referred to as large pore micelle templated silica (LP-MTS). The LP-MTS have been used to immobilize invertase enzyme [32] (Scheme 10). The immobilized enzyme was active, stable and could be stored for over 20 days and was reused without significant loss of its catalytic efficiency.

Moreover, CNSL as a templating agent has been used to prepare novel, heterogeneous copper(II) Schiff base catalysts (Scheme 11) and the catalyst employed in the oxidation of maleic acid, at room temperature, using H_2O_2 as an oxidant. This catalyst showed an excellent catalytic efficiency with yields of up to 90 % and turn over number (TON) of ~1000 in 10 min [33].

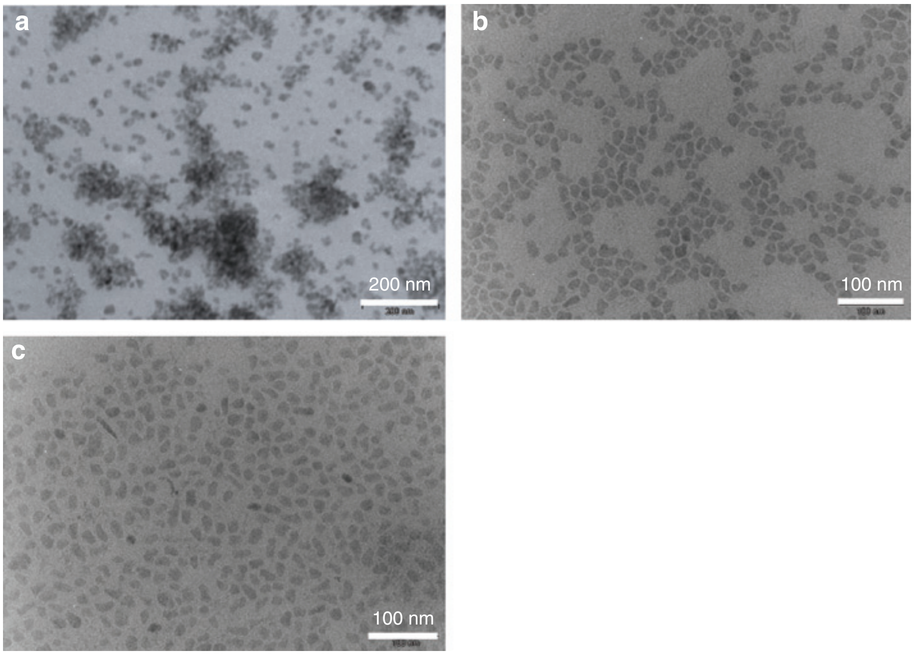


Fig. 3: TEM (a, b, c) images of anacardic acid capped CdSe, CdTe and CdS, respectively.

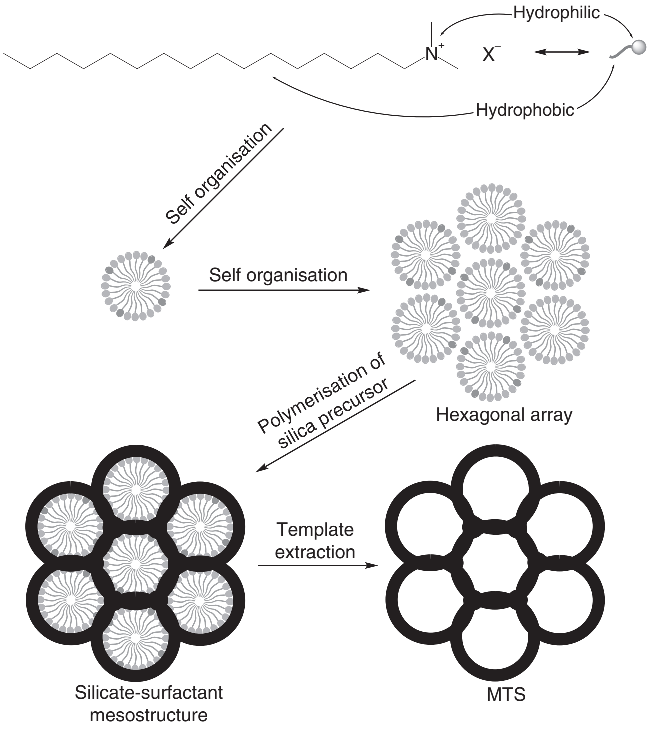
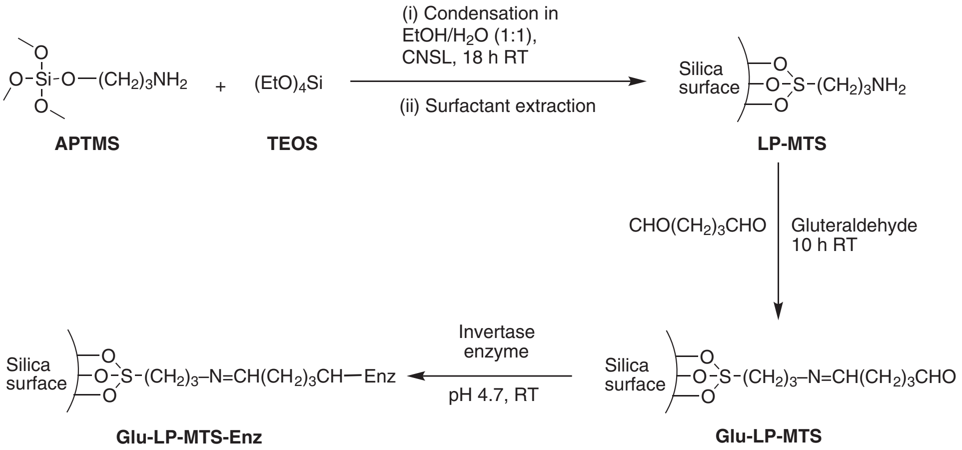


