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ARTICLE TYPE

Naturally Occurring Phenolic Sources: Monomers and Polymers

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Exploration of sustainable alternative to chemicals derived from petro-based industries is the current challenge for maintaining the balance between needs of changing world while preserving the nature. The major source for sustainable chemicals is either the natural existing plant sources or waste generated from agro-based industries. The utility of such resources will supplement new processed materials with different sets of properties, and environmental friendliness due to their biodegradability and low toxicity during preparation, usage and discard. Amongst other day to day use polymers, phenolic resins account for vast usage. Replacement of petro-based monomers such as phenol and its derivatives either partly or completely utilized for the synthesis of such resins is ongoing. Extraction of naturally phenolic components from cashew nut shell liquid (CNSL), lignin, tannin, palm oil, coconut shell tar (CST) or from agricultural and industrial waste, their utilization as a synthon for the preparation of a bio-based polymers and properties obtained is reviewed in this paper. This review article is designed to acknowledge efforts of researchers towards 3C motto - not only trying to Create but also adapting the principles to Conserve, and Care for a sustainable environment. This review paper describes how extraction, separation and recovery of desired phenolic compounds occur recently? How substituted phenol compounds unmodified/modified act as monomer for polymerization? How the presences of sustainable phenolic material affect properties of polymer? There are about 600 references cited and still there is lot to unfold in this research area.

Keywords: natural phenols, cardanol, lignophenol, tannin, sustainable polymers, phenolic resin

1. Introduction

Over a decade, there is a continuous surge in petro-products prices due to more dependence and high depletion rate of non-renewable fossilized reserves. In addition, awareness about environmental protocols for greener earth could be achieved mainly by reduction of greenhouse gases, and generation and usage of biodegradable products.

Exploration and utilization of alternative renewable feed stocks of monomers for the chemical industry; in particular, polymer industry is a necessary step towards the sustainable development. It provides new significant synthetic aspects and helps to produce partly green goods with a finite content of renewable or recyclable material extracted without odour problems and less use of fossil fuel reserves.

Bimlesh Lochab did M. Sc. (1997-1999) and M. Tech. (1999-2000) from IIT, Delhi, India. She held Felix scholarship for her D. Phil. Degree (2002-2006) from the University of Oxford on the topic of polymers for electro-optic applications under the advisement of Professor Paul Burn. She did her PDF in University of Oxford and University of Nottingham, UK. After her return to India, she received Young Scientist Award to research on cardanol based benzoxazine polymers. In 2012, she has joined as an Assistant Professor, Shiv Nadar University (SNU), UP, India. Her research interests include polymers using intermediates from sustainable origin; dendritic architectures and polymers for PVs and OLEDs, and nanoparticles for nanocomposite applications.

Swapnil Shukla completed her B.Sc. and M.Sc. degree in chemistry from University of Delhi, India. Her specialization during M.Sc. was organic chemistry. She is currently in second year of her Ph. D. programme at Shiv Nadar University, UP, India. She is pursuing research in the field of green polymers based on renewable sources and synthesized in accordance with the tenets of green chemistry under the supervision of Bimlesh Lochab. Her research interests involve exploration the realms of sustainable chemistry with an emphasis on synthesizing polymeric materials.

Literature in past,[1] showed utility of polymers based on naturally occurring plant oils such as soya bean, castor, linseed, sunflower, mustard, palm oil; amines such as fatty amines; polyols such as glycerol, ethylene glycol; alkenes such as limonene; diacids such as succinic acid, citric acid, tartaric acid etc. However, there is a need to explore alternative materials which are generated either from waste or substances of non-food origin. The main aim should be exploration of the possibility to produce sustainable polymers massively and economically which compete successfully with petro-based polymers. In past two centuries, there is a change in dependence of sources of raw materials for chemical industries with time and it showed a closed loop cycle.[2] Renewable feed stocks were of interest in early 1850s, but the non-renewable coal tar based materials were simultaneously explored and reached maxima of usage in 1930s. In the meantime natural gas and oil based resources started gaining importance from 1930 onwards. However, the problems associated such as dwindling and not easily replenishable feed stocks of non-renewable resources have necessitated the use of renewable feed stocks, thereby closing the loop. Currently, research efforts are focused interest for either partial or complete replacement of chem-stocks of petro-based industries.

There are several problems associated to extract the desired monomer or chemical intermediate from naturally occurring renewable resources.[3] The main limitations are *(i)* poor knowledge about the occurrence, chemical content and composition in the natural source, *(ii)* its varying percentage with species, geographical area, and climatic conditions, *(iii)* same chemical extraction process cannot be applied from species to species, *(iv)* requirement for optimization of extraction process, *(v)* extraction of desired chemical recovery from the usual complex chemical composition involves higher costs, *(vi)* low percentage of the desired chemical species requires further processing costs and *(vii)* development of non-destructive techniques to analyse and quantify the content easily.

In this review article, we will focus on phenols derived from easily renewable natural resources such as cashew nut shell liquid (CNSL), lignin, tannin, palm oil, coconut shell tar (CST) or from agricultural and industrial waste and their use as monomer with or without modification for the synthesis of a sustainable polymers. The hydroxyl functionality, side groups and aromatic ring available in these naturally occurring phenolic derivatives could be tailored to design new monomeric structures which need to be explored.

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Several classes of phenolic polymers have been developed in the past hundred years. Phenolic resins, the first synthetic polymer was developed more than a century ago by Baekland.[4] Since then phenols have been utilized for the preparation of other polymers such as polyesters, polycarbonates, epoxy resins, poly(phenylene oxide), polyurethane etc.

2. Sources of Naturally Occurring Phenol

Earlier, the waste generated by agro-based industries such as empty fruit bunches,[5] seed,[6-7] fibre, shell,[8] wood, bagasse[9] are mainly utilized either to generate local source of energy by incineration[10] or as natural fertilizer. The waste is found to be rich in phenolic derivatives such as cresol, catechol, guaiacols, syringol, eugenol etc. which can promisingly substitute petro-based phenol in the phenolic polymers. The sources of naturally occurring phenolic compounds that will be considered are CNSL, lignin, tannin, palm oil and CST.

2.1 Cashew Nut Shell Liquid (CNSL)

It is a reddish brown viscous liquid, having the honey comb structure of the shell of cashew nut obtained from cashew tree grown in coastal areas of Asia and Africa, Mozambique, India and Brazil. India is a leading exporter of CNSL and had exports 13575 M.T. in 2011-12 and expected to increase nearly by 1500 M.T. per annum.[11] The estimated growth rate in demand is 7 to 8% per annum. The noxious saps of numerous members of the *Anacardiacae*, such as Japanese lac, poison ivy, cashew nut shell liquid, etc., contain phenolic compounds in which benzene ring substituted with long unsaturated alkyl side-chains.[12]

2.1.1 Structure

CNSL is alkyl phenolic oil contained in the spongy mesocarp of the cashew nut shell from the cashew tree *Anacardium occidentale L.* It is a by-product of the cashew nut processing industry, obtained as a dark brown, viscous, vesicant liquid.

CNSL derived from the most diffused roasted mechanical processes of the cashew and is a powerful phenolic pollutant of the cashew agro industry. It is a mixture of anacardic acid (71.7%), cardanol (4.7%), traces of cardol (18.7%), 2-methylcardol (2.7%),[13] and remaining 2.2% is unidentified polymeric material as shown in Fig. 1.

The pentadecyl alkyl side chain (R) of each of them may be saturated, mono-olefinic, di-olefinic or tri-olefinic with a high percentage of the components having one or two double bonds per molecule of CNSL. In total, it is a mixture of 16 phenolic components with varying percentages.

Amongst other components in CNSL, anacardic acid is highly corrosive and poisonous material. It is of less use commercially but has medicinal effects such as antimicrobial,[14] antitumour[15]and molluscicidal activities. It is a potential enzyme inhibitor for tyrosinase[16] and acetytransferase[17] and showed other potential therapeutical[18] and antioxidant[19] benefits.

The presence of dual functionalities in cardanol and cardol namely phenolic and long-chain alkyl/alkylene moieties has been widely utilized as such or modified further for applications[20] mainly as plasticizers[22-25], adhesives,[26] fuel additives,[27] surfactants,[28-35] resin additives[36-39] and intermediates which act as precursors for other chemicals such as formation of cardanol based fullerenes and porphyrin derivatives.[40-41]They also act as material for a variety of soft nanomaterials[42] such as nanotubes, nanofibers, gels.[43] Cardanol and cardol are the major constituents of cashew nut shell oil and have shown both high cetane number and heating value (36 - 40 MJ/kg) equivalent to that of fuel oil along with excellent solubility in diesel[44] and light lubricating oils. The presence of strongly polar phenol group also induces antioxidant properties thereby contributing to high stability at room temperature. However storage at high temperature leads to polymerization accounting for increase in oil viscosity.[45]

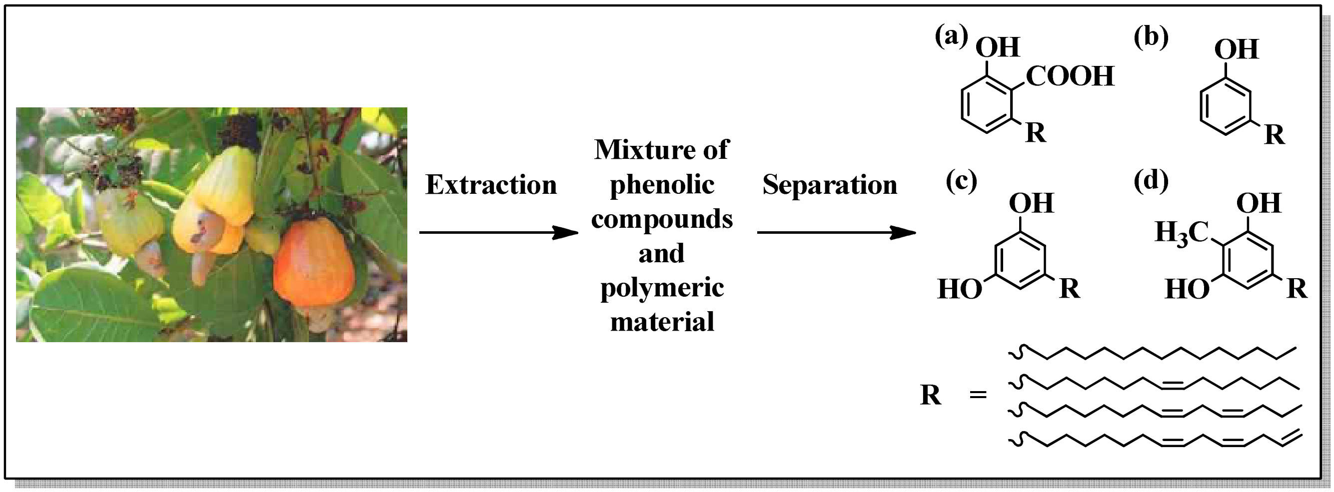


Fig. 1 Components in CNSL: (a) anacardic acid, (b) cardanol, (c) cardol, and (d) 2-methylcardol

2.1.2 Extraction and Characterization

Extraction of CNSL from cashew nut shell and its isolation into it components were carried out by techniques such as solvent extraction, pyrolysis, heat and supercritical carbon dioxide extraction. CNSL is commercially produced in two ways and available in two grades[46] (i) *Natural grade:* the cold-processed CNSL, obtained by solvent extraction of the cashew nut shells, has anacardic acids (60-70%) and cardols (20-25%)[47] as major components; (ii) *Technical grade:* the hot-processed/heat extraction CNSL, which oozes out of the shells during roasting of the nuts for separation of the kernels. The major components of the hot-processed CNSL are cardanols (60-70%) and cardols (20-25%) with minor quantities of 2-methylcardols**.**

Tyman *et al*.[48-49] investigated solvent extraction of CNSL from the shell material using organic solvents (carbon tetrachloride, light petroleum, or diethyl ether) and extracted CNSL in 15–30% yield using long extraction times ranging from 1–14 days. Higher yields of CNSL can be achieved by changing the polarity of organic solvents, longer extraction runs, and using finely ground shells. However this method requires harsh mechanical pre-treatment and further, use of organic solvents tend to extract undesirable coloured compounds from the shell material. Thus, the use of organic solvents for separating CNSL from cashew is mainly suitable for small scale analysis rather than for large scale processing due to use of organic solvents which accounts for high cost and non-green solution. In another procedure, solvent extracted CNSL using soxhlet apparatus,[50-51] was separated into various constituents namely anacardic acid, cardanol, cardol using alanine as an extractant to facilitate the separation of monohydric and dihydric phenols and removal of polyhydric phenols. Decarboxylation of anacardic acid in CNSL can also be achieved in toluene as solvent using dean-stark apparatus in 3h. Cardanol was obtained in 50% yield when decarboxylated CNSL was heated at reflux in methanol:formaldehyde:diethylenetriamine (200:20:3 v/v) solution for 2h.[49]

Typically, the composition of heat-extracted CNSL is approximately 52-60% cardanol, 10% cardol and 30% polymeric material. In heat-extraction procedure, CNSL is extracted from shell at a high temperature in range 80-200°C. Once it reaches a temperature of 180^{o}C it is kept for 2-3 h to ensure decarboxylation process. During this process the percentage of cardanol is increased to ~68% at the expense of thermal decarboxylation of anacardic acid. Heat-extracted CNSL is often further processed by distillation to give distilled technical grade at reduced pressure to remove the polymeric material. The composition of the distilled technical grade CNSL is about 78% cardanol, 8% cardol, and 2% polymeric material.

Extraction by vacuum pyrolysis at 500 °C at 720 mmHg mainly contained cardanol, cardol along with substituted phenols and phthalates. The maximum yields of about 40% (~16% obtained up to 150 ^{o}C plus 24% obtained on pyrolysis) have been achieved.[44,52]

Green extraction procedures such as use of supercritical carbon dioxide (Sc-CO$_2$) were also explored for the extraction of CNSL. It was found flow rate 4-5 kg/h at 40 °C and 250 bar yielded 19% phenolic lipids in 17.5 h.[21] The process conditions were further modified and optimized and it was found that the fraction mainly contained cardanol (70–90%) with traces of anacardic acid and cardol at a flow rate of 0.8-1.3 kg/h at 50 °C, 300 bar in 0.9 h.[54] A much higher percentage of cardanol (85%) was obtained at 300 bar and 60 °C using Sc-CO$_2$ extraction. The yield obtained was much higher than that of the technically distilled grade CNSL.[55] Chemical degradation, especially decarboxylation of the anacardic acid, did not occur during the extraction with Sc-CO$_2$ solvent in pressure profile separation method.[54,56] The latter method involves penetration, dissolution, expansion and rupture of the shell matrix due to depressurization of the CO$_2$ to increase mass transfer and phase contact area. CNSL extracts obtained with the pressure profile method using pressurization–depressurization steps with CO$_2$ at a flow rate 5 L/min, 60 °C at standard atmospheric pressure and followed by depressurization to 0.1 MPa lead to extraction of cardanol (19-22%), cardol (26-32%) and anacardic acid (46-52%).

Extraction of cardanol from natural grade CNSL requires separation of anacardic acid as a salt followed by use of different solvents to separate other components. Anacardic acids can be isolated from CNSL by its precipitation as either calcium[57] or lead[58]anacardate on treatment with corresponding hydroxides. The salt of anacardic acid was filtered, dried and treated with hydrochloric acid to release free anacardic acid from the mixture. The acid-free CNSL was treated with liquor ammonia and extracted with hexane:ethyl acetate (98:2) to separate the mono phenolic component, cardanol. Subsequently, ammonia solution was extracted with ethyl acetate: hexane (80:20) to obtain cardol.[59] Anacardic acids can also be separated from solvent extracted CNSL by column chromatography using silica gel with ethyl acetate:hexane (1: 3) v/v and triethylamine (0.5%) as eluent mixture to elute cardanol and cardol followed by elution with acidic (acetic acid, 1%) eluant mixture.[27]

Separation of cardanol especially from cardol is based on physical processes such as vacuum distillation[6] or a chemical process[13] or a chemical treatment have been described in the literature.[47,60] The 3-pentadecadienylphenol was obtained as the main fraction when CNSL was distilled at 205-219 °C at 1.5 mm Hg.[6]

The purity and identity of components and their derivatives was confirmed by HPLC,[57-58,61,53] Mass analysis,[27] IR,[52] ^{1}H-NMR[52,58,27] and ^{13}C-NMR[52] spectroscopy.

In HPLC purification of CNSL, a gradient elution system was used either with a mixture of solvent such as acetonitrile:water:acetic acid in the ratio 80:20:1;[57,62] or 66:22:2 with tetrahydrofuran (THF)[58] or THF[61] alone at a different flow rate of 1.8, 2.7or 0.8 mL/min respectively. HPLC trace showed four different peaks at retention times ranging from 3.5-10.7 min corresponding to first elution of cardanol-triene (39.6%) followed by other fractions namely diene (20.2%), monoene (31.4%), and saturated (2.7%) akyl side chain respectively.

GC-MS analysis showed *m/z* at 304 and 320 corresponding to saturated cardanol and cardol respectively.[62] Tyman *et al.*[58] reported *m/z* ratio of cardanol, cardol and 2-methylcardol with monoene, diene, and triene constituents at 304.1, 302.2, 300.1, 298.1; 320.2, 318.2, 316.2, 314.2; 334.4, 332.4, 330.4, 328.4 respectively. The four *m/z* values which differs by 2 units for each component confirms the presence of four different alkyl chains which differ by a double bond. ESITOF MS[27] also showed *m/z* at 297 [(M - H)- of cardanol], 299 [(M - H)- of cardanol], 301 [(M - H)- of cardanol], and 303 [(M - H)- of cardanol which further confirms the variation in double bond in side chains.

FTIR of cardanol[52] showed characteristic peaks due to O-H stretch (3363 cm^{-1}), C–H vibration of the unsaturated hydrocarbon moiety (3010 cm^{-1}), C-H asymmetric and symmetric stretching vibrations of alkyl side chain (2930, 2849 cm^{-1}), C=C and aromatic stretching bands (1601, 1454 cm^{-1}), terminal vinyl group (907 cm^{-1}) and also the vinyl peak (630 cm^{-1}). In another publication C-H vibration peaks at 994, 976, and 912 cm^{-1}, ascribed to the conjugated *cis-trans* double bond, non-conjugated *trans* double bond, and terminal vinyl group in polycardanol, respectively.[63]

A typical ^{1}H-NMR spectrum[52,58,27] of cardanol diene showed signals due to terminal -CH$_3$ group centered at 0.85 (CH$_3$, *t*), long aliphatic side chain methylene protons in three different environments observed at 0.88–1.59 (n-CH$_2$, *m*, 27H),1.85–2.25 (CH$_2$CH=, *m*, 4H), and 2.9 [CH$_2$(CH=)$_2$, *m*], benzylic protons at 2.56(CH$_2$Ar, *t*, 2H, *J* = 7.4 Hz), olefinic protons were at 5.05–5.42 (CH=, CH$_2$=CH–, *m*, 4H), and aromatic protons appeared as a multiplet at 6.63–6.80 (HAr, *m*, 3H), 6.95–7.05 (HAr, *m*, 1H).

A ^{13}C-NMR[52] for cardanol diene and cardol monoene was reported with aliphatic signals ranging from 11-38 ppm and aromatic from 112-155 ppm respectively.

Both CNSL and cardanol are considered a sustainable, low cost and largely available natural resource by-product. Cardanol possesses interesting functional structural features that allow chemical modification to generate a range of amphiphiles and useful monomer structures.

2.2 Lignin

Lignin is an aromatic polymer which mainly found in the cell walls of secondarily thickened cells, making them rigid and impervious. It is synthesized in plants by enzyme catalysed oxidative combinatorial coupling of 4-hydroxyphenyl propanoids units.[64-65] The molecular weight of lignin ranges between 600-15000 KDa. Lignin is usually exploited as an energy source in paper mills and bio-ethanol industries and it is a residue of alcohol and sugarcane industries, paper and pulp mill waste water discharge. Nearly 40-50 MT/annum waste lignin is generated by pulp and paper industry. These wastes are chiefly used an energy source by combustion and only 5% is used for other purposes.[66]

2.2.1 Structure and source of chemicals

Lignocellulosic biomass is made up of three main components: hemicellulose, cellulose and lignin, of which the lignin fraction can account for up to 40% of its dry weight. Lignin is an amorphous biopolymer in which hydroxylphenyl propane units are connected with ether and partial carbon–carbon bonds in a helical structure.[67] Lignins are highly functionalized bio-macromolecules possessing primarily alkyl-aryl ether linkages, aliphatic and aromatic hydroxyl groups and low polydispersity, which offer potential for high value-added applications in renewable polymeric materials development. Lignocellulosic materials have been proposed as large renewable resources for chemicals and sugars to reduce society’s dependence on non-renewable petroleum-based feed stocks.

The major chemical functional groups in lignin include hydroxyl, methoxy, carbonyl and carboxyl in various amounts and proportions, depending on genetic origin and extraction processes. Phenolic chemicals can be obtained from lignin by chemical disassembly processes.

Although lignin is the most abundant natural phenolic polymer, its phenol activity is extremely low due to etherification of phenolic hydroxyl groups of lignin precursors in the biosynthetic process. The basic building blocks of lignin can be schematically simplified into “C9” units made up of a phenolic moiety bearing three aliphatic carbons. The aromatic components are moreover differently substituted by methoxy groups, whereas the aliphatic portions are characterized by the variable presence of C=C unsaturations, hydroxyl functionalities, and other less frequent substituents.[68-70] A representative structure of lignin[71] is shown in Fig. 2.

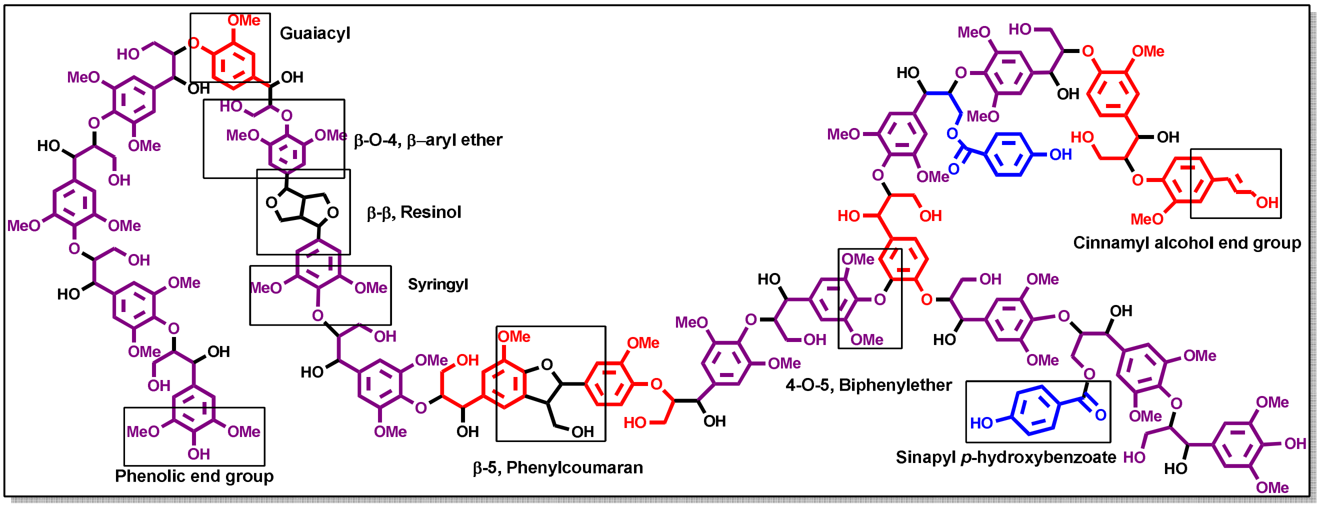


Fig. 2 Structural representation of a lignin polymer from poplar wood, as predicted from NMR-based lignin analysis.[71]

The polyphenolic structure of lignin is chemically stable and therefore vigorous reaction conditions are needed to modify or transform its structure. The presence of oxygen during transformation prevents its depolymerisation into simple green monomers. The highly reactive radical reaction intermediates during thermal conversion resulted in oligomers products of increased molecular weight e.g. tars or solid chars. Utilisation of reactive additives[66] such as radical scavengers e.g. phenol, supercritical water-phenol mixtures; reactive hydrogen containing compounds e.g. tetralin, 9,10-dihydroanthracene; and hydrogen in presence of metal catalysts prevents degradation of vinyl and allyl substituents by means of hydrogenation and capping radicals. Lignin pretreatment, dissolution and catalytic treatment is an important area for production of substituted phenols and other important chemicals.[72] The basic aromatic phenols[66, 73-74] obtained from lignophenols are structurally represented in Fig. 3.

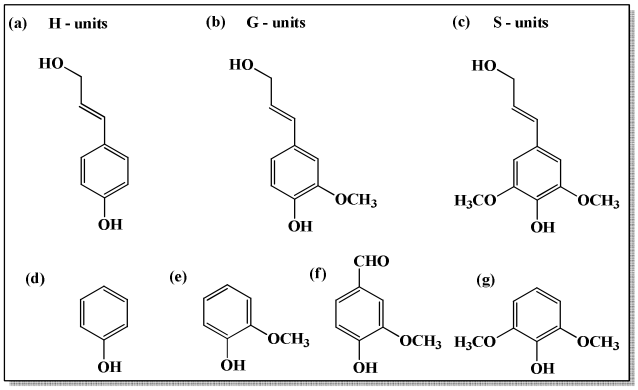


Fig.3 Lignophenol:- Basic units(a) H:*p*-Coumaryl alcohol (*p*-hydroxyphenyl derivative), (b) G:Coniferyl alcohol (guaiacyl derivative), (c) S:Sinapyl alcohol (syringyl derivative); Structures of phenols derived from basic units are (d) phenol, (e) guaiacol and (f) vanillin, (g) syringol from (a, b and c) respectively.[65,71]

The three basic units namely (a) H: *p*-Coumaryl alcohol (*p*-hydroxyphenyl) (b) G: Coniferyl alcohol (guaiacyl) and (c) S: Sinapyl alcohol (syringyl) are differentiated by the presence and position of methoxy group. In comparison to H units, the aromatic ring of S and G units substituted phenols is more electron rich to facilitate electrophilic attack but former phenolic H units derivative is less sterically hindered for ring substitution.

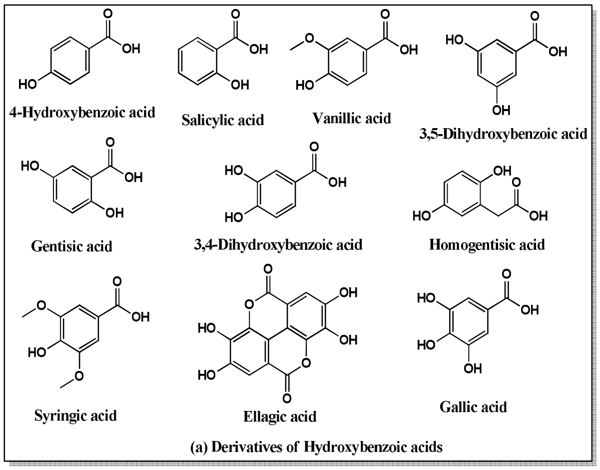
A generalized chemical structure of sustainable and valuable aromatic chemicals obtained by cleavage of aryl ethers and aryl–alkyl linkages from lignin is shown in Fig. 4.

The lignin fraction in these materials contains numerous phenolic components, mainly acids such as ferulic, *p*-coumaric (PCA), syringic, vanillic and *p*-hydroxybenzoic acid. Ferulic acid (FA) and PCA are the major phenolic compounds present in sugarcane bagasse.[75] In addition, there are certain substituted phenolic compounds with alkyl/alkylene chains present in palm, soybean, maize, sunflower rapeseed etc. These classes of phenolic compounds are called as tocols such as alpha, beta, gamma-tocophenols and tocotrienols, Fig. 5.

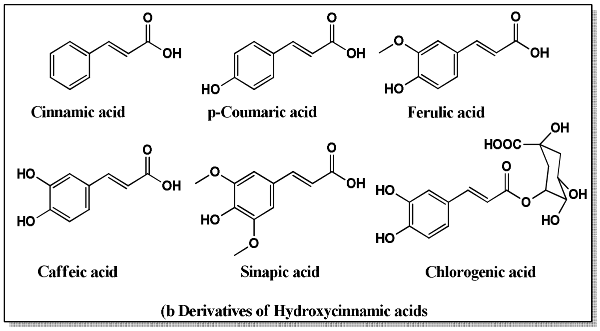
2.2.2 Nature of wood

Lignin, the second major component of cell walls of hard and softwood as well as lignocellulosic fibres of annual plants, is a highly branched and amorphous macromolecule, whose structure varies with the vegetable species. Lignins are complex aromatic biopolymers that vary in composition and structure as a function of genotype, phenotype, and environment, as well as with the cell type and maturity of the plant tissue, and genetic improvement of plants.[76-77]

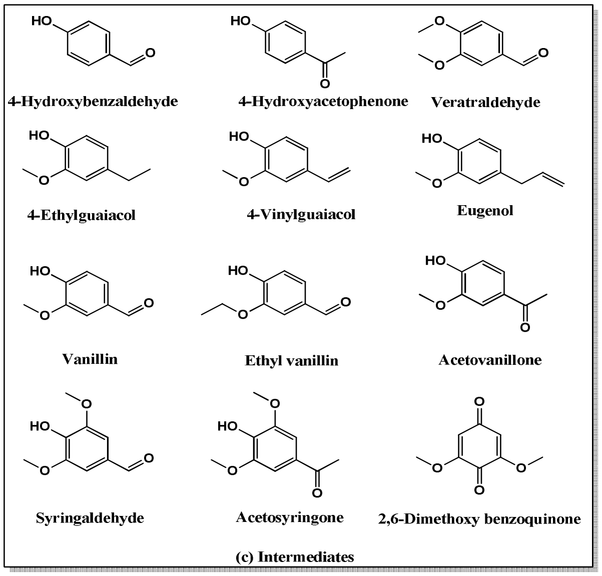
The H, G, and S units are not discrete within either the cell or a given lignin molecule, and the compositional ratios of these three moieties can vary significantly. This inherent complexity and heterogeneity of lignin, both in structure and composition, make it extremely difficult to develop a conversion technology that can



(a) Derivatives of Hydroxybenzoic acids



(b Derivatives of Hydroxycinnamic acids



(c) Intermediates

Fig.4 Naturally occurring phenolic compounds from various biological origin obtained from lignin as derivatives of a) Hydroxybenzoic acids b) Hydroxycinnamic acids and c) Intermediates.[176,75, 186-187, 233]

efficiently process a wide range of sustainable feedstocks cost-effectively. Genetic engineering strategies are involved to design the lignin polymer so that the development of feedstocks can be tailored for efficient biofuel, optimal and selective chemical feedstock production.[53]

Major constituents of some wood and agricultural-based materials are shown in Table 1.[73,79-87]

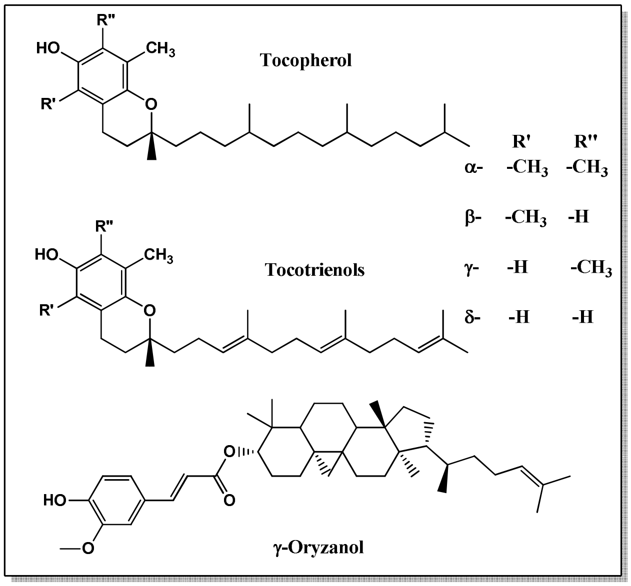


Fig. 5 Phenolic derivatives present in rice bran and other plant derived oils

Hardwood is derived from trees like aspen, poplar, birch, elm, maple while softwood is from pine, spruce, cedar, fir, larch, douglas-fir etc. The composition of the cell wall changes with the kind of tree or plant but in general 40–45% of wood is cellulose, 25–35% hemicellulose, 15–30% lignin, and up to 10% other compounds. Apart from woody biomass many other biomass feedstocks have been used in the production of phenolic precursors. The distribution of the various constituents varies depending on their origin ranging from *Gramineae* (grass and cereals, non-woody biomass) to *Gymnosperms* (softwoods) and *Angiosperms* (hardwoods) family. Moreover the lignin content of softwoods is generally higher than the lignin content of hardwoods (Table 1). Grasses are built up from H, G, and S units; softwood lignins essentially consist of G units with low levels of H units; hardwood lignins of G and S units with traces of H units[88- 91](Fig. 3), except for commelinid monocots which has high abundance of hydroxycinnamic acids.[92,71]

Lignins from monocots grasses incorporate G and S units at comparable levels and more H units than dicots.[66] Softwoods may yield more reactive phenolics than hardwoods due to the relative lack of S with one methoxy group in softwood derived liquids compared to G with two methoxy groups derived from hardwood. Lignin extracted from sugarcane bagasse[93] has the major proportion of H units in comparison to other sources. The most widely employed feedstocks to date for productions of pyrolytic lignins are hard and softwoods due to consistency, widespread availability and extensive referencing. In addition lignin and lignin enhanced biomass are difficult to characterise and to process thermochemically. It was observed that the amount of S and G decreased with increase in pyrolysis temperature, guaiacol derivatives are formed at lower temperatures while syringol derivatives, phenol and catechol are formed at higher temperatures. Guaiacols undergo secondary decomposition reactions to form catechol.[94]

In grasses, *Poaceae* family is rich in hydroxycinnamates namely

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Table 1 Constituents of lignocellulosic wood and specific fibres[73,79-87]

Wood/Fibre	**Polysaccharides (wt%)**[a]	**Lignin (wt%)**	**Wood/Fibre**	**Polysaccharides (wt%)**[a]	**Lignin (wt%)**
Softwood			***Plant materials***[c 83]		
Bark [73]	30-48	40-55	*Alfalfa*	--	12-15
			(Medicago sativa L.)		
Wood [73]	66-72	25-30			
PinusRadiata[b80]	-	28	*Red clover*	--	7
			(Trifolium pratense L.)		
Pinus Taeda[79]	-	27-30	*Bromegrass*	--	10-13
Hardwood			*(Bromusinermis Leyss.)*		
Bark [73]	32-45	40-50	*Cornstalk*	--	8
			(Zea mays L.)		
Wood[73]	74-80	18-25	*Oat straw*	--	14-17
			(Avena sativa L.)		
Eucalyptus regnans[60]	-	23-33	*Wheat straw*	--	14-18
Fagus sylvatica[27]	52[c]-68	40[c]-31	*(Triticum aestivum L.)*		
Fibre[82]			*Cereal straw*[82]	53-76	12-20
			Barley straw[84]		
Jute	75-91	12-13		65-73	15-16
			(Hordeum vulgar L.)		
Sisal	76-92	10-14	*Paddy straw*[85]	56	6
			Rice husk[86]	51-57	16-24
			Sugarcane bagasse[87]	80-75	20-25

a.(Cellulose and Hemicellulose) *b. Wood meal* c. g/Kg cell wall determined by Klason method c. Heat treated

ferulates (trans-4-hydroxy-3-methoxycinnamate) and *p*-coumarates (trans-4-hydroxycinnamate).[95] Lignin obtained from other non woody biomass i.e. wheat straw and sakanda grass (*S. munja*) of Indian origin (ALM lignin) is reported to be richer in phenols as compared to lignin residue (ETEK lignin) obtained as a byproduct from ethanol production industry based on softwood of Sweden origin.[96]

Besides hardwood, softwood and non-woody biomass lignins are structurally different in their phenolic component ratios; they also differ in their linkages with cellulosic components. This account for their different properties and extraction strategies for the phenols from them. The difference in aromatic ring structure in woody biomass affects compositions of the types of the linkage with phenylpropane units.[97] The biphenyl type contents of the condensed structures are usually lower in hardwood lignins and as requires different pyrolysis condition. The most abundant lignin linkage is the arylglycerol-β-aryl ether (β-O-4) linkage (Fig.6a) and it consists of two diastereomers, erythro and threo forms. Softwood lignin has almost an equal amount of the two forms but erythro form is predominant in hardwood lignin.[98]

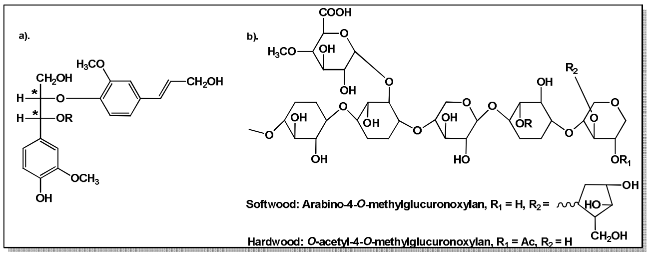


Fig.6 Chemical structure in woody biomass: a) β-O-4-linkage b) hemicelluloses

The hemicelluloses component in hardwoods mainly contains xylan (*O*-acetyl-4-*O*-methylglucuronoxylan) units, while softwoods have galactglucomannan and xylan (arabino-4-*O*-methylglucuronoxylan) as major and minor components respectively, Fig. 6b.[99] The content of acetyl group in hardwood hemicellulose is usually higher than that of softwood hemicellulose.[100-101] Since the chemical structures of hemicellulose in hard and softwood are different accounting for different linkages in their backbone. In case of hardwoods, xylan chains contain 4-*O*-methylglucuronic acid with α-(1→ 2) glycosidic linkages and *O*-acetyl substitution at C2-C3. Softwoods xylans lack acetyl units and have arabinofuranose units linked by α-(1→ 3) glycosidic linkages. [102, 103] In woody biomass, phenolic acids mainly PCA and FA, have been found to form cross-links between lignins and polysaccharides and in non-woody biomass (wheat straw), PCA is mainly ester-linked while FA is ether-linked to lignin and ester-linked to hemicelluloses forming lignin–carbohydrate complexes (LCCs), as shown in Fig. 7.[104-107] In addition to PCA and FA, even *p*-hydroxycinnamic acids and diferulates[108] are abundant in non-woody plants to form cross-linkages between lignin and polysaccharides.[105, 109- 113]

Structural differences between softwood, hardwood and non-woody biomass account for different physical properties. Woody structure is physically larger, structurally stronger and denser than agricultural biomass.[114] Softwoods are generally more resistant to hydrolysis as compared to hardwoods. Straw lignin is known to possess characteristic alkali solubility and alkali treatments have been used to increase the digestibility of the complex ligno-cellulosic chemical network.[115-116] The solubility of straw lignin in alkali has been attributed mainly to the presence of significant amounts of H residues, which are bound to lignin as *p*-coumarate units.[91] Non-woody biomass (straw, grasses or stalks) are more easily treatable than wood (milder temperatures and lower reaction times), and its fermentation conditioning steps are less expensive and efficient.[117-119] The thermoplastic region of softwood lignin is in the range 170-175°C and hardwood in 160-165 °C. Softwood lignin have stronger intermolecular hydrogen bonding between the phenolic and biphenol moieties thereby restricting their thermal mobility and leading to a higher glass transition temperature (T_g) than that of hardwood lignin. SKL shows a T_g of 119°C higher than that of HKL 93°C.[120] Differential scanning calorimetry (DSC) analysis of pine softwood, eucalyptus hardwood and switchgrass showed softwoods to be the most recalcitrant material and thereby requiring alternate strategies prior to its use as a source for phenols and fuel.[121]

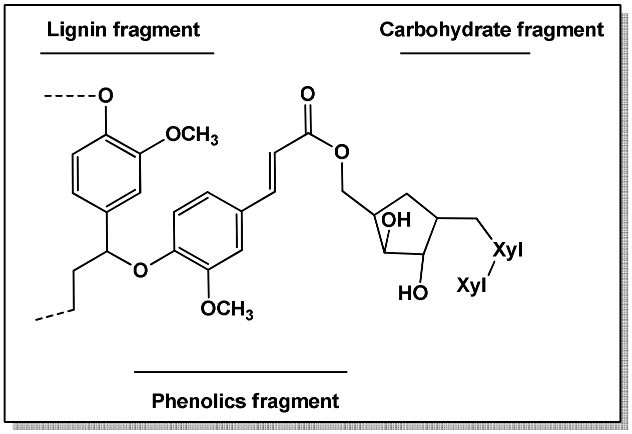


Fig. 7 Lignin phenolic carbohydrate complex (LCC) in wheat straw (non woody biomass)

Photodegradation of softwood hinoki (*Chamaecyparis* sp.) and hardwood maple (*Acer* sp.) lignin revealed that the phenolic hydrogen abstraction reacted faster than the β-aryl ether linkage cleavage resulted in formation of more non-conjugated carbonyl products than hardwood. In addition, the guaiacyl structure in hardwood degraded faster than the syringyl unit.[122]

2.2.3 Extraction

Several processes have been used for the extraction of lignophenols from lignin. These include phase separation, pyrolysis, thermochemical methods, ultrasonic irradiation, solid state fermentation (SSF), enzymatic modification etc.

Lignin exists in plants as complex polymer and has attached polysaccharides, cellulose and hemicellulose. In order to liberate lignin-derived phenols requires a pretreatment step which involves removal of polysaccharides followed by conversion of lignin to high molecular weight, lignophenols and low molecular weight substituted phenols. The nature of biomass dictates the pretreatment strategy and conditions, through depolymerisation process. In general, hardwood required harsher conditions than softwood and non-woody biomass. The extent and rate of depolymerization influence pretreatment time and temperature. For example, ionic liquid pretreatment is effective in terms of depolymerizing switchgrass and pine at 120°C, and 160°C for eucalyptus.[121]

Phase-separation system is a process where cellulose and hemicelluloses are hydrolyzed to sugars and lignin is converted to a light-colored functional phenolic polymer, lignophenol. The first step in the phase-separation process is based on solvation of lignocellulosic materials by phenol derivatives, resulting in successive cleavage of ether linkages of lignin, swelling and hydrolysis of carbohydrate by concentrated acid. The second step is cleavage of Cβ aryl-ether linkages by switching functions of lignophenol under the mild alkaline condition. The third step is demethylation of the aromatic methoxy groups in presence of boron tribromide from lignophenol depolymerised products. The methoxy group of guaiacyl aryl coumaran was effectively demethylated to give catechol type arylcoumaran dimer. In the process, native lignin was modified by phenol derivatives to selectively grafted benzyl position, the most reactive sites, to give 1,1-*bis*(aryl) propane type lignin based recyclable polymer, lignophenol that has the original inter-unit linkage of lignin and have high phenolic content and may partially substitute phenol in resins (Fig. 8).[69]

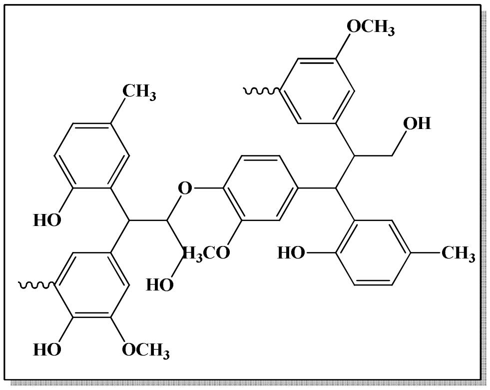


Fig.8 Conversion of native lignin to lignophenol derivatives ligno-*p*-cresol[69]

Through the phase-separation process, lignocellulosics were converted and separated to lignin-based polymers (lignophenols) and hydrolyzed carbohydrates. The resulting lignophenols have unique functions such as high phenolic characteristics, very light colors and high stabilities. Phase separating procedure involves the addition of drops of bio-oil to a large amount of water, followed by filtration and drying of the filtrate, the resulting insoluble fraction is commonly referred to as pyrolytic lignin devoid of cellulose and hemicellulose.

It was observed that lignophenol is converted to monophenols only under hydrothermal conditions after the phase-separation process. Cupric oxide[123-124] oxidized lignin to form aromatic phenol derivatives such as vanillyl (vanillin, acetovanillone, and vanillic acid) and syringyls (syringaldegyde, acetosyringone, and syringic acid). Other inorganic salts including organometal compounds such as methyltrioxorhenium (MTO), salen complexes, polyoxometallates (POMs), metalloporhyrins, and enzymes[125] such as laccase, peroxidase oxidise lignin to several other organic compounds are also studied.[126]

Liquefaction of ligno-celullosic materials such as corn,[127] sawdust, woodchips, agricultural residues and peat moss represents another route for obtaining phenolic resin precursors. It is generally performed under high pressure (10–20 MPa) at 290–350 °C and followed by a separation process.

Lignin depolymerisation under pyrolytic conditions leads to high amount of char generation and poor yield of low molecular chemicals. However, there has been particular interest in the use of such pyrolytic lignin as a renewable resin from pyrolysis of biomass due to the high yield of pyrolytic lignin and its ease of assimilation into phenol formaldehyde formulations.[73] Fast pyrolysis, as name suggested is carried out in absence of air, is a relatively recent thermochemical conversion technology. Fast pyrolysis trials were carried out in a small vortex reactor with a capacity of 10–20 kg/h operated at 480–520 °C to produce optimum yields of pyrolysis oil (55 wt.% on a dry basis). The vortex reactor transmitted very high heat fluxes to the biomass causing primary depolymerisation of the constituent polymers into monomers and oligomers. Fluidised bed pyrolysis, though it is not a pure pyrolysis process as a small amount of air is employed, the oxygen only represents an order of 5% of stoichiometric combustion requirements and the process is therefore quite close to standard fast pyrolysis. Identified compounds are claimed to be all polymerisable with, on average, two positions available for methylene linkages versus three for phenol. Rapid Thermal Processing (RTP™) is a method of preparing phenolic precursors by liquefying wood, bark and forest and wood industry residues using a patented fast pyrolysis process. Pyrolysis time (oven dried/N_2/600 °C/40–600 s) dictates the nature of products from monomer i.e. phenolic derivatives (<120 s) to polyaromatic hydrocarbons (>120 s).[128] Pyrolysis reaction pathways have been determined on model compounds to postulate lignin chemical decomposition.[129] The pyrolysis kinetics[130] of lignin using thermogravimetric analysis (TGA) has also been reported to understand formation of compounds as a function of both rate and change of temperature. Fast pyrolysis of lignocellulosic biomass produces a renewable liquid fuel called pyrolysis oil that is the cheapest liquid fuel (as elaborated in section 2.2.5) produced from biomass today, which can be converted into industrial commodity chemical feedstocks.[131] Reviews have been published on fast pyrolysis processes of lignin,[132] applications of fast pyrolysis liquids including resins and on the production of monomeric phenols by thermochemical conversion of biomass. The production of monomeric phenols through hydrogenation of lignin has been the subject of much research, some of it indicating the potential for substantial yields of phenol and benzene. When heated, lignin component depolymerises to form monomeric and oligomeric phenolic compounds. Lignocellulose biomass on treatment with flash pyrolysis and steam gasification yield substituted phenols and nature of phenol generated depend upon temperature of treatment.[133] The importance of kinetic study, degradation mechanism, chemicals products obtained based on the type of thermal treatment has been reviewed.[94] Gani *et al.*[134] studied the effect of lignin and cellulose content on pyrolysis and combustion behaviour for woody (Hinoki sawdust, larch bark and palm oil fiber) and non-woody agriculture biomass (rice husk, sugar cane bagasse, rice straw and corn stalk). Pyrolysis of softwood and hardwood lignins showed substantial mass loss occurred at 400 – 500 °C due to loss of propyl, methoxy and hydroxyl moieties. At pyrolysis temperature ≥500 °C, lignin was converted into fused polyaromatic complexes and it changes to coke like product at

~900 °C.[135]

In addition to fast pyrolysis, vacuum pyrolysis has been investigated as a means of producing phenolic resin precursors from lingo-cellulosic materials. In comparison to fast pyrolysis, longer residence times, of the order of 40 s, are employed in vacuum pyrolysis. The vacuum suppresses condensation reactions in the vapour, as the concentrations of reactants and therefore reaction rates are lower.

Thermal treatment in a hydrogen atmosphere leads to formation of chemicals like phenols, while oxidative atmosphere produces phenolic aldehydes and acids. Reviews on catalytic treatment of lignin[102,136] mainly hydrodeoxygenation (HDO) process led to formation of higher percent of phenolic compounds under comparatively milder conditions.[137-142] Lignin depolymerisation using catalyst system such as silica-alumina, and further catalytic cracking lead to formation of phenols,[142,128] alkoxy phenols, coke and aromatic hydrocarbons.[143-151] In general, the structure of lignin extracted from each method varies with nature of wood and processing conditions such as temperature, solvents, reaction time, catalyst, concentration etc. Catalytic processing of lignin depends upon the nature and morphology of the catalyst such as acidity and pore size. For instance, silicalite catalyst favours formation of alkoxy phenols due to stabilization of such structures by the catalyst under fast pyrolysis of lignin however absence of such catalysts lead to higher char formation.[73,152] This process will lead to the formation of lignin samples with varying functional groups both amount and nature (phenolic and aliphatic hydroxyl groups), molecular weight, polydispersity index, anti-oxidant activity.[153]

Thermochemolysis is a chemically assisted pyrolysis with the use of chemicals such as tetramethylammonium hydroxide (TMAH) (Py/TMAH) has been used to characterize a variety of natural polymers, including lignin.[154-159] Amen-Chen *et al.*[160] reviewed the production of monomeric phenols from thermolysis of lignin. Thermochemolysis product of guaiacyl dehydrogenation polymer in presence of TMAH lead to the formation of (E)-5-formyl-2,3,3′,4′-tetramethoxystilbene as major product.[161]

Alternatively, purification process needs modification due to generation of multi-component and multi-functionality organic compounds. Techniques such as ultrafiltration and nanofiltration retentate of waste water from a thermo-mechanical pulp mill showed potential of recovery of 11 Kg of hemicelluloses and 8 Kg of aromatic compounds (lignin) / tonne of pulp.[162] The cost of lignin production from non-woody lignocellulosic feedstock (*Miscanthussinensis L.*) via ultrafiltration of lignin fractions obtained by organosolv pre-treatment is estimated as 52 €/tonne.[163] Lignin recovered from different industries has different sets of properties which may be attributed to the presence of residue materials such as water and coexisting carbohydrates. For example, industrial hydrolysis lignin (HL) obtained from bio-ethanol production plants showed a lower T_g - 25 to 90 °C value than that of other industrial lignins, such as kraft lignin or lignosulfate.[164]

The scaling up of a high temperature process for recovery of chemicals from lignin may not be viable on a commercial scale due to high energy requirements. Therefore, low temperature processes are encouraged to obtain desired chemicals from degradation of lignin. Greener methods such as use of supercritical and ionic liquid solvents[165] over organic solvents, enzymatic hydrolysis over metal/acid/or alkaline catalysts and use of microwave reactor[166] over traditional reactors are explored either for extraction of lignin from lignocellulosic biomass or utilized for recovery of chemicals[165] from lignin.

Lignin decomposition is also facilitated by green solvents mainly supercritical water (Sc-H_2O).[167] It was found to contain catechol (28 wt%), phenol (8 wt%), *m*, *p*-cresol (8 wt%) and *o*-cresol (4 wt%) along with other phenolic substituted compounds.[168] Catechol undergoes further decomposition in Sc-H_2O to form phenol as suggested by change in percentage of phenol at expense of catechol.[169] Catalytic hydroprocessing of lignin into liquid products in supercritical ethanol overcome the problems associated with the low lignin conversion (<20%) and char formation at higher temperatures in hot compressed water.[170] Organosolv lignin undergoes depolymerization using catalytic hydrothermal process such as Ni/active carbon and Ru/γ-Al_2O_3 as catalysts lead to significant reduction of char formation and high yield of degraded lignin (DL) with weight average molecular weight 568g/mol and number average molecular weight 181g/mol upon treatment in water–ethanol and pure ethanol media under sub/supercritical condition in hydrogen atmosphere.[171]

Ionic liquids, such as 1-butyl-3-methylimidazolium chloride (BMIMCl) and 1-allyl-3-methylimidazolium chloride (AMIMCl),[172] Mn(NO_3)$_2$ in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [EMIM][CF_3SO_3][173] and renewable cholinium amino acids [Ch][AA][174] either under microwave irradiation and/or pressure are good source of either lignin or lignin based phenols or cellulosic compounds. Ionic liquid,1-ethy-3-imidazolium acetate treatment break lignin aggregates to nm size subunits of different shapes.[175]

Enzymatic processes such as SSF is a bioprocess for synthesis of phenolic compounds from agro-industrial residues and plants including cereal and vegetable wastes such as straw, bagasse, stover, cobs, husks.[176] The process involves digestion of organic polymer molecules by enzymes. The degradation of organic matter is both enzyme and condition specific such as temperature, moisture, concentration, incubation time etc. The presence of different weight percent of lignocellulosic biomass ratio mainly of cellulose, hemicelluloses and lignin dictates the digestibility. Lignin obtained by enzymatic hydrolysis could be a novel source for the production of many aromatic phenolic compounds at ambient conditions.[144] Both fungi[178-180] origin enzymes such as phenol oxidases (manganese and lignin peroxidases), laccase or their isoenzyme and bacterial strains[181-182] such as *Streptomyces viridosporus T7A*, *Nocardia*, and *Rhodococcus* are known to oxidise lignin G and H units to produce compounds such as ethyl salicylate, coumaric, cinnamic, ferrulic acid, gentisate, 3-hydroxybenzyl alcohol etc.[183] Therefore, in order to achieve selective or to increase the percentage of specific organic compound from enzymatic assisted degradation of lignin, development of improved microbial strains has come up an attractive and importantarea for research.[184] The mechanism of biodegradation of wheat straw by *Streptomyces viridosporus T7A* was studied and observed functional group changes in the lignin structure mainly carbonyl and methoxy groups.[185] Enzymatic modification of lignophenols is a potential way to convert lignin into chemicals for industrial applications.[186] Phenolic compounds comprises a variety of odorants which can form, be degraded or be modified during processing. Vanillin and other aromatic aldehydes are produced from lignin degradation during wood cooperage and can be released into the wine during barrel ageing.[186-187]

2.2.4 Characterization techniques

Concentrations of lignin from wood pulp samples can be determined[188] both by non-invasive[77,189] and invasive methods.[78,190] The non-invasive methods are based on the fact that chemical structure of lignin allows them to absorb electromagnetic radiation in specific region. The production of characteristic spectra in a specific region (wavelength, wave number or chemical shift) features will be proportional to amount of lignin in sample is determined by either utilizing molar extinction coefficient (UV-visible spectroscopy), or overlap intensities of modified and unmodified matrix infrared (IR) and near-infrared spectroscopy (NIR)[191-192] or integration of specific peaks in solid state nuclear magnetic resonance (NMR) spectra[193] with the sample of known lignin content. The non-invasive methods dictate whether the extraction of lignin from wood is economical and cost-effective.

On the other hand, invasive methods are based on volumetric titrations or gravimetric techniques using specific chemical treatments such as acetyl bromide or thioglycolate. The lignin content was estimated by the gravimetric Klason procedure.[194] The lignin structure can be investigated by chemical methods such as thioacidolysis,[126-127] Copper oxide oxidation,[197-204] nitrobenzene oxidation (NBO), and derivatization followed by reductive cleavage (DFRC).[205] The composition (H/G/S) of the lignin polymer and its quantification was achieved by DFRC method using pyrolysis-gas chromatography-mass spectrometry (GC-MS). This involved nitrobenzene oxidation, pyrolysis (GC-MS), thioacidolysis and DFRC.[206] This analytical process involves lots of time for preparation and analysis due to multi-step process. A streamlined thioacidolysis method and near-infrared reflectance-based prediction modeling allows quicker analysis.[207]

A spectroscopic technique such as FTIR, NMR etc. is used to differentiate the nature of wood. FTIR spectra of softwood box (*Buxus sempervirens*) and hardwood aspen (*Populus tremula*), in the fingerprint region 1800-800 cm^{-1}, showed prominent differences in the transmittance values. A reduced intensity of the band at 1740 cm^{-1} is slightly higher in aspen than in box which can be attributed to a greater number of acetyl groups in case of former.[208,209] The difference in the guaiacyl content between softwood and hardwood is elaborated by a doublet detected at 1610–1595 cm^{-1}, while only one band at 1595 cm^{-1} respectively.[210] Generally hardwood shows an equal intense peaks at 1595 and 1510 cm^{-1} attributed to the predominant syringyl unit, while in the softwood the band at 1510 cm^{-1} is more intense than at 1595 cm^{-1}, attributable to a higher content of guaiacyl units.[211]

In softwood kraft lignin (SKL), the 1269 cm^{-1} band (guaiacyl ring breathing with carbonyl stretching) is more intense than the 1214 cm^{-1} band and has no syringyl absorption at 1327 cm^{-1}, whereas the opposite is true for hardwood lignins, that is, a weak 1269 cm^{-1} band, a strong band at 1215 cm^{-1}, and a syringyl absorption at around 1327 cm^{-1}. The presence of a syringyl unit in hardwood lignin is also evident from the higher intensity of the band at 1462 cm^{-1}.[120] The presence of higher percentage of methoxy groups in hardwood is indicated by the peak near 1600 cm^{-1} due to aromatic–OCH$_3$ stretching.[210-211]

NMR spectroscopy provides information about the structural configuration, quantification, chemical composition, and linkages present in lignin sample.[212-214] ^{13}C-^{1}H correlated (HSQC, HMQC),[215-216] and ^{13}C-NMR[217-221] both solution and solids state are reported in literature to elucidate the structure of lignin. NMR studies confirmed the higher concentration of methoxy signals in hardwood kraft lignin (HKL) as compared to SKL due to predominance of both G and S units in the former. It is observed that purified isolated lignins, namely, “cellulolytic enzyme lignin” gave good quality spectra as they are devoid of cellulosic component. Cell wall polymers lignin and polysaccharides in native state are also identified and characterized during hydrothermal treatment of wheat straw lignin using solution state 2D-NMR spectroscopy.[222] Non-woody biomass such as corn stover was studied for the structural changes showed by lignin and LCCs characterized by alkaline nitrobenzene oxidation, ^{13}C, and ^{1}H–^{13}C HSQC NMR studeis.[223]

The composition and nature of lignin phenols are also determined by compound-specific radiocarbon analysis (CSRA) technique.[224-225]

Microscopy techniques such as confocal microscopy along with Histochemical Mäule staining provides indication for S-units in composition of lignin at cellular level.[226-227] The H/S/G composition can also be determined by laser capture microdissection combined with the microanalysis of lignins.[227]

Mass spectrometry (MS) techniques such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and Time-of-flight secondary ion mass spectrometry (ToF-SIMS)[228-229] were used for the analysis of the depolymerized fragments of lignin polymers, structural determination of monolignols, syringyl to guaiacyl (S/G) ratio[230] in order to obtain information on the complex polymer structure of lignin present in plant cell walls. It was found that rupture of inter-unit linkages at 8-O-4' , 8-1', 8-5', and 8-8' in lignin showed *m/z* 137 and 151 due to guaiacyl ring.[229] FT-ICR MS of wheat straw lignin showed some regularity with a difference of 44.026 *m/z* (C_2H_4O) units suggesting lignin is not a completely random polymer.[230-231] Other MS technique such as jet-cooled thermal desorption molecular beam (TDMB), secondary ion MS (SIMS), synchrotron vacuum-ultraviolet secondary neutral MS (VUV-SNMS) were also used to understand the fragmentation mechanism of monolignols under different energetic processes. The positive ion SIMS spectrum of coniferyl alcohol showed characteristic peaks at *m/z* 137 and 151.[232] A study on wheat straw lignin using atmospheric pressure photoionization quadrupole time-of-flight mass spectrometry (APPI-QqTOF-MS) provided evidence that grass lignin is composed of repeating phenylcoumaran units, which are formed from two di-coniferyl units linked by the C8–C′5 covalent bond and the ether C7-O-4′ linkage, forming a furan-like ring attached to an aromatic coumaran ring.[233] Py-MBMS of grass bagasse gave a distinctive fragmentation pattern with high m/z 114 consistent with expected xylan enrichment, and fragments at *m/z* 150 and 120 indicated coumaryl derivatives, presumably from the hydroxycinnamic acid groups, PCA and FA.[234]

Simple techniques such as GC-MS analysis of pyrolysed softwood and hardwood sample confirmed the presence of syringyl and guaiacyl groups in hardwood and softwood lignin.[235] Non-wood fibers such as hemp, flax, jute, sisal and abaca, alkali lignins have been analyzed. Hemp and flax have low S/G ratios, while jute, sisal and abaca showed high S/G ratios, as revealed by Py-GC/MS and FTIR analysis. Py/TMAH showed a significant amount of PCA in the abaca lignin and much lower cinnamic contents in the other lignins. This analysis also confirmed that PCA is attached to cell walls through ester bonds, while FA through ether-linkage except sisal where, the linkages are found to be in reverse order.[236] Softwood lignin pyrolysis afforded coniferyl derivatives while hardwood lignin coniferyl and sinapyl derivatives and grass lignin *p*-vinylphenol as confirmed by GC-MS studies.[237]

Thermal characterisation such as DSC[120-121] and TGA, and thermorheological analysis can also provide insight about nature of wood. The yield of carbon generated from SKL and soda hardwood lignin was found to be 37% and 34% as analyzed by TGA studies at 900^{o}C.[238] The viscosity of softwood and hardwood lignin was found to be considerably different due to their different chemical structures and molecular weights and former shows a lower value 2.8 poise while later has 3.5 poise at 1.8 s^{-1} at 225 ^{o}C.

2.2.5 Lignin Pyrolysis Oil

The properties of lignocellulosic biomass such as carbon neutrality, relative abundance, renewability and non-food competition[239-240] have considered them as an important primary feedstock for generation of renewable fuels and chemicals. Amongst various possible extraction techniques, pyrolysis has come up as an economically viable option for the generation of lignin pyrolysis oil by the virtue of low capital and operating cost.[241] Apart from addressing the sustainability issue, lignin pyrolysis oils have also been of economic relevance due to their attractive fuel selling price of $2.48/ gallon as supported by PNNL (Pacific Northwest National Laboratory).[242-243] The cost of final oil product range between $2.11-3.09/gallon, depending on source of biomass.

Amongst prominent lignocellulosic fractions, cellulose is primarily used for pulp and paper production (5–36 × 10^8T/annum,[244] cellulose[245-246]and hemicellulose, can be also hydrolyzed to fermentable sugars that can be either fermented to produce ethanol or butanol, or transformed by hydrogenation or dehydration methods to yield intermediates important for chemical syntheses and fuel purposes. The upgradation strategies are different for lignins being phenolic in nature whereas cellulose and hemicelluloses are polysaccharides. Bio-oil yielded from lignocellulosic biomass via fast pyrolysis technique comprises of both water soluble and insoluble fractions out of which former with high oxygen content are derived from cellulose and hemicelluloses fraction of biomass. Cellulose being a pure polymer of glucose can be converted to high quality bio oil. Under rapid pyrolytic conditions pure cellulose yields levoglucosan which can easily be hydrolyzed to glucose but generally due to the presence of small amount of alkali, hydroxyacetaldehyde is formed instead.[247] Catalytic pyrolysis of cellulose has also confirmed it to be the highest hydrogen producer amongst all the biomass components.[248] Apart from thermal treatment, microbial methods[249] and chemo-catalytic conversions[250-251] have also been explored to effect the conversion of cellulose to biofuel. Cellulose and hemicellulose have received widespread attention as possible fossil fuel alternatives due to their easy convertibility[252] but lignin has largely remained under-utilized except for possible applications in paper pulping, bioethanol fermentation or a low-value fuel because of its inhomogeneity and resistance to degradation.[253]

The conditions of pyrolysis of lignin to generate oil depend on feedstock composition and experimental conditions, such as temperature, residence time and nature, morphology and type of catalyst which are different than for their use for generation of chemical intermediates as discussed in earlier section i.e. 2.2.3. The chemical nature of pyrolysis products from lignin contains mainly water insoluble heavy oil (65–85 wt.%),[254-255] whereas tannin and cellulose yield mostly water soluble light oil, which contains >60 wt.% of water and water soluble components such as methanol, levoglucosan and catechol. In comparison to lignin, pyrolysis of tannin and cellulose yield,~78 wt% and ~85 wt% of light oil respectively.[256-257] This accounts for the analysis and development of new and different process technologies for conversion of lignin to pyrolysis oil in comparison to whole lignocellulosic biomass in terms of chemistry, mechanism, upgradation, catalysts etc.[258]

In comparison to traditional oils, pyrolysis oils have high oxygen and unsaturated content apart from several other drawbacks such as poor volatility, corrosiveness, viscosity, thermal instability, high coking tendency, low heating value, and immisciblity with petroleum fuels.[131] This hampers the prospects of their commercialization thereby necessitating the utilization of upgrading technologies that convert pyrolysis oils to a potential substitute for diesel and gasoline. The upgrading process stabilizes the pyrolysis oil, reduces or eliminates the inferior properties mentioned above enhancing its compatibility with gasoline. Several upgradation techniques ranging from catalyst cracking, hydrodeoxygenation (HDO), to hydrotreatment are under exploration.

The use of zeolite cracking is one of the most widely explored upgradation catalysts for pyrolysis oil. It was found that H-ZSM-5 zeolite improves lignin depolymerization[143] and leads to complete deoxygenation[143,147,149] of liquid phase producing simple aromatics and naphthalenic structures. Modification of ZSM-5 zeolite with substitution of metals such as nickel, cobalt, iron, and gallium resulted in highest, ~16wt % of hydrocarbons.[259] Also, pyrolysis of several biomasses such as, corn stalks, cassava rhizome, hybrid poplar wood, rice husks and pine wood with ZSM-5 zeolites resulted in lowering of oxygen content. The use of nickel salt additive along with zeolite resulted in an improvement in the decomposition of aliphatic hydroxyl, carboxyl, and methoxy groups and ether bonds in the lignin.[260] The variation in the ratio of Si:Al in zeolite have shown a profound effect in cracking reactions during thermal treatment of biomass. The lowering of Si:Al ratio in H-Beta zeolites resulted in formation of less organic oil, more water, and polyaromatic hydrocarbons.[261] The pyrolysis of SKL in presence of various H-ZSM-5 zeolites with different $SiO_2:Al_2O_3$ mole ratios ranging from 23:1-280:1 at 600 °C was studied. H-ZSM-5 zeolites lead to an almost complete decomposition of aliphatic hydroxyl and carboxyl groups and the content of polyaromatic hydrocarbons in pyrolysis oil was found to decrease with increase in $SiO_2:Al_2O_3$ ratio. Also, an 8-16 % decrease was observed in the molecular weight in presence of zeolites.[262] Mixing of H-ZSM-5 with organosolv lignin extracted from prairie cordgrass (PCG) in a ratio of 5:1 at 650° C resulted in a 13 wt% yield of PCG lignin. Aspen (woody biomass) showed a two-fold increase in the total aromatic hydrocarbon yield obtained from organosolv lignin pyrolysis in presence of H-ZSM-5 as compared to PCG lignin (non-woody biomass). However the content of oxygen in the volatile emissions during catalytic pyrolysis was found to be lowered in case of PCG as compared to aspen thereby enhancing the quality of pyrolysis oil.[263] Zeolite frameworks also influence the pyrolysis mechanism. FAU and BEA zeolites were found to improve the cleavage of aromatic–methoxy and other ether bonds in the lignin yielding pyrolysis oil with gasoline range molecular weight. Hence, upgraded pyrolysis oil could be used as the precursor of gasoline and possible substitution of petrochemicals. Similarly, other zeolite frameworks such as MFI, FER and MOR zeolites could more efficiently decompose the carboxyl groups thereby reducing the acidity of pyrolysis oils making it more suitable for use as a biofuel.[264] The cost effectiveness for zeolite cracking process can be achieved by the requirement of low amount hydrogen gas and regular non-pressurized reactor. However, the produced oil is of low quality[265] and showed higher coke content. Moreover, although zeolite is effective in deoxygenation of small oxygenates molecules such as aldehydes and ketones but its capability is limited for deoxygenation of phenolics due to its small pore size.[266-267] This was accounted to the difference in reaction pathway goverened by reactivity-selectivity principle. When the pore size is small selectivity increases but reactivity decreases due to different diffusion rates. Zeolites can also be used as a catalyst support for such process. It was observed that the modification of zeolite into mesoporous structure significantly increased the reactivity. The dehydration and transalkylation reaction mainly occur on the acid site. In addition, the stronger acidity or bonding with reactants reduces the desorption rate and lower the reaction rate which implies that acidity and surface area are two key parameters for support material characterization.

Hydrodeoxygenaton (HDO) is another popular upgradation process which involves hydrogenation of the unstable unsaturated bonds and reduction of oxygen in the pyrolysis oil. It produces high-quality oil, but it requires hydrogen under pressure as one of the major reactant. In contrast to zeolite cracking, the cost for hydrogen and pressurized reactor reduces the viability of this process. Commonly used catalysts in HDO process are sulfided and transition metal catalysts. Sulfided catalysts such as $NiMoS/Al_2O_3$, $CoMoS/Al_2O_3$ etc. are more often used due to their low costs over other transition metal catalysts. Although widely used for petroleums, this class of catalysts suffers from certain disadvantages owing to the unique nature of pyrolytic oils. The presence of water, high oxygen and coke content,[268] in raw pyrolytic oil[269-270] are the factors which may lead to rapid catalyst deactivation resulting in poor yields. In comparison to sulfide catalysts, transition metal catalysts, such as platinum, palladium, ruthenium, rhodium, etc. can easily be utilized in presence of water. They also showed higher reactivity for hydrogenation and require moderate reaction conditions.[271-272] But this class of catalysts also suffers from certain disadvantages such as high costs due to demanding catalyst recycle technique and its sensitivity to sulfur present in kraft lignin. Therefore, feedstock requires special treatment to remove the sulfur before treatment with HDO process.

Spectroscopic techniques are widely employed to elucidate chemical structure and composition of lignin pyrolysis oil as compared to chromatography and MS techniques. The simplest and most commonly used GC technique can detect only 10–40% of the content of pyrolysis oil due to its complex nature.[273-274] The addition of flame ionization detector (FID) to GC leads to an improvement in detection to a 30%.[275] NMR spectroscopy such as ^1H-, ^{13}C-,[275] HSQC- and ^{31}P- were found to be a better characterization techniques both for chemical structure elucidation and quantification. ^{31}P-NMR spectroscopy is widely used technique, both for studying chemical changes during pyrolysis of biomass and quantification of hydroxyl groups. This analysis is based on the phosphitylation of hydroxyl groups with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) to form phosphorous linked groups to the bio-oil.[276] The effect of catalyst (viz. zeolites) on the pyrolytic mechanism,[262,264] variation in the bio-oil quality with the nature of biomass (woody Vs. non-woody)[263], order of bond cleavage,[277-284] primary cleavage products,[254,277-284,285-286] favourable decomposition steps,[287,254,277,279] an efficacy of a particular extraction methodology[255] etc. were comprehended using these spectroscopic methods. GPC analysis is another technique employed to zero down on optimal pyrolytic condition viz. temperature, time duration,[254] nature of catalyst[264] etc. thereby enhancing the properties of pyrolytic oil.

2.3 Tannin

Tannins are natural phenolic structures present in numerous wood species particularly in the southern hemisphere.[288] They are useful for helping the plants to fight against insects and fungi. Furthermore, their astringent character limits the consumption of tannin-rich vegetables by herbivorous animals.[289] Although, distributed all through the cytoplasm of any vegetal cell,[290] the highest concentration of such compounds is generally found within tree barks including black mimosa bark (*Acacia mearnsii),* quebracho wood (*Schinopsis batansae),* oak bark (*Quercuss* spp.), chestnut wood (*Castanea sativa),* pines (*Pinus radiata* and *Pinus nigra)* and fur etc. Brazil, India, Zimbabwe, Tanzania are amongst leading producers for mimosa tannin, Argentina for quebracho tannin and Slovenia for chestnut wood tannin amongst others.[288] The qualitative and quantitative analytical differences between tannins from plant polyphenols of other types arise from their affinity to bind with proteins, basic compounds, pigments, metallic ions and macromolecular architectures including anti-oxidant activities, etc. The specific binding properties are utilized for their quantification protocols. As a result of which the quantification of tannins is based on their binding activity unlike the analysis of polyphenols.[291]

Traditionally tannin have found use in leather manufacturing due to their ability to precipitate proteins in the animal hide.[288] Other uses for tannins range from cement plasticizers, ore floatation agents, wine additives to pharmaceutical applications. Also, tannins are explored as green renewable material for novolac adhesives,[292] and for formation of resole resins. Their utilization for partial replacement of petro based phenols viz. in wood adhesive formulation lead to reduction of pressing and gelation time and also lowered formaldehyde emissions adding to their ecological relevance.[293]

Tannins can be classified as hydrolysable (HTs) and condensed tannins (CTs) (Fig. 9).[292] The molecular weight of vegetable tannins range between 500-3000 Da.

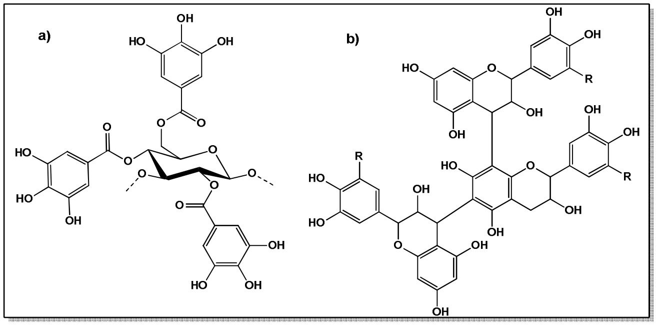


Fig. 9 Chemical structure of a) hydrolysable tannin (HT) and b) condensed tannin (CT; when R = H, catechin)

HTs are sourced from chestnut (*Castanea sativa*), myrabolans (*Terminalia* and *Phyllantus*), divi-divi (*Caesalpina coraria*), tara, algarobilla, valonea, oak etc. They contain either gallatotannins (monoester, Fig. 9a) or ellagitannins (diester) which on hydrolysis in acidic/basic or enzymatic conditions produce glucose and gallic or ellagic acid. In addition to gallic and ellagic acid, the other phenolic acids such as valoneic, nonahydroxytriphenoic, hexahydroxydiphenoic and flavogallonic acid have also been obtained due to the hydrolysis of ester linkages in HTs (Fig. 10).

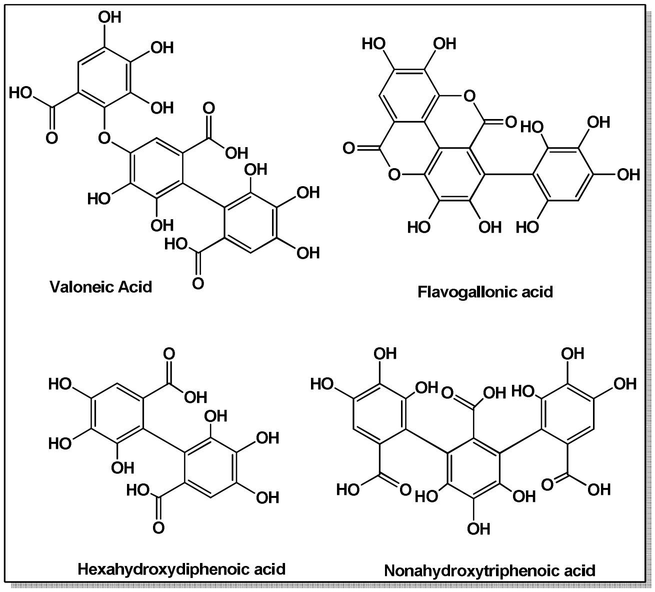


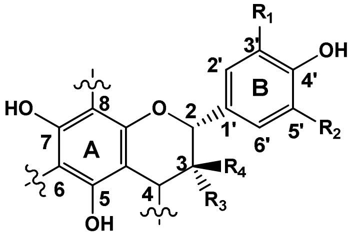
Fig.10 Phenols and phenolic acids obtained in low molecular weight fractions of HTs[288]

The presence of ester linkages explains their susceptibility to acidic, alkaline and enzymatic hydrolysis. However, HTs not as commercially viable as CTs due to their lack of macromolecular structure, low level of phenol substitution, low nucleophilicity, limited worldwide production and relatively high price. The commercial HTs obtained from chestnut tannin extract contains positional isomers namely castalagin (14.2%) and vescalagin (16.2%), positional isomers castalin and vescalin (6.6%)[136],gallic acid (6%) and pentagalloyl glucose monomer (3%).

CTs constitute more than 90% of the total world production of commercial tannins (2 x 10^5 tons/ year).[294]The main source of CTs are wattle or mimosa *(Acacia)*, quebracho (*Schinopsis*), hemlock (*Tsuga*), sumach (*Rhus*) and various pine (*Pinus*)species. CTs are the polymers of a mixture of either flavan-3-ols or flavan-3,4-diols and are most frequently linked either via C4-C6 or C4-C8 bonds (Fig. 11).[295-296] They are also called as flavolans or proanthocyanidins such as procyanidins, propelargonidins, prodelphinidins, profisetinidins and prorobinetinidins.[297] Catechin, gallocatechin and epigallocatechin are all precursors of CTs. The structure of flavonoid monomer is represented in Fig. 11.

The flavonoid structure (Fig 11) comprises of two aromatic rings namely A- and B-ring, which differ in number of hyroxyl groups. A-ring may have one (resorcinol) or two (phloroglucinol) hydroxyl groups while B-ring can have two (catechol) or three (pyrogallol) hydroxyl groups. In addition to this structural variation, A- and B-ring can be linked resulting in formation of different flavanoid monomer structures which differ in reactivities. Such difference in number and position of hydroxyl groups in the two rings dictates their reactivity towards aromatic electrophilic substitution reaction, A-ring tend to be more reactive than the B-ring.[294] Mimosa tannins are mainly based on prorobinetinidine, being the association of a resorcinol A-ring with a pyrogallol B-ring. In mimosa bark tannin extract, the repeating units are mostly 4,6-linked and sometimes 4,8-linked.In mimosa bark, 70% of CTs contain A and B rings as resorcinol and pyrogallol, 25% contains resorcinol and catechol respectively while rest percentage contains are the non-tannins (carbohydrates, hydrocolloid gums and small amino and imino acid fractions).[294] The hydrocolloid gums account for high viscosity of tannin extract even though they are present in low (3-6%) percentage. The properties of CTs depend on the structure of monomer units, degree of polymerization (DP) and the linkage-type between flavan-3-ol units accounting for a considerable range of structural variation.[298] CTs are oligomeric compounds characterized by sequences of units bearing two or more OH groups per aromatic moiety with DPs varying considerably (2-30) from species to species.[299-300] The soluble extract fraction of mimosa and quebracho tannins contains oligomers of flavonoid unit (2–11)[294,301] with an average DP of 4–5, while pine tannins have ~30 units with an average DP of 6–7.[302] The most common classes are the procyanidins, which are chains of catechin, epicatechin, and their gallic acid esters, and the prodelphinidins, which consist of gallocatechin, epigallocatechin, and their galloylated derivatives as the monomeric units.[303] In CTs, the presence of phenolic –OH, number and free aromatic ring position accounts for high reactivity and its economic usage for the preparation of adhesives, resins and other applications apart from traditional leather tanning for which HTs are well suited. The CTs have the capability to replace up to 90% of phenols in phenolic resins.[304]

In general, tannins could be structurally modified by acetylation, hydrolysis, condensation, polymerization reactions.[305-308] They may also be copolymerized with isocyanates, formaldehyde, aminoplast or phenolic resins to yield thermosetting binders for particle panels.[294,304, 308]



	R1	R2	R3	R4
(+)-Afzelechin	H	H	H	OH
(-)-Epiafzelechin	H	H	OH	H
(+)-Catechin	H	OH	H	OH
(-)-Epicatechin	H	OH	OH	H
(+)-Gallocatechin	OH	OH	H	OH
(-)-Epigallocatechin	OH	OH	OH	H
Epifisetinidol	OH	H	H	OH
Epirobinetinidol	OH	OH	H	OH

Fig.11 Mononmeric unit containing flavonoid units

In addition to the commonly used classification as HTs and CTs, tannins can also be categorized into Type A and Type B based on the chemical structure variation with seasonal changes. Polyphenols of constant chemical structure are categorised as Type A and polyphenols of variable composition as Type B. All ellagitannins belongs to Type A tannins. The structures and compositions of type B tannins from a particular plant species behave in a transient manner which varies with season, growth conditions of the plant, and extraction methods. Examples of Type B tannins are HTs from Chinese and Turkish gallotannin.[291,309]

2.3.1 Extraction and characterization

Similar to cardanol, isolation of tannin from the biomass utilize extraction techniques such as conventional methods,[310] extraction[311] and green methods such as utilization of microwave and ultrasonic wave,[312-313] and sub-critical solvents.[314]

In conventional methods, the effect of solvent polarity on the extraction of gallic acid, ellagic acid and corilagin from *P. niruri* was studied using polar solvents such as water, water-ethanol mixture, ethanol, and non-polar solvent such as hexane.The yield of extraction was found to be maximum in polar solvents such as water (26%), followed by aqueous ethanol (27%) and least in hexane (~2%) due to higher salvation of polar tannin phenolics structures.[315] Other solvents systems such as acetone and diethyl ether either alone or in combination with water and ethanol were also reported for the extraction of phenolics from pomegranate aril.[316] Industrial tannin production largely employs and prefers hot water extraction technique over organic solvents to reduce both VOC emission and cost. This process requires extraction at 70 °C with longer extraction times, and high water to solid weight ratio. These parameters require optimization to improve both the yield and quality of tannin extract. However, poor extraction efficiencies may be accounted due to either dilute extraction conditions, prolonged heating duration or use of temperatures > 70 °C which may lead to degradation of phenolics.[317] Norway spruce (*Picea abies*) bark appears to be a promising source of tannins by industrial extraction (10.7%) and extraction yield was scaled up to a promising 50% with profound temperature control at a pilot scale.[318]

An alteration in pH of aqueous extracting solvent from neutral to slightly alkaline using aq. Na_2CO_3 (10%) showed an increase in extractives concentration from 25% to 49%. This increase in extractive percentage was due to partial cleavage of pyran rings of phlobaphens (~ polyphenols) assisted by alkaline pH resulting in enhanced water soluble intermediates. However, with increase in concentration of base in solvent there is a simultaneous increase in undesirable non-tannin percentage which found to inhibit the utility of extract for adhesive applications.[319] It was found that by alteration of the nature of base to a mixture of aqueous Na_2SO_3:$NaHSO_3$ (1:1, 0.25%) and NaOH (1%) at 70/80 °C also led to extraction of tannin. The function of NaOH is to increase the alkalinity to improve tannin yields in the extract while sulphite-bisulphite mixture led to decrease in extract viscosity thereby stabilizing the extracted mass.[320] A bi-component solvent system, acetone-water with bisulphite method is also reported for tannin isolation.[321]

Microwave assisted extraction (MAE) offers several advantages over conventional extraction techniques viz. shorter extraction times, lower solvent consumption, better efficiency and higher yields.[322] Rosemary (*Rosmarinus officinalis*) biomass subjected to MAE in presence of alcohol such as methanol and ethanol showed a two-fold higher extraction yield (951 mg of chlorogenic acid/100g) as compared to ultrasound assisted extraction (UAE). However the extraction yields of microwave and soxhlet extraction were found to be similar.[323] Besides usage of naturally occurring source as such, grape pomace residues obtained from wine manufacturing units are also found to be rich in CTs. Their extraction using conventional methodology required harsher conditions (100 °C, high base concentration 2.5-7.5%).[324] While optimal MAE conditions are milder (100 °C, 1:8 solid to solvent ratio, 1.25% Na_2CO_3, 8 min.) and gave higher polyphenolic and consequently tannin yields from 0.6, 1.6 and 1.5% for grape red marc, white marc and pomace respectively.[325] *Agrimonapilosa*

Ledeb known for its high tannin levels yielded 128.7mg/g of tannin under MAE conditions optimized to irradiation power of 500 W, at concentration of solvent to mass ratio as35 mL/g at 30 °C in 15 min.[326] Response surface methodology (RSM) could be used as an important method for optimization of extraction process.[325,327] MAE process optimized by RSM for cherry laurel (*Prunus laurocerasus*) leaves suggested the most economic conditions of extraction are a power of 307.6 W, a very dilute concentration conditions of 0.17 g/mL in17.1 min.[328]

In addition to MAE advantages, UAE is another promising technique for tannin extraction owing lower equipment costs, simplicity of operation, and better extraction quality. Ultrasonic waves requires shorter extraction times and lower temperature for leaching out of tannin as compared to other extraction techniques viz. maceration, hydrodistillation, low pressure solvent extraction etc., making it suitable for extraction of thermally sensitive organic compounds.[329-330] Cavitational effects of ultrasound waves facilitate the release of extractable compounds and enhance mass transport by disrupting the plant cell walls.[331] Highly solvating solvents lead to better swelling and accounted for higher extraction efficiency and/or reduced extraction times.[332] In myrobalan, a 4.5 times enhancement in the extract yield (90%) was observed without external heating due to ultrasonic treatment as compared to conventional methods (21%).[333] Quantitative extraction of polyphenols from jatoba (*Hymenaea courbaril L.*) bark using UAE process at 60 W,50 °C, 40 min. and a solvent to feed ratio of 20 showed improved yields as compared to conventional agitation process.[334] A variation in ultrasonic method extraction parameters such as temperature (0–75 °C), output amplitude (20, 50 and 100%), duty cycle (0.2 s, 0.6 s and 1 s), quantity of sample (0.5–2.0 g), and total extraction time (3–15 minutes)was studied for tannin extraction of grapes. It was found 6 min. extraction time using acidic pH (2) ethanol:water (1:1) at 10 °C gave optimal tannin extraction yields[335] where as conventional extraction process required stirring and 60 min. to attain the similar yields.[336-337]

Not only the use of greener methods allows better yields at milder extraction conditions, even the utilization of either green or low volatile solvents such as ionic liquids is also a current area of research to supplicate tannins to meet commercial requirement for material applications.[338-339] The extraction efficiency of HTs materials from plant sources such as catechu (*Acacia Catechu*) and myrobolan (*Terminalia Chebula*) was found to be 85% using a distillable ionic liquid, N,N-dimethylammonium N′,N′-dimethylcarbamate (DIMCARB) at room temperature as compared to the conventional extraction methods which utilize bulk quantities of solvents.[338] Ionic liquid extraction of tannin from Gallachinens is using simultaneous ultrasonic and microwave assisted extraction technique yielded ~630 mg/g of tannin content. which was ~22% more efficient than the conventional techniques along with reduction in extraction time from 6 h to 1 min.[340] Although, ionic liquids have come up as an attractive alternative to the existing solvents, due their high boiling points and solvation capability however they suffer from the major drawback for their removal to isolate the target compounds. Macroporous resin adsorption technology in addition to ionic liquid based UAE and MAE increased the tannin content in *Gallachinensis* extract from 70 to 85% with a solvent recovery of 99%. Preliminary extraction of tannins by 1-butyl-3-methylimidazole bromide and its subsequent removal from *gallachinensis* extract using macroporous resins.[341] The use of low temperature, greener processing condition is also important from industrial scale up methods. CTs undergoes depolymerisation in presence of thiols to from monomeric phenols under mild conditions at 40 °C in 2h using ethanol as a solvent.[342]

Supercritical fluids (SCF) can also be used as solvents for extraction as they provide an environmentally viable and commercially feasible option due to use of lower temperature and their easier removal, unlike ionic liquids, after completion of extraction process by altering the operating conditions. The lower critical temperature 31 °C and moderate critical pressure (7.28 MPa) of carbon dioxide makes it an ideal solvent for compounds that may suffer thermal degradation esp. phenolics. In addition, CO_2 processing creates a medium without oxygen where oxidation reactions can be avoided, which is of paramount importance during antioxidant extraction.[343] The non-polar nature of carbon dioxide and polar nature of phenolic extractive is a mismatch for its usage as the only extraction solvent. In order to enhance the polarity of carbon dioxide alcoholic co-solvent such as methanol or ethanol showed better extraction yields.[343] The percentage of ethanol in Sc-CO_2 showed a profound effect in the chemical component extracted. Gallic acid, epigallocatechin and epigallocatechin gallate were extracted at 300 bar, 50 °C and 20% of ethanol while epicatechin yield was optimum at 250 bar, 30 °C and 15% of ethanol.[344]

Several methods are reported in literature to determine both the amount and analysis of CTs, HTs or total phenolics in a sample. In general, HTs are apparently more difficult to analyse than CTs due to theirs sensitivity to hydrolysis by acids, bases or enzymes. The nature of analytical data critically depends on appropriate sample preparation, storage conditions, extraction techniques and prior knowledge of the reactivities of tannins. The amount of tannins in a sample can be measured by general tannin assays, such as precipitation with metals[345] or proteins.[346] It is important to select appropriate assays for measurement of the quantity and activity of CTs.[347]

Colorimetric assays are widely used for comparison of tannin content in various samples. Most widely used colorimetric assays that are used to quantify tannins are based on reaction of phenolic moieties with specific reagent and colour change was monitored and analyzed at specific wavelength by UV-visible spectroscopy.[348] Assay such as Folin Ciocalteu,[349] CUPRAC,[350] Trolox equivalent antioxidant capacity,[351] and free radical scavenging assay such as 2,2-Diphenyl-1-picylhydrazyl (DPPH)[352-354] and Oxygen radical absorption capacity (ORAC)[355] are well cited in literature.

Characterization of tannic component in extracts is a complex process due to the co-existence of a large number of isomeric molecules and high molecular weight species. They are often unstable under heat, in acids and bases, or easily oxidized. Characterization techniques such as FTIR, NMR, MALDI-ToF along with chromatography techniques (HPLC, SEC) are useful tools to study, identify, and determine the purity the tannin composition in the extract. SEC is mainly used to determine average DP of CTs.

The nature of resin condensed or HTs can be analysed by UV-visible spectroscopy by analyzing the ratio of λ_{max}: λ_{min} centered at 276 nm and 256 nm respectively. It was found that HTs showed lower ratio values (1.03-1.35) while CTs showed a higher value in the range of 1.67-2.15.[356]

IR spectroscopy of tannin extract from grape pomace origins showed catechinic acid rearrangement under alkaline extraction conditions as suggested by the weak IR peak development at 1750 cm^{-1}. IR peaks at 1308, 1264 and 1212 cm^{-1} indicated pyran ring opening during the sulfitation process of flavonoid tannins.[357] The C=O or C-C stretch vibration in CR_2-CHR-$CR(SO_3)^{2-}$was accounted to peak at 1260 cm^{-1},[358] while peak at 1440 and 1495 cm^{-1} [357] were due to C-H deformation and aromatic ring vibration respectively. These peaks were only detected for extracts obtained with 1% NaOH along with $NaHSO_3$/Na_2SO_3due to lower lignin content as impurity.[320]

The accurate analysis of tannins requires conjunction of chromatography along with MS techniques. Chemical methods involving acid depolymerisation of CTs to form carbocation intermediate which is trapped with phoroglucinol and derivatized followed by capillary GC separation and detection by flame ionisation. Such processes are tedious, however very sensitive and detect ~100 ng CT in a sample.[359] Mass spectrometry techniques such as LC-MS/MS, MALDI-ToF provide a good insight for the structural analysis of tannins. The fragment pattern *m/z* 301, 317, 285 was attributed to the fragment patterns of myricetin, quercetin and kaempferol, respectively as confirmed from further fragment ions for quercetin (*m/z* 121, 151, 179, 245, 273, 301), myricetin (*m/z* 137, 151, 179, 271, 289, 299, 317), kaempferol (*m/z* 187, 93, 285).[360] MALDI-TOF for non-purified industrially extracted maritime pine polyflavonoid tannin indicated procyanidins oligomers composed of catechin/epicatechin, epigallocatechin and epicatechingallate monomers. These oligomers contain 20–21 monoflavonoid units having catechingallate dimer (528–529 Da) as major repeat units which has lost both the gallic acid residues and a hydroxyl group along with a small proportion of fisetinidin units.[361] MALDI-TOF spectrometry demonstrated that the grape pomace tannin extracts contained oligomers up to 6 repeating flavonoid units, with dominant procyanidin with a minor amount of prodelphinidin units.[357] Post source decay fragmentation of data obtained from MALDI-ToF allowed analysis of sequential loss of monomers from CTs polymers. This technique confirms the major polymeric architecture present in willow (*Salix alba*) and lime leaf (*Tilia cordata*) contain procyanidin units while for spruce needle (*Pacia abie*) and beech leaves (*Fagus Sylvatica*) have both procyanidin and prodelphinidinin varying ratios.[362] Two-dimensional chromatography (Hydrophilic Interaction Chromatography with Reversed-Phase Liquid Chromatography) coupled with MALDI-ToF allowed analysis and accurate mass detection of procyanidins which comprise tannins up to a DP of 16.[363] HPLC-ESI-ToF allowed identification of major monomeric components of chestnut shell and pine bark tannins tannin extract as catechin/epicatechin and dicatechin (*m/z* 289.08) andgallocatechin/epigallocatechin (*m/z* 305.07).[361] HPLC/DAD and MS provides both qualitative and quantitative analyses of polyphenols, HTs and CTs in the extract. Chestnut (*Castanea sativa*) bark samples showed first time detection of the presence of 1-O-galloyl castalagin along with other components vescalin, castalin, gallic acid, vescalagin, castalagin and ellagic acid which were both separated, quantified and identified using HPLC-DAD/ESI-MS.[364] Normal-phase HPLC was found to be more suitable over reverse phase for pine bark (*P. maritime L.*) tannic acid extracts analysis and revealed that extract was mainly composed by polyflavanols (containing 2-7 units) and tannic acid as glucose gallates (containing from 3-7 units of gallic acid).[365] Mass spectrometry profiling followed by preparative HPLC in peel and flesh of mango fruits showed HTs glycones as a major class of compounds. MS signal was observed at 332.07, 636.09, and 788.11 Da corresponding to galloyl-, trigalloyl-, and tetragalloyl-glucose respectively. HPLC trace of these samples showed different peaks with different retention times corresponding to each m/z value suggesting the co-existence of isomeric structures.[366] Myrtle and pomegranates tannin extracts showed the [M-H] peak at *m/z* 343.2 (due to galloylquinic acid) and 169.2 (due to the loss of quinic acid),[367] at 633 (due to galloyl HHDP-glucose isomers)and [M-H] at *m/z* 481.3 and 483.2 (due to the loss of a gallic acid) and 301.1 (due to lactonized form of the HHDP-unit i.e. ellagic acid). The mass spectrum also confirmed the major tannic compound in pomegranate peel extracts, [M-H] peak at 1083.2 (due to β-punicalagin), and 781.2 (due to loss of 301 *m/z* fragment of ellagic acid).[368] The peel extracts and seed extracts showed a reversal in relative abundance of gallic:ellagic acid derivatives as 29:71 and 61:39 respectively.[369]

^{13}C NMR spectroscopy confirmed the presence of procyanidinin the leaves and needles of willow (*Salix alba*), spruce (*Picea abies*) and beech (*Fagus sylvatica*) while prodelphinidin was only present in the latter two. NMR signal between 70 and 90 ppm demonstrated the presence of stereoisomers (catechin/epicatechin; gallocatechin/ epigallocatechin).[362] The proanthocyanidin tannins in quebracho (*Schinopsis lorentzii*) heartwood and black wattle (*Acacia mearnsii*) bark showed signal at 118 or 105 ppm due to presence of catechols (quebracho) or pyrogallols (wattle) respectively.[370] ^{13}C-NMR analysis of chestnut tannin extract confirms procyanidins and prodelphinidins as major components with small amounts of prorobinetidins due to the presence characteristic bands of a typical CT pattern.[371-374] The presence of carbohydrate content in tannins is confirmed due to characteristic signals in 65–85 ppm.[375]

2.4 Palm oil

Palm oil is an agricultural product from palm tree, *Elaeisguineensis* which is mainly produced in East-South Asian countries, such as Malaysia and Indonesia. Oil palm fruits lead to

Table 2 Chemical compositions of lignocellulosic biomass in Malaysia [162]

Wood/Fiber	**Polysaccharides**	**Lignin (wt**

	(wt%)[a]	%)
Oil palm fronds [380]	86.5-83.5	14.8-20.5
EPFB [381-382]	82.4	17.6-25[382]
Oil palm fibres[383]	59.6	28.5
Oil palm shells [384]	43.5	50.7
Oil palm trunks [385]	75.6	17.1
Coconut husk Cocosnucifera L. (fiber)	50.9 [386]	32.8[387]

formation of two types of oil derived from mesocarp and kernel. Both Indonesia and Malaysia is the leading producer of palm oil accounting for nearly 80% world production, 21-23 MMT in 2013 by Indonesia alone.[376] In Malaysia, lignocellulosic biomass availability is nearly 47,402 dry Kton per year. Agro-waste generated from oil palm mill industry and agricultural fields (oil palm fronds, OPF and empty fruit bunches, EFB) is considered as a poor source for fertilizers, animal feed or incineration due to very low nitrogen content and smoke problems respectively. However they are rich in lignocellulosic material therefore can act as a renewable source of chemicals at low cost for green material applications.[377-378] The lignin and polysaccharide content variation in palm tree is shown in Table 2.[379]

In general, palm waste has nearly 60-80% cellulose and 30-20% lignin content accounting them as a good source of both glucose[388] and phenolic compounds. Lignin content was found to be maximum in oil palm shells followed by fibres, EPFB and OPF and trunks respectively. Iraqi date palm, *phoenix – AustaOmran* showed highest lignin content of 36% as determined by Klason lignin method.[389]

Extraction of lignin from palm fruit essentially requires a pretreatment step. This process allows the release of fermentable sugars from the plant polymers and an easy separation of lignin from cellulose in a lignocellulosic biomass. Hydrothermal treatment is generally used to obtain sugars and proved to enhance the enzymatic digestibility of the solid residue.[390-391] Glucose acts as a reserve source for second generation bio-alcohols, methanol, ethanol[392-393] using hot compressed water or ionic liquids,[394] acetic acid and substituted phenols. Thermal cracking mainly produced a solid residue and is not a suitable method for recovering desired chemicals.[128] Palm oil is obtained from palm shell by fluidized-bed fast pyrolysis technique[2, 73] with a maximum liquid product yield of 58 wt % at 500°C. Fast pyrolysis[395] of EFB is good source for renewable chemicals such as phenols, acetic acid, methanol, 2-furaldehyde and ethyl acetate depending upon nature of catalyst in catalytic cracking, pyrolysis temperature, ratio of steam to oil, time factor etc.[396]

Solid support catalysts such as zirconia supporting iron based catalyst (Zr/FeOx, Zr-FeOx or Zr-Al-FeOx)[396-397] and rare earth metal exchanged Y-type (REY) zeolites[398] such as nickel supporting REY zeolites and FeOOH catalyst lead to formation of methanol, acetic acid and phenols, ketones from oil palm shell waste. Unlike thermal cracking or when FeOOH catalyst is used alone, it was found there is generation of solid residue which prevents easy recovery of desired chemicals. Solid supports not only allows easy recovery but also believed to enhance the activity of FeOOH catalyst.

The pyrolyzed palm shell oil contains high percentage of phenol and its derivatives, such as Fig. 12 substituted cresol, pyrocatechol, guaiacol, syringol, eugenol.[2] Solvolysis liquefaction process of EFB in presence of ethylene glycol followed by extraction in acetone showed the presence of phenol, syringol, eugenol, propenyl and propenoic substituted phenols as confirmed by FTIR and analytical pyrolysis GC/MS analysis.[399] Processes such as caustic pulping[400] or use of organic acids[401] (formic and acetic acid) leads to delignification of lignocellulosic biomass. The nature of base in alkaline liquefaction also affects the nature of product. Potassium carbonate favours phenol while sodium hydroxide mainly yields esters.[402] The organic acids act both as solvent and acid in the process. They are attractive due to significant amount of material dissolution at low processing temperature, no requirement for use of mineral acid catalyst and cause depolymerisation of lignin and hemicelluloses. Acidic phenolysis of oil palm EFB in presence of phenol, sulfuric acid as catalyst (8 wt% of phenol) showed 96% liquefaction at 150 °C in 90 min.[128] The reaction follows second order kinetics with an activation energy of 50.7 and 18.1 kJ/mol when the catalyst concentration was 5 and 8%, respectively.

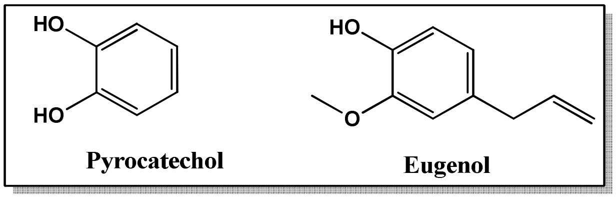


Fig.12 Structures of phenols extracted from palm oil[2]

Organosolv methods give rise to lower molecular weight lignins that are soluble in most organic solvents[403] and the presence of phenolic hydroxyl groups and oxidized groups favour their incorporation into polymer formulations and their chemical modification.[404] Among organosolv pulping methods EFB was subjected to pulping with organic solvents with a high boiling temperature (ethylene glycol, diethylene glycol, ethanolamine and diethanolamine), showing the pulps from amines to have better properties than the ones from glycols.

Delignification of OPF black liquor using Kraft, soda and organosolv pulping process showed the presence of H:G:S ratio as 21:6:51, 30:21:49 and10:23:67 respectively. It was found that OPF lignin obtained by alkaline pulping method (Kraft and soda) gave higher phenolic OH, thermal stability and molecular weight to that of the organosolv method.[405] The presence of G- type unit in OPF lignin structure with a free C5 position, could give highly potential active sites for polymerization process such as in phenol–formaldehyde condensation reactions. While S-type unit (C3 and C5 positions are linked to methoxy group) tends to show a low reactivity toward formaldehyde. Besides, higher amount of phenolic hydroxyl in the OPF lignin structure can activate the free ring positions. Thus, it promotes better non-covalent interactions with formaldehyde to form a stiffer lignin–phenol–formaldehyde (LPF) macromolecules resin.

Palm oil mill effluents (POME) are also found to be good source for water-soluble phenolics which can be separated by simple separation techniques[142] in combination such as centrifugation and membrane filtration technologies.

The advantages of supercritical solvents in liquefaction process are extraction of liquid products from waste at low temperature and faster conversion rates of the order of seconds (at 380°C and 100 MPa for 8 s).[406] Liquefaction of palm waste with Sc-H_2O[407] or sub/supercritical methanol, ethanol, acetone and 1,4-dioxane[408] showed promising results. The treatment of palm oil waste with supercritical solvents showed water-insoluble portion on further fractionation into methanol-insoluble residue was mainly composed of lignin (> 84 wt%) and the phenolic hydroxyl contents.[406-407]

Lignin[409] or substituted phenols obtained from palm waste is structurally characterized by FTIR,[399] ^{1}H-NMR[397] and ^{13}C-NMR spectroscopy, and analytical pyrolysis GC-MS spectrometry.[399] The two dimensional GC-ToF-MS chemical characterization of bio-oils[410] indicated that the major classes of components are ketones, cyclopentenones, furanones, furans, phenols, benzenediols, methoxy- and dimethoxy- phenols and sugars. In addition, esters, aldehydes and pyridines were also found for sample obtained from empty palm fruit bunch. The high quantity of phenol in the bio-oil of EPFB is of interest because phenol isolated from the bio-oil could provide an alternative to the phenol obtained from petroleum.

2.5 Coconut shell tar (CST)

Materials based on the coconut tree form a major renewable resource of the tropical regions of the world. Coconut shells are produced as waste of about 4.2 million tons per year. Destructive distillation of coconut shells give coconut shell char, which is used as filler in plastics and for the development of activated carbon. CST is a byproduct obtained during the distillation process and was considered as a waste so far. The CST is tarry oil, dark brown in colour with a characteristic unpleasant empyreumatic odor. Except for some identification of the components, not much work has been reported so far in the literature.

Distillation of CST[153] was performed at atmospheric pressure unlike CNSL, and fractions were collected at 100 °C (water, 22%), 103-105 °C (crotonaldehyde, 3%), and 118-120 °C (acetic acid, 11%). The residue was treated with 3% sodium hydroxide for 2 h and neutralized with glacial acetic acid. It was dissolved in acetone and filtered to remove free carbon. The filtrate, after the removal of acetone, was used for polymerization. It is reported to contain many monomers, the major one being phenolic in nature (~45%).

Green coconut husk, an abundant agro-industrial residue in Brazil, is a potential source of FA, from which vanillin is produced via microbial fermentation.[401] It was found that coconut husk is a very rich source for 4-hydroxybenzoic acid (13mg/g) on alkaline treatment.[411] Coconut husk has maximum percent of lignin content nearly 33%, (Table 2) among naturally occurring plant material and therefore a valuable source for generation of phenolic compounds. However, its exploration is not much in literature and therefore needs to be researched on.

3. Modifications of Naturally Occurring Phenols

The functionalities present in agro-waste such as lignin, cardanol, tannin, palm oil and CST offer a wide variety of structural modifications to synthesize new bio-based renewable structures. The functionalities varies from phenolic –OH, aromatic ring, aliphatic side chains (saturated or unsaturated bonds), carboxylic, carbonyl groups etc. which could be either used as such or further chemically transformed. These chemicals may then acts as monomers or oligomers or intermediates which could be further explored for a range of polymers. Modifications of such naturally occurring phenolic compounds can be classified into three categories namely reaction due to *(i)* phenolic hydroxyl group *(ii)* aryl group *(iii)* side chains which are described in below section.

3.1 Reaction due to –OH group

The phenolic hydroxyl group can react with different structural modifiers and lead to different molecules via nucleophilic substitution (S_NAr/S_N) or condensation reaction. A generalized scheme for the possible modifications of –OH groups in naturally occurring phenolic compounds is shown in Fig. 13. The structure of monomer can be tailored by using various electrophilic centres with different substitution groups attached, which could be further altered by using additional polymerisable sites to affect the curing process.

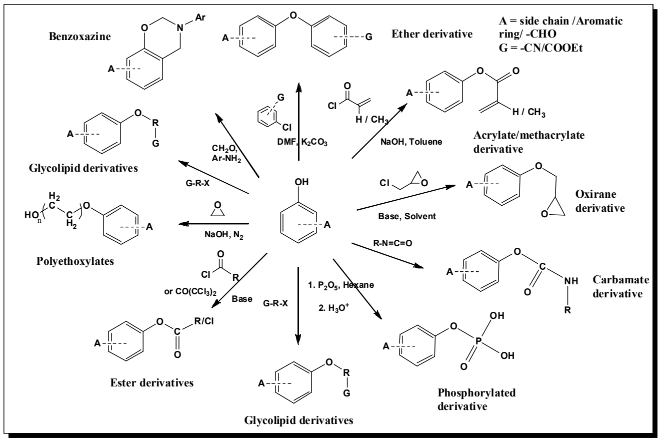


Fig.13 Molecular flexibility provided by hydroxyl group modification

Cardanol or other renewable phenolics is modified to various new chemical structures[42] which find applications as surfactants, glycolipids, and polymers derived from cardanol, and their subsequent self-assembly into functional soft materials such as 4-aminodiphenyl ether,[412] 4-nitro-3′-pentadecyldiphenyl ether,[413] 3,5-dinitro-N-(4-(3-pentadecylphenoxy)phenyl)benzamide,[413] cardanol glycolipids (GlyLip),[414-415] polyethoxylates,[58,416] acrylate/methacrylates,[417-418] epoxide,[419] phosphorylation,[420] chloroformate[421] etc. Cardanol based surfactants showed comparable and better biodegradable properties in comparison with commercially available petro-based nonylphenol polyethoxylates.[58,416] The formation of new synthetic structure, which can be used as such or modified further to, imparts new characteristics to the monomer. Acryloylation,[417,421] epoxidation[419] and phosphorylation[420] of cardanol were also reported as some of synthetic procedures of structural modification. However, cardanol, being less reactive, undergoes epoxidation to a smaller extent than phenol or bisphenol-A. Although cardanol epoxides do not form cross-linked networks due to being mono-functional, they are found to be effective in producing relatively flexible systems when reactive blended with commercial diglycidylether of bisphenol-A (DGEBA). Phosphorylation[420] of phenolic hydroxyl group introduces hetero-atom in the phenolic monomer, which impart flame retardant properties. However, in case of cardanol simultaneous oligomerization is noticed and this could be accounted by a carbonium ion-initiated mechanism of oligomerization of long alkylene side chain due to acidic nature. The phosphorylated monomer is highly reactive with aldehydes, amines, and isocyanates. In addition, the presence of double bond opens up further modification possibilities.

The reactivity of *Sarkanda grass* lignin for epoxidation with epichlorohydrin was found to be comparatively higher than *Wheat straw* and *Protobind 1000* lignin.[422] Lignin hydroxyl groups can be modified to epoxy followed by treatment with diamine leading to amination.[423] Lignin undergoes structural modification on reaction with carboxylic acids, carboxylic acid halides, or anhydrides.[424]

Mannich-like condensation reaction of phenolic –OH group with formaldehyde and an amine[209-210] form new bicyclic heterocycles, benzoxazines (Bz) monomers (Fig. 14). The structure of Bz monomer can be tailored by using various phenols and amines with different substitution groups attached, which could be further altered by using additional polymerisable sites to affect the curing process.

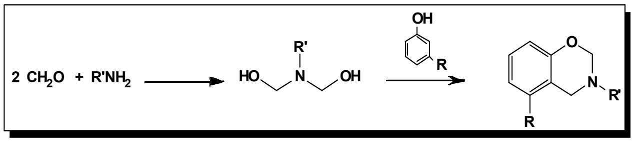


Fig.14 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines

Renewable benzoxazine monomers based on reaction of formaldehyde with phenolic -OH from renewable source such as cardanol, syringol, lignin[427] and ammonia[13] or amine (aniline[428] or diamines[429] and further higher functionality amines[430]) led to a new class of renewable monomers which undergoes Ring Opening Polymerisation (ROP) to form sustainable polymers.

3.2 Reaction due to –aryl group

Electrophilic aromatic substitution reaction modifies the aryl group present in cardanol, lignophenol, tannin, palm oil and CST. A generalized reaction pathway possible for such structural modifications is shown in Fig. 15.

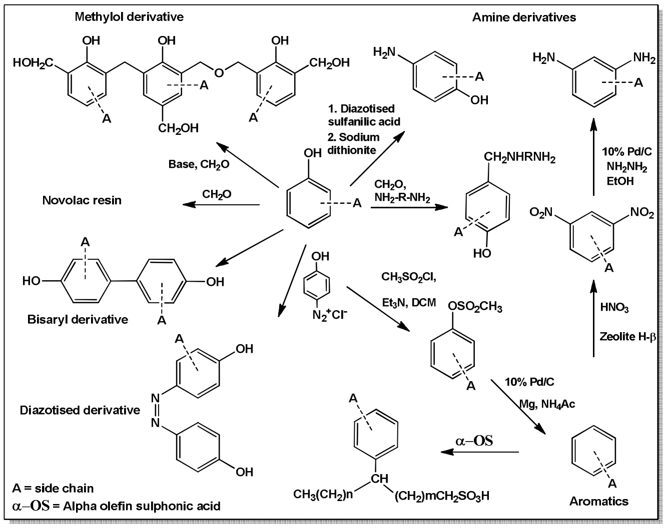


Fig.15 Molecular flexibility due to aromatic ring modification

The main reaction studied for lignophenol,[423,431] cardanol,[420,432] EPFB[433-434] and CST[435] is the condensation of phenolic compound with formaldehyde. This resulted in formation of water soluble methylol derivatives of phenols (resoles) or relatively high molecular mass novolac resins. Modification of lignin prior to resin synthesis has typically been performed by reacting lignin with phenol in the presence of organic solvents such as methanol or ethanol. This process is called phenolysis. Initially, lignin was allowed to react with phenol before performing a condensation reaction with formaldehyde. Lignin was added to a mixture of phenol dissolved in ethanol, such that the lignin/phenol weight ratio was varied and known. Phenolysis of the lignin was carried out at 70°C for a few hours. Organosolv Alcell lignin was also used as a replacement for phenol in PF resins.[436]

Besides Cardanol–Formaldehyde (CF) resins there are several other electrophilic reactions of cardanol were also reported such as diazotization of cardanol with different aromatic amines[437-438] and electrophilic substitution of nitro group in benzene ring.[412,439] Aryl coupling to form bisaryl derivatives lead to different set of monomers due to addition of functionality,[440] from a monophenol to diphenol. Electropolymerisation of vanillin, eugenol to form polyvanillin[441] and polyeugenol[442] is also gaining importance for completely green polymers. Sulphonation of phenols extracted from the pyrolysis oil of palm shells using simultaneous sulphonation alkylation process in presence of alpha-olefin sulphonic acid may find applications as surfactant in oil fields.[28]

3.3 Reaction due to side chain

Depending on the source of phenolic compound (i.e. cardanol, palm oil, lignophenols) the side group may be alkyl (-CH_3, $C_{15}H_{31}$), alkylene (-$C_{15}H_{29}$, -$C_{15}H_{27}$, $C_{15}H_{25}$, -CH=CH-COOH), ether (-OCH_3), aldehyde group, carboxylic group etc. Cardanol double bond may be epoxidised[443] or undergo olefin-metathesis reaction[444] which may act as modified monomer for the formation of different set of polymers. The modification of alkylene side chain by ozonisation[445] has been carried out to introduce alcohol, aldehyde and carboxylic etc. functionalities, Fig. 16.

Ruthenium catalyzed olefin metathesis has been successfully applied to the synthesis of biscardanol derivatives and cardanol-based porphyrins using Grubbs catalyst.[446-447]

Cardanol and its derivatives were used as the precursor for the synthesis of fulleropyrrolidines which could be used in medicinal chemistry, pharmaceuticals and photovoltaic applications.[40]

4. Polymers Derived From Naturally Occurring Phenolic Derivatives

Amongst the various phenolic monomers, cardanol has dual phenolic and alkenyl side chain which makes it an ideal natural raw material for the synthesis of water-resistant resins and polymers. The polymers obtained from the phenolic monomers either crude or modified are shown in Fig. 17.

Besides these general modifications certain specialised naturally occurring phenolic biopolymers are designed to have a different set of specialised properties (as elaborated in miscellaneous section).

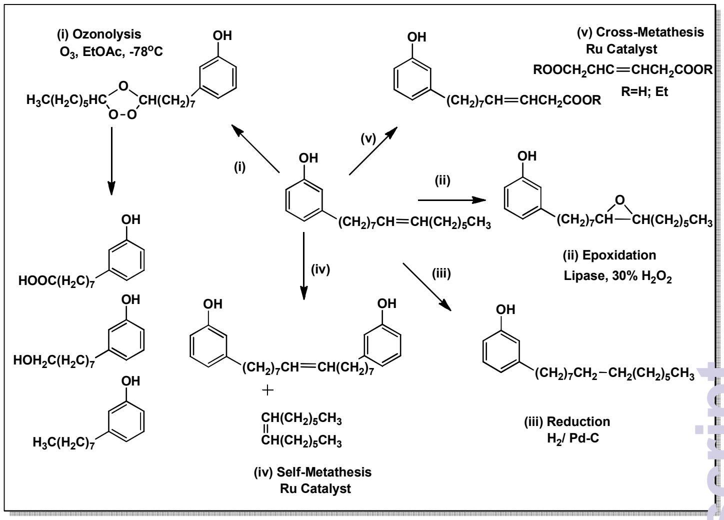


Fig 16: Chemical modification of alkyl/alkylene chain reaction to form intermediates

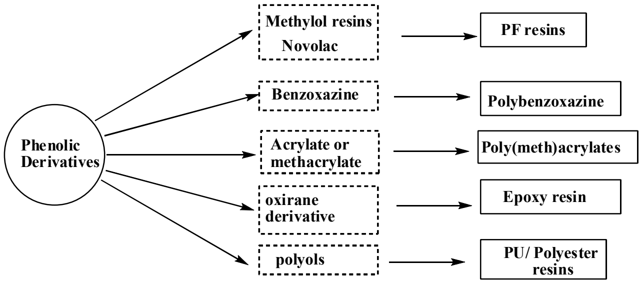


Fig.17 Scheme depicting polymers obtained from naturally occurring phenolic monomers

4.1 Addition Polymers:

4.1.1 Carbocationic polymerisation

Cardanol undergoes polymerisation through the side chain double bonds of alkenyl group either by heat (180 °C) or using cationic initiators such as diethylsulphate:sulphuric acid/ phosphoric acid,[448] $BF_3.OEt_2$[449-450] etc. to form polycardanol, Fig. 18.

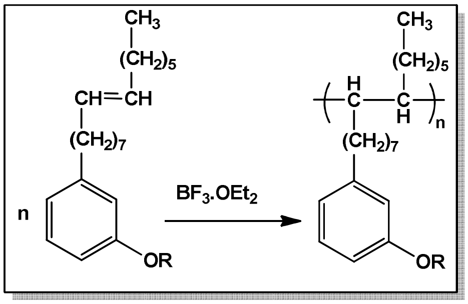


Fig. 18 Carbocationic polymerization of cardanol

The acid assisted oligomerization is a slow process resulted in an average molecular weight (1200 to 11507) increase only by 46% when heated at 140 °C for 40 h. Low molecular weight of polymer could be accounted due to bulky nature of the side chain and presence of 1, 2-disubstitution at the double bond. Steric hindrances may also restrict the molecular weight attainable in oligomerization. The formation of low molecular weight species could also be accounted due to chain transfer to monomer. The presence of double bond in alkylene side chain in cardanol may also yield oligomers via carbocationic polymerization (Fig. 19).[448]

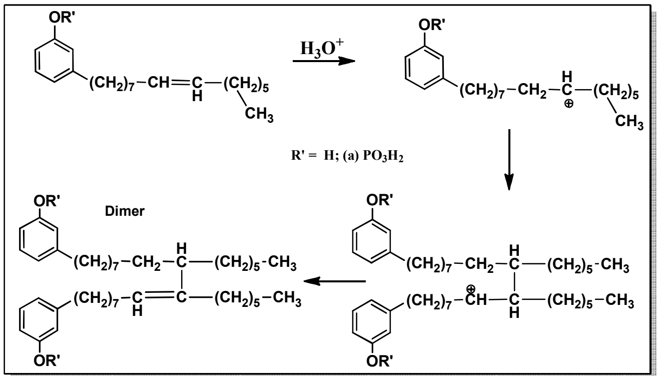


Fig.19 Low molecular weight species generation via carbocationic mechanism

Free radical initiators such as benzoyl peroxide (BPO) or 2, 2′-azobisisobutyronitrile (AIBN) do not initiate polymerization or cross-linking to form polycardanol. The phenolic moiety of cardanol, because of its antioxidant nature, can act as a radical scavenger and prevents polymerisation.

Bulk polymerization[451] of cardanol is facilitated by < 5 wt% of a cationic initiator consisting of a strong acid, a lewis acid and a lewis acid complex and the obtained cardanol polymer has a number average molecular weight of 10,000-100,000. Tyman has reported oligomerization of CNSL through unsaturated side chain during distillation process.[452]

4.1.2 Oxidative polymerisation

Oxidative polymerisation of cardanol both in solution and bulk (r.t. / 80 °C) is catalyzed by metal complexes such as complex of iron with *N,N′*-ethylenebis(salicylideneamine) (Fe-salen) and hydrogen peroxide[453] or enzymes such as *Soybean/fungal peroxidise*[454-456] to give a soluble polymer number average molecular weight $2 \times 10^3 - 6 \times 10^3$ (PDI 2-3) in good yield, Fig. 20.

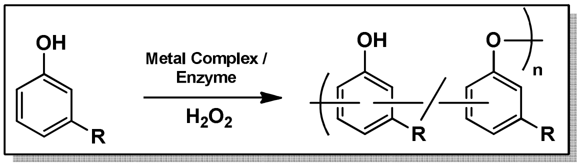


Fig. 20 Oxidative polymerization of cardanol

Phenolic moiety was polymerized and the carbon-carbon unsaturated group in the side chain of cardanol remain unaffected during the polymerization. The polymer was subjected to the hardening by cobalt naphthenate[453] catalyst or thermal treatment or methyl ethyl ketone peroxide to give the cross-linked film (artificial urushi)[457] with high hardness and gloss surface. The alkenyl side chain was modified by epoxidation[456] using *C. antarctica* lipase assisted catalysis in presence of acetic acid and hydrogen peroxide to introduce epoxy functionalities in polycardanol followed by curing with phenalkamine at 150 °C.

Enzyme catalyzed oxidative polymerize phenols lead to formation of polyphenols which are attractive due to their high thermal stability. Beside this advantage, they are considered as an alternative resins to phenol formaldehyde due to absence of toxic formaldehyde. Enzyme catalyzed oxidative polymerization may not be suitable for phenolic monomers with longer alkylene chain due to their low solubility in aqueous polymerizing medium. Fe-salen can be used as an alternative to assist such polymerization.[63]

Peroxidase-catalyzed polymerization of phenols is a popular method to give phenolic polymers, lignocresol, which was prepared by lignin and p-cresol, in methanol–phosphate buffer solution system to give cross-linked polymers.[458-459]

Lignin-based macromonomer such as lignocatechol and lignourushiol undergoes catalytic polymerisation using oxidoreductase laccase. The polymer formed showed high thermal stability due to formation of highly cross-linked network. The polymers had the affinity for bovine serum albumin (BSA) and glucoamylase.[460]

4.1.3 Polycardanylacrylate

A linear organic solvent soluble polymer, poly(cardanyl acrylate) (PCA) was obtained by solution[417] polymerization of the cardanyl acrylate (CA) using free radical initiator (0.8% AIBN/BPO), Fig. 21.

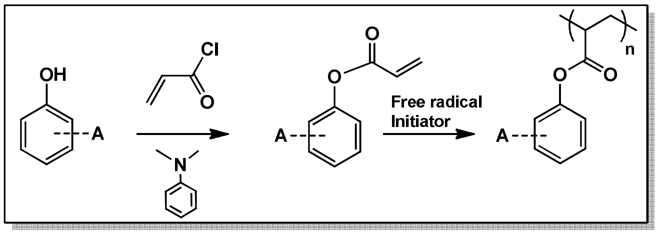


Fig. 21 Polymerization of cardanyl acrylate

PCA undergoes cross-linking on exposure to air (or UV light) on removal of solvent to give an insoluble infusible transparent film. However, in bulk/ and suspension (2 wt% PVA) [461] polymerization of CA, the polymer undergoes in-situ cross-linking in the absence of any cross-linking agent. Copolymer beads of methyl methacrylate (MMA) and styrene with CA were prepared by suspension polymerization using free radical initiators and studied by SEM and optical micrograph images. A copolymer of CA (0.05-0.08 mole fraction) with MMA in bulk at 80 °C using 2% BPO as an initiator resulted in significant improvement in the thermal stability of poly(methyl methacrylate) (PMMA).[462] This was accounted due to the participation of olefinic double bonds of alkyl group in cardanol in copolymerization, thereby making the side chain less flexible and more stable.

Auto-oxidation (cross-linking) of PCA produced various free-radicals which were used as a tool to reduce metal salts to prepare and stabilize the gold and silver nanoparticles *in situ*. This sustainable approach avoided the use of external hazardous reducing and stabilizing agents.[463]

4.2 Condensation Polymerisation

4.2.1 Phenolic resins

Phenolic resins are well known example of commercially exploited condensation polymers formed by electrophilic substitution reaction of the phenolic derivatives and aldehydic compounds. The reaction was initiated with acid and basic catalysts such as NH_4OH, NaOH, oxalic acid, or H_2SO_4. The condensation of phenol and formaldehyde resulted in formation of water soluble methylol derivatives of phenols (resoles) or relatively high molecular mass novolac resins. Phenolic resins prepared from cardanol either alone or in combination with other phenols, and HCHO are known since 1968. Cardanol formaldehyde (CF) resins have the usual characteristics of PF resins but a much better flexibility**.** However, the disadvantages of CF resins as compared to phenolic resins are lower tensile strength and thermal stability.[248] This may be attributed to C-15 side chain which imparts steric hindrance and reduction in intermolecular interactions. An optimum percentage replacement of phenol by cardanol is required, which possibly can achieve some specific properties and overcome some disadvantages of pure phenolic resins. Phenolic resins (resoles) containing cardanol (<15 wt. %) distinctly improved the chemical resistance and mechanical properties (tensile, flexural, and Izod impact strengths) compared to neat PF resin.[465]

The cardanol based resins were found to be more heat and oil reactive than resins obtained from the usual *p*-substituted phenols such as *p*-tert-butylphenol, *p*-tert-amylphenol, and *p*-phenylphenol, possibly due to side chain unsaturation and the trifunctional nature of resin.[466] Varnishes prepared from the cardanol resin compared favourably with similar products derived from other alkyl phenols.

Misra *et al.*[467] reported on the kinetics of the formaldehyde condensation and cardanol by determining the concentration of formaldehyde present in the reaction mixture with time. A theoretical model based on RSM[468] was found to be in good agreement with experimental data, between the process variables and the extent of conversion was established for different types of cardanol-phenol formaldehyde (CPF) (novolac) resins.

Swain *et al.*[469-470] have reported the synthesis, characterization, thermal, ion-exchange, bactericidal and fungicidal properties of the resins based on hydroxyl aromatic compounds, formaldehyde/furfural and substituted aromatic compounds in the presence of acids and bases as catalysts. They found copolymer of cardanol/*p*-hydroxyacetophenone/formaldehyde to be more thermally stable. In analogy to cardanol, furfural is also obtained from renewable resources such as vegetable waste like cane sugar, bagasse, rice hulls, maize cobs, and other such cellulosic waste materials.

Insulating enamel vanish based on poly(vinyl formal) (PVF) modified by CPF resins was found to improve physico-mechanical properties, heat resistance and electrical properties of the insulating enamel varnish for copper wires.[471]

Thermal characterization of the cyanate esters derived from CPF novolac resins and the corresponding cured phenolic-triazine networks indicated a detrimental effect of cardanol on the thermal stability and char residue of the resins.[472] Effect on the structure and properties of CNSL-novolac resins prepared using succinic acid as catalyst has also been reported.

Flame-retardant polymers based on cardanol modified with hetero-atoms such as phosphorus (MCPAF) and bromine (BrMCPAF) followed by polymerization with formaldehyde have been reported (Fig. 22).[420, 432] Thermal stability of MCPAF resin was found to be higher than CF resins above 500°C. Char yields and limited oxygen index (LOI) values of resin based on MCPAF are 21 and 27 while in case of BrMCPAF resins higher values (27 and 49 respectively) were observed.

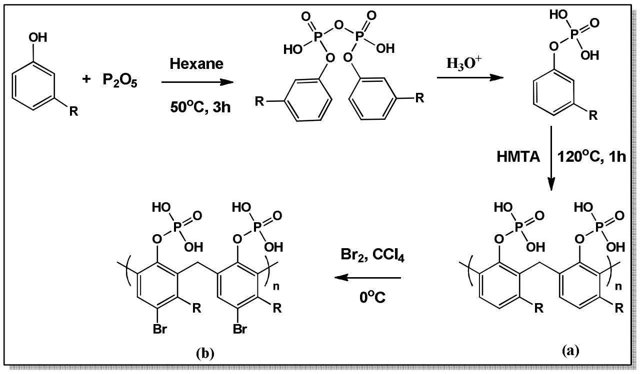


Fig.22 Preparation of *(a)* MCPAF and *(b)* BrMCPAF[204]

Applications of reinforced composite of epoxy modified CF resin (~ 40% of cardanol by weight) using surface treated natural fibres such as short ramie, flax, hemp, and jute with higher renewable content were also explored.[473] Pressure sensing materials have been prepared by *in-situ* blending of CF with polyaniline (PANI) doped with H_2SO_4 and casted into poly(propylene) cups.[474] Condensation of diazotized cardanol with formaldehyde yielded diazotised CF resin.[475] CNSL and cresol based Novolac copolymers showed applications as photoresists for microlithography applications.[476]

Lignin and phenol can undergo hydroxymethylation to form LPF copolymer in the presence of NaOH and excess of formaldehyde.[477-478] DSC scan of LPF resoles showed onset of curing (T_o) at 150–175 °C, which is typical of the conventional phenolic resole resins. A secondary peak at 135–145 °C was observed which could be accounted due to the exothermic reactions between the free formaldehyde with phenol or lignin to form methylol phenols. The replacement ratio of phenol with lignin should be less than 50 wt% due to mainly lower thermal stability of such resins. However properties can be improved by purifying the lignin feedstock before the resin synthesis.[479] The lower values of decomposition temperature obtained for the LPF resin with respect of the PF resin also supports this explanation, since the thermal stability of a resin is increased as the degree of branching and molecular weight of the resin increases.[480]

Lignin based novolac-phenolic prepolymers with 25-45 wt% replacement of phenol from different origin (Kraft pine, soda/anthraquinone flax, and sulfonated SKL) showed lower T_o and gelation time but with a higher volumetric shrinkage than reference PF resin.[475] Ligno-*p*-cresol with the reactive sites on the C1-cresolic and the terminal phenolic units were hydroxymethylated (HM) to give network polymers by heating. On the other hand, ligno-2,4-dimethylphenol, with reactive sites only on the terminal phenolic units, gave linear-type polymers. The polymerisation of lignophenols could be controlled by mixing with HM-ligno-p-cresol and HM-ligno-2,4-dimethylphenol. The recyclable composites[481] with high dimensional stability were prepared by the combination of cellulose and HM-lignophenols (HM-LPs). Under alkaline conditions, the resulting polymers were depolymerised and re-separated effectively to small fragments (lignophenols and cellulose) by the switching function (nucleophilic attack of C1-phenolic nuclei to C2).

Lignophenolic thermoset obtained from lignophenol extracted from sugarcane bagasse have similar izod impact strength as phenolic thermoset.[482] Sisal fiber natural biocomposites based on lignophenolic resin showed good adhesive properties. Phenol extracted from black liquor of oil palm EFB had replaced commercial phenol (1:1) to form LPF resin. In comparison to PF resin, LPF resin showed a higher bonding strength and lower kinematic viscosity over 21 days storage time.[433] Enrichment and polymerization of the phenolic components of CST showed a 2.4 fold higher lap shear strength than PF resin.[435] This showed the possibility of lignin utilisation and successful replacement of 50% petro based phenol for adhesive applications. The reason for good adhesion properties is attributed to the presence of higher hydroxyl to methoxy group ratio[483-484] and lower molecular weight of resin which seeps easily into the pores of binding substrate to from better cross-linked channels. LPF resins which have either high viscosity due to their high molecular weight or lower thermal stability account for not suitable for adhesives for coating wood and the hot-pressed composites which requires both high temperature and longer processing time.[485-486] Laccase modified lignin also showed better adhesion properties than unmodified LPF resin.[487] A 30% replacement of phenol with oxidatively degraded lignosulphonate in phenolic resole based foams showed similar properties as traditional ones.[488]

CTs are more suitable than HTs for use in manufacturing a phenolic-type polymeric matrix, due to the presence of phenolic rings with a larger number of free aromatic positions and activating hydroxyl groups to facilitate electrophilic attack[489] thereby, exhibiting a potential for use in the reaction with formaldehyde.[490] However, tannins are large rigid aromatic structures with restricted rotation around their backbone bonds[491] therefore they require high temperature for curing reactions with formaldehyde. As a result, resins become rapidly immobilized due to the premature gelation, while not being further extended due to the restricted backbone mobility and multiple reaction sites. This leads to brittle materials with less stability and short shelf-life making them unsuitable for industrial applications. This behaviour can be explained on the basis of two steps namely, methylolation and condensation leading to the formation of tannin–formaldehyde resins.[492] The reactivity of tannins can be enhanced by acid hydrolysis which opens up the heterocyclic ring of polyflavonoids, with the formation of a carbocation intermediates.[493] Also, improvement in the performance of a tannin-based adhesive is observed by subjecting tannin extracts to acetic anhydride and subsequent alkaline treatment.[308] Monomeric phenols such as pyrogallol derived from HTs may also acts as a phenol substitute in the PF resin.[494] The requirement of exploring tannins as alternate phenolic feedstock also stems from the fact that formaldehyde based resins despite of their superior bonding properties and low costs are associated with health hazards. Tannins can partially be substituted in industrial PF adhesives, due to their ability in reducing gel time and pressing time.[495-497] Tannins-based rigid foams are also an important class of compounds by the virtue of numerous applications such as floral foams, ion adsorption, packaging, crash protection or insulation material with superior properties like their great thermal and fire resistance, good mechanical resistance under compression, lower cost and ease of preparation along with an important advantage of being sourced from inexpensive and renewable, environment friendly raw materials.[498-499] Recent studies on tannins based foams formulated without formaldehyde and very volatile blowing agents[500] and by addition of small percentage of multiwall carbon nanotubes have focussed on enhancing the environmental relevance and mechanical properties of tannin based foams.[501-502]

4.2.2 Benzoxazines

Benzoxazines (Bz)[425] are a class of phenolic compounds which have better thermal properties and flame retardance than phenolics. They provide huge potential for exploration due to better mechanical performance and molecular design flexibility for advanced composites. They undergo ROP[503-506] accounting for nearly zero shrinkage in cured product, Fig. 23.

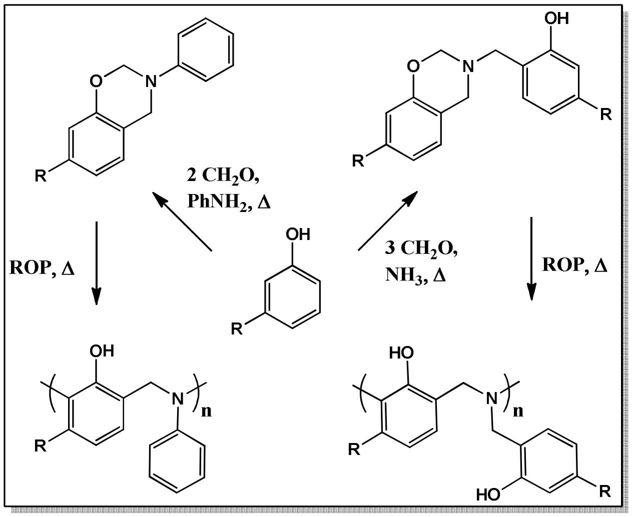


Fig.23 Synthesis of cardanol based benzoxazines and polymers by heat assisted ring-opening polymerisation

The phenolic component is varied from cardanol,[13,429,507-508] cardbisphenol[509] to lignin derived compounds such as guaiacol, FA, coumaric acid, phloretic acid etc. and amines were also varied from petro-based monomers such as monoamine (aniline), diamines [4,4′-diaminodiphenyl methane(DDM), 4,4′-diaminodiphenyl sulphone (DDS)] etc. and higher functionality amines[430] to sustainable amines such as furfurylamine, stearylamine[510] to lower the curing temperature and enhance thermal stability.

Polybenzoxazines based on cardanol were investigated both as resin for making composite[13,428] and as a reactive diluent (a liquid monomer) for the solventless synthesis[428] of higher viscosity monomers. Biobased based Bz monomers showed very high T_o which is lowered either by adding catalysts or curing promoter (methyl *p*-toluenesulfonate)[511] or by incorporating certain monomers having acid functionalities.[512]

Polybenzoxazines based on esters of ferulic, coumaric, and phloretic acids showed superior T_g values than prepared by unsubstituted monofuctional benzoxazine.[513]

Cardanol based polybenzoxazine were explored as composites,[514] coatings,[509] binder and adhesives[515] applications. They showed good mechanical properties, decreased water absorbability, increased resistivity and dielectric strength, decreased dielectric loss and dielectric constant and exhibited high resistance to both corrosion and organic solvents.

Formation of benzoxazine of the hydroxyl groups of condensation polymer of phenol or cardanol with furfural showed T_o as 198 and 225°C and 5% weight loss ($T_{5\%}$) as 432 and 383 °C respectively.[516]

Cardanol is not only used for Bz monomer synthesis, there are other reports where usage of other renewable sources were also utilised for the formation of PBz. Urushiol, natural product, react with monamine, aniline to form benzoxazine which showed a T_o 210 °C and temperatures corresponding to $T_{5\%}$ and $T_{10\%}$ weight loss are 325 °C and 357 °C, respectively.[517] Blends of urushiol benzoxazine based on diamines such as DDM and 3,3′-phenylmethanebis(3,4-dihydro-2*H*-1,3-benzoxazine) have lower curing temperature 180 °C.[518] The lower T_o in latter Bz monomer structure could be due to formation of bis-oxazine over mono-oxazine in former. Another renewable source based Bz monomer of methylester of renewable diphenolic acid (DPA) (MDP-Bz) showed a T_o of 220 °C and T_g of 303°C and $T_{10\%}$ 386 °C.[519]

4.2.3 Epoxy resins

Epoxies derived from vegetable oils have been studied extensively for several interesting properties[520-521] but lack of aromatic structure results in poor thermal and mechanical resistance thereby limiting their industrial applicability. This has paved way for the exploration of bio-based epoxy polymers with a high aromatic density[522] obtained by the epoxidation of natural phenolic compounds such as cardanol, tannins,[523] and other phenols which have either double bond or hydroxyl group which can undergo epoxidation, Fig. 14 and 17.

Epoxide-containing polycardanol (EPCD)[58] was enzymatically synthesized using two different enzymes, viz. lipase and peroxidase. Curing either using phenalkamine or thermal treatment resulted in transparent polymeric films with a high gloss surface and higher pencil scratch hardness as compared with polycardanol.

Bisphenol-A based epoxy resin having 20 mol% of cardanol epoxide cured by a polyamine hardener exhibited reduced tensile, impact and compressive strengths.[524] However, the resin showed considerable improvement in elongation-at-break without much decrease in energy absorption.

An epoxy–cardanol resin developed using epichlorohydrin, bisphenol-A and cardanol and hardened with an aromatic polyamine adduct exhibited better binder media for paints and showed better mechanical and anticorrosive properties as compared to epoxy resin.[419]

Cationic photo-polymerization conversion of epoxidised cardanol (CE) containing 10 wt% CE and 5 wt% hydroxy-functional reactive diluents as a function of relative humidity was determined for thin film materials. CE imparted balanced physiochemical properties to the cationic UV curable materials thereby showing a great potential as a reactive ingredient in cationic UV curable materials.[525]

Blends of epoxy with CF and PF resole resins were prepared and it was found that an increase in energy absorption and elongation at break reach a maximum at 60% cardanol content in cardanol-phenol modifier resin as compared to unmodified epoxy resin.[526]

A nanocomposite obtained by in-situ polymerization of a blend of nanoclay (6 wt%), cardanol-modified-resole (15 wt%), epoxy and polyamide as hardener showed improvement in mechanical properties of the glass-fiber-reinforced epoxy-composite system.[527]

Cardanol epoxidised benzoxazine (CBO) resin displayed a T_g of 76.6 °C whereas the CEO gave a value of 29.5 °C. A maximum T_g of 82.1 °C was observed for a composition of 70–30 where the epoxy content is 70%.[443] Cardanol benzoxazine with two double bonds in alkylene side chain and CEO monomer has T_o 225 and 93 °C respectively, $T_{5\%}$ 347 and 305 °C respectively.

Eugenol epoxy and the bisphenol-A type epoxy have similar reactivity, dynamic mechanical properties and thermal stability.[528] This showed a good possibility of replacement of non-renewable phenol with renewable phenol in polymers.

Lignin epoxidized with epichlorohydrin and cured with 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole showed 70% of the flexural strength of the petroleum-based epoxy resin.[529] Lignin epoxy resins[530-531] were synthesized and characterized. The final properties of resin depend upon the physical, chemical properties of the lignin, which depends upon sources and method of purification therefore leading to different set of thermal, structural and chemical properties.

Catechin based epoxy (GEC) monomer can replace up to 50% of DGEBA usage in epoxy resin formulation resulted in a decrease in swelling percentage suggesting formation of higher cross-linked network. However no effect on T_g was observed with 50% replacement.[532] Glycidylation of green tea extract, catechin with epichlorohydrin yield epoxy pre-polymers, Fig. 24. Further cross-linking with isophorone diamine (IPD) results in formation of aromatic biobased cross-linked polymer which exhibited a 3-5 fold higher cross-link density and a higher char yield than commercial epoxy, DER352.[533]

Allylation of gallic acid followed by epoxidation yieded a tetra-epoxy monomer which also showed comparable curing charateristics as DGEBA with IPD.[534] Epoxy thermosets based on gallic acid and gallotannins have also been synthesised.[535]

4.2.4 Polyester

Polyester obtained by reaction of diazotised cardanol and *p*-aminobenzoic acid showed liquid crystalline behavior.[536] Similarly, a copolymer based on oxidized cardanol i.e. 8-(3-hydroxyphenyl) octanoic acid and *p*-hydroxybenzoic acid showed a thermotropic liquid-crystalline behaviour.

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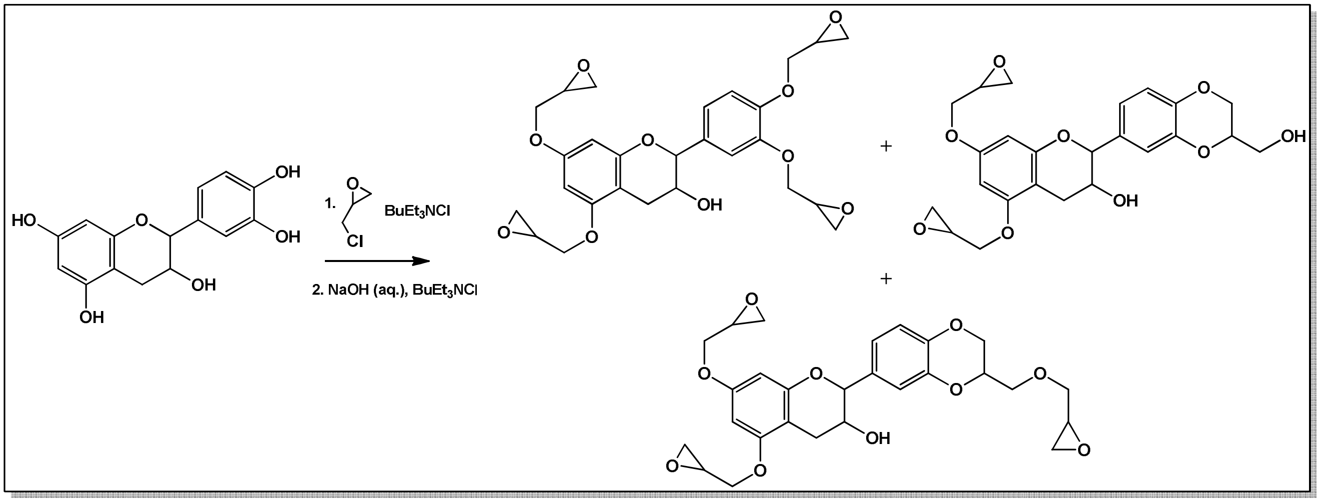

Fig. 24 Epoxidation of catechin to form epoxy monomers

A copolyester was synthesized by solution polycondensation of terephthaloyl chloride with 4-[(4-hydroxy-2-pentadecenylphenyl)diazenyl] phenol (HPPDP) and 1,4-butane diol.[537] Polymer showed short range crystallinity as indicated by melting temperatures (63 and 127 °C) in DSC scan but no crystallinity was observed by wide-angle X-ray diffraction (WAXS).

Lignins can undergo polyesterification reaction when they have a sufficient and an appropriate number of hydroxyl groups present as observed in the case of wheat lignins.[538] Biodegradable polyester (Biopol D 400P) films containing plasticizers (5-10%) and hydroxyl group protected lignophenol exhibited tensile strengths better than those of Biopol films without the plasticizer.[539] Lignophenols or their carboxymethylated derivatives are chemically modified with polyalkylene glycol diglycidyl ether to form a cross-linked hydrogel network[540] which showed nearly tens to thousand times higher water absorption as compared to their dried weights.

4.2.5 Polyurethane

Polyurethanes have been synthesized using hydroxyalkylated CF resins/ commercial polyol (PPG-2000) and diphenylmethane diisocyanate (MDI). Polyurethane prepared using a higher mole ratio of cardanol/formaldehyde of hydroxyalkylated CF resin is found to possess better thermal and mechanical properties than the polyurethane prepared from a lower mole ratio.[541]

Polyurethane based on high-ortho novolac CF polyol resin and polypropylene glycol-2000 (PPG-2000) condensed with MDI showed lower tensile and tear strength. This could be due to low molecular weight between the cross-links and higher cross-link density. However a 75% increase in elongation at break was observed due to the flexibility of the chain introduced by the polyol.[542]

Polyurethanes based on HPPDP was prepared by the treatment with MDI in N,N′-dimethylformamide as solvent at 80-90 °C, Fig. 25. The HPPDP was obtained from diazotized cardanol and a polyether prepared by condensing cardanol with epichlorohydrin and polymerizing through ROP.[438] WAXS study of PU showed a broad amorphous halo indicative of absence of crystallinity in the polymer, which has been explained as due to strong hydrogen bonding in the hard phase. This suggests sustainable PU can be explored for nonlinear optical applications.[437]

Double bonds present in side chain of cardanol in cardanol-glycols-based polyurethane (CGPU) films[543] were cross-linked on treatment with cobalt octoate due to autooxidation-polymerisation mechanism. The increase of molecular weight of glycols leads to a decrease of cardanol content in CGPUs and hence decreases cross-linking density of the films, which strongly affects T_g and swelling behaviour. A Co^{+2} catalysed and unanalysed CGPU film showed a T_g 15-40 °C and -30 to 15 °C respectively.

PU prepared by reaction of cardanol polyols (diol and triols), Fig. 26, with MDI at an NCO/OH (1/1) using dibutyltin dilaurate as catalyst showed a linear increase in T_g with an increase in the hydroxyl value of the polyol and higher thermal stability in comparison to the PPG-based polyurethanes.[544]

Solvent induced self-assembly was observed in cardanol-urethane methacrylate comb polymers based on isophorone diisocyanate (IPDI) exhibited three-dimensional honeycomb morphology in chloroform, whereas in tetrahydrofuran, they formed spheres and tubes.[545]

Polyurethane based on reaction of prepolymer based on demethylated lignin with toluene-2,4-diisocyanate (TDI) and polyethylene glycol has led to 6.5 fold increase in modulus.[546] Electro-spun kraft lignin materials showed moisture responsive reversible shape change behaviour and this is attributed to both

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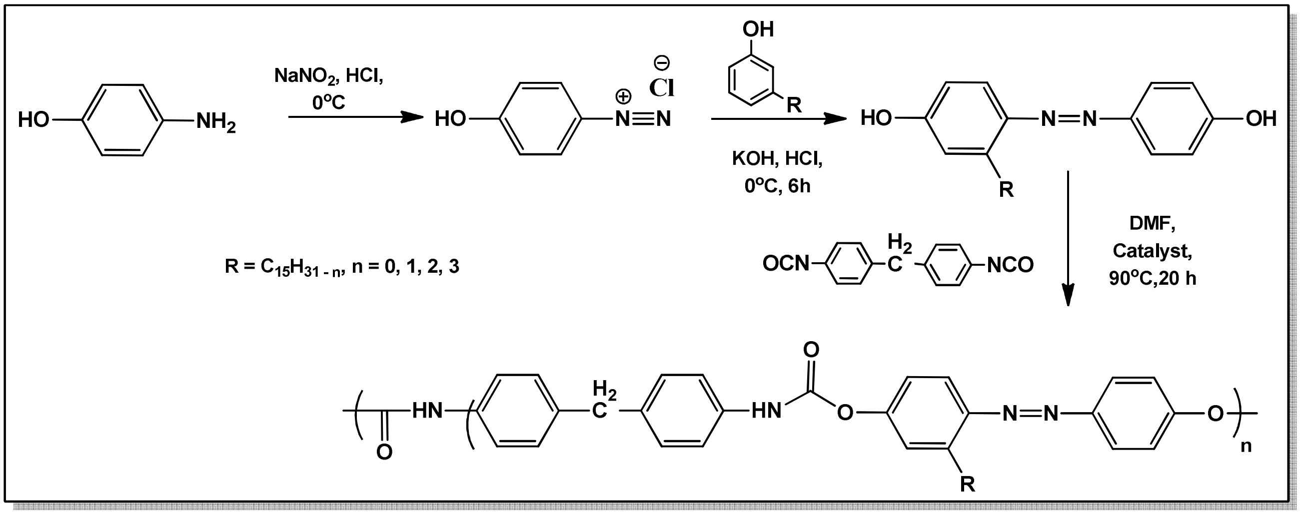

Fig. 25 PU resin based on diazotized cardanol

the chemical structure and physical properties of lignin fractions.[547] PUF based on sodium ligninosulphonate and ethylene glycols/ diethylene glycol/ triethylene glycol/polyethylene glycol were synthesized. The T_g was found to be in the range of 37 to 117 °C and is dependent upon the mixing rate and molecular mass of glycols.[548] The hydroxyl goups of lignin can be utilized to replace petroleum-based polyol in PU.[549-552]It was observed 25-30% w/w replacement of polyol with hardwood ethanol organosolv lignin (HEL) or 19-23% w/w HKL can lead to similar properties as a polyol based PU foam.[553-554]

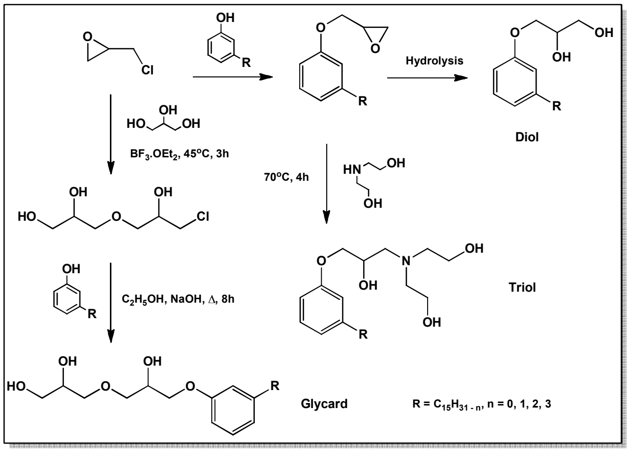

Fig. 26: Preparation of cardanol polyols[544]

4.3 IPNs

Semi-interpenetrating polymer networks (Semi-IPNs) were reported in literature of phenolic resins mainly with vinylic polymers such as PMMA[555] and polyurethanes.[556-559] CF-PMMA showed an unusual increase in T_g of CF from 128-144 °C suggesting thereby restrictions in the segmental motion of the CF phase obtained by mixing with another rigid polymer such as PMMA.[555]

Semi-IPNs have also been prepared from castor-oil-based polyurethane with acetylated and phosphorylated cardanol derivatives.[556] CF-substituted aromatic compounds copolymerized resins with castor oil polyurethanes semi-IPNs using ethylene glycol dimethacrylate (EGDM) as a cross-linker showed a higher thermal stability.[557] The wide angle X-ray diffraction analysis of semi-IPNs prepared by condensing CF novolac resins and PUs prepared from castor oil and diisocyanates of varying NCO/OH ratio has also been investigated.[558]

Semi-IPNs were synthesized by reacting castor oil based polyurethanes and a cardanol and furfural based phenolic resin. The semi-IPN containing 75% cardanol-furfural resin was stable up to very high temperatures, due to formation of highly cross-linked network. The degradation mechanism of these semi-IPNs was suggested based on the kinetic parameters evaluated from computer simulations of TGA data.[559]

4.4 Rubber

Rubber can be physically or chemically modified with phenols obtained from renewable resources. CNSL has been used as an additive that improves the moisture resistance of the rubber to explore its usage for electrical insulation. The phosphorylated derivative of cardanol (Anorin-38)[560-571] is found to behave as a multifunctional additive when physically/chemically added to rubber during compounding. However, physical blending of cardanol or its derivatives usually associated with incompatibility of the additive onto the rubber resulting in poor and complex mixing, handling problems, time consuming and cost extensive, leaching problems during storage and use. In order to improve the compatibility, natural and synthetic rubber was chemically grafted[572] with cardanol, Fig. 27 or its phosphorylated derivative in both solid state/solution, in the presence of free radical initiator. Importantly, such rubber variant have high plasticity (57-59) lower Mooney and melt viscosities or viscosity (35-43), better cure properties as compared to conventional virgin or plasticized natural rubber (NR). Moreover, upon vulcanization the above grafted rubber is found to have superior tensile properties, better ageing resistance and higher flame retardancy.

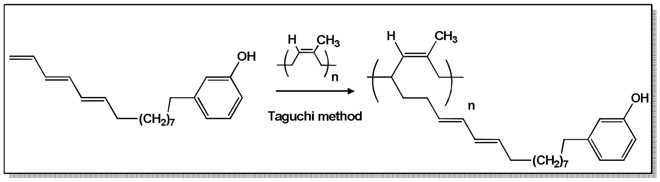

Fig. 27 Chemically grafting of natural rubber with cardanol triene

CF and cardanol glycidyl ether (CGE) have been synthesized for reinforcing NR, a blend of NR and styrene-butadiene rubber (SBR), and nitrile-butadiene rubber (NBR).[573] In comparison to novolac CF resin, resolic CF acts both as a reinforcing agent and a cross-linking agent for NBR due to reaction of the methylol groups of CF with the nitrile group of NBR.

Adhesive properties of blends of PF/CF copolymer resin with polychloroprene rubber was studied using different substrates. A 80:20 phenol:cardanol ratio was found to be optimum for shear strength of aluminum-aluminum bonds, while a 60:40 ratio is the best for peel properties.[574]For SBR-SBR and SBR-Al bonds, a 60:40 ratio is optimum for both peel as well as shear strength. The copolymer based on phenol, cardanol and formaldehyde is a better choice for the resin than either of the individual condensation products of phenol or cardanol with formaldehyde. The addition of 3-aminopropyltriethoxysilane[575] to the adhesive formulation improves the bond strength of metal-to-metal specimens.

4.5 Miscellaneous

Several other renewable source phenolic monomers derived from agro waste have come up in recent past showing a variety of applications with promising commercial viability.

Vanillin based polymers such as vinyl ester resins,[418] vanillin-chitosan hybrid,[576-578] neat-[440,579]or chitosan–vanillin Schiff-base biopolymers[580]may find applications in metal ion removal. Polymers formed by methacrylation of hydroxyl functionality or to a carbonate ester[421] have been explored for molecular imprinting applications. Poly(dihydroferulic acid) may act as a substitute to polyethylene terephthalate (PET) formed by reaction of vanillin and acetic anhydride which then subjected to the Perkin reaction followed by hydrogenation to afford acetyldihydroferulic acid, Fig. 