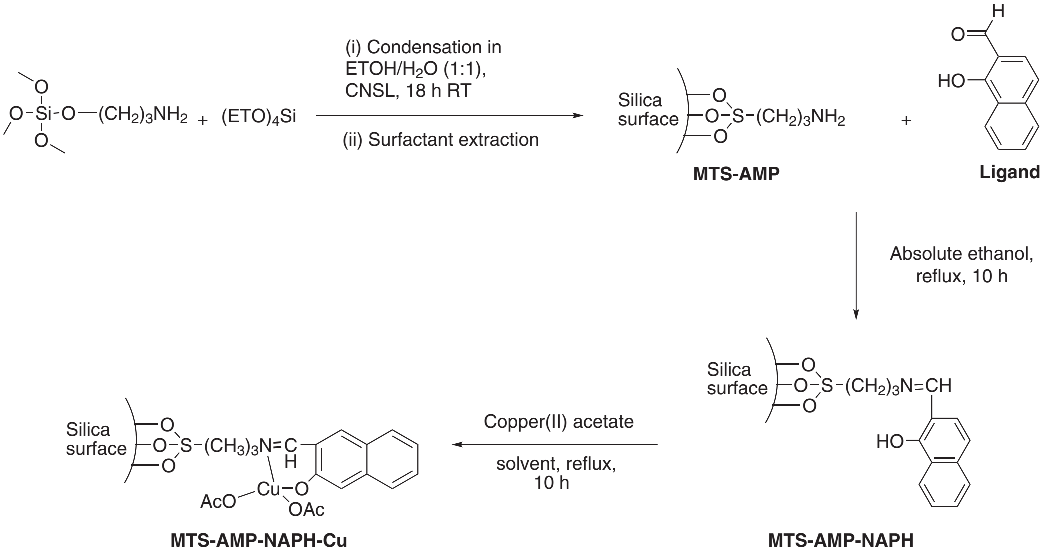
Fig. 4: Graphical representation of the MTS formation.



Scheme 10: Preparation of LP-MTS immobilized invertase enzyme.

Conclusion

This paper reports transformation of CNSL constituents into useful and important chemical products using chemistries such as metathesis and polymerization. We have demonstrated that CNSL components isolated from CNS waste are good feedstocks and can be used to synthesize interesting fine chemicals, derivatives and hybrid chemicals using various catalytic approaches. The paper further reveals that transformation of CNSL components into useful chemical products is feasible. Indeed, based on these developments, it is clear that cashew nut shells (CNS) are a potential renewable resource for production of cashew nut shell liquid (CNSL) that can replace non-renewable resources to synthesize multitude bio-based chemicals and products. This approach does not only replace petroleum based resources but also comes up with a waste disposal strategy



Scheme 11: Synthesis of MTS-AMP-NAPH-Cu catalyst.

by adding value to CNS wastes in the cashew nut processing factories chain. The use of bio-renewable waste raw material in the production of interesting functional chemicals is clearly seen in this paper. Overall, the starting materials such as unsaturated cardanol or anacardic acids from CNSL are among cheap and abundant renewable natural resources thereby making the production costs of produced chemicals and products greener and cheaper than petroleum based starting materials.

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References

[1] S. E. Mazzetto, D. Lemonaco, G. Mele. *Quim. Nova* **32**, 732 (2009).
[2] A. P. Chaudhari, N. J. Thakor, D. M. Mahale, P. M. Haldankar, S. P. Sonawane. *IJAIEM*. **1**, 172 (2012).
[3] R. A. Rajapakse, P. A. Gunatillake, K. B. Wijekoon. *J. Natn. Sci. Coun. Sri Lanka* **5**, 117 (1977).
[4] *FAOSTAT data, 2013,* http://faostat3.fao.org/download/Q/QC/E, accessed on 09/03/2015.
[5] J. Y. N. Philip, J. Buchweishaija, L. L. Mkayula. *Tanz. J. Sci*. **28**, 105 (2002).
[6] O. P. G. Mwangi, P. G. Kareru, G. Thiong'o, A. N. Mohammed. *JAGST*. **15**, 28 (2013).
[7] C. K. S. Pillai. *Journal of Intellectual Property Rights*. **4**, 199 (1999).
[8] G. C. J. Mwalongo, L. L. Mkayula, B. Dawson-Andoh, E. B. Mubofu, J. Shields, B. A. Mwingira. *Green Chem*. **1**, 13 (1999).
[9] B. F. Hamad, E. B. Mubofu. *Int. J. Mol. Sci*. **16**, 8569 (2015).
[10] Y. Guo, G. Mele, F. Martina, E. Margapoti, G. Vasapollo, W. Xiao. *J. Organometallic Chem*. **691**, 5383 (2006).
[11] G. Vasapollo, G. Mele, R. Del Sole. *Molecules* **16**, 6871 (2011).
[12] G. Mele, G. Vasapollo. *Mini-Rev. Org.Chem*. **5**, 243 (2008).
[13] J. H. Tyman, L. S. Kiong. *Lipids*. **13**, 525 (1978).
[14] R. Paramashivappa, P. P. Kumar, P. J. Vithayathil, A. S. Rao. *J. Agric. Food Chem*. **49**, 2548 (2001).
[15] P. P. Kumar, R. Paramashivappa, P. J. Vithayathil, P. V. S. Rao, A. S. Rao. *J. Agric. Food Chem*. **50**, 4705 (2002).
[16] E. Bursell, A. J. E. Gough, P. S. Beevor, A. Cork, D. R. Hall, G. A. Vale. *Bull. Entomol. Res*. **78**, 281 (1998).
[17] I. Ujváry, G. Mikite. *Org. Proc. Res. Dev*. **7**, 585 (2003).
[18] J. A. Mmongoyo, Q. A. Mgani, S. J. M. Mdachi, P. J. Pogorzelec, D. J. Cole-Hamilton. *Eur. J. Lipid. Sci. Technol*. **114**, 1183 (2012).
[19] C. Jiménez-Rodriguez, G. R. Eastham, D. J. Cole-Hamilton. *Inorg. Chem. Commun*. **8**, 878 (2005).
[20] M. R. L. Furst, R. Le Goff, D. Quinzler, S. Mecking, C. H. Botting, D. J. Cole-Hamilton. *Green Chem*. **14**, 472 (2012).

[21] J. E. Mgaya, E. B. Mubofu, Q. A. Mgani, D. B. Cordes, A. M. Slawin, D. J. Cole-Hamilton. *Eur. J. Lip. Sci. Technol*. **117**, 190 (2015).
[22] S. Perdriau, S. Harder, H. J. Heeres, J. G. de Vries. *Chem. Sus. Chem*. **5**, 2427 (2012).
[23] S. Baader, P. E. Podsiadly, D. J. Cole-Hamilton, L. J. Goossen. *Green Chem*. **16**, 4885 (2014).
[24] S. Gopalakrishnan, T. L. Fernando. *RJPBCS*. **1**, 252 (2010).
[25] T. K. Das. *Int J Appl Sci Biotechnol*. **2**, 176 (2014).
[26] R. Ikeda, H. Tanaka, H. Uyama, S. Kobayashi. *Macromol. Rapid Commun*. **21**, 496 (2000).
[27] F. Cardona, C. Moscou. Synthesis and characterization of modified Phenolic resins for Composites with enhanced mechanical performance, In: 20th Australasian conference on the mechanics of structures and materials (ACMSM20), (2009).
[28] S. Mlowe, A. A. Nejo, R. Pullabhotla, E. B. Mubofu, F. N. Ngassapa, P. O'Brien, N. Revaprasadu. *Mat Sci. Semicon. Proc*. **16**, 263 (2013).
[29] S. Mlowe, R. Pullabhotla, E. B.Mubofu, F. N. Ngassapa, N. Revaprasadu. *Int. Nano Lett*. **4**, 106 (2014).
[30] J. Akhtar, M. A. Malik, P. O'Brien, K. G. U. Wijayantha, R. Dharmadasa, S. J. O. Hardman, D. M. Graham, B. F. Spencer, S. K. Stubbs, W. R. Flavell, D. J. Binks, F. Sirotti, M. El Kazzi, M. Silly. *J. Mater. Chem*. **20**, 2336 (2010).
[31] D. J.Macquarrie. *Phil. Trans. R. Soc. London A*. **358**, 419 (2000).
[32] E. B. Mubofu, J. E. G. Mdoe, G. Kinunda. *Catal. Sci. Technol*. **1**, 1423 (2011).
[33] F. B. Hamad, E. B. Mubofu, Y. M. M. Makame. *Catal. Sci. Technol*. **1**, 444 (2011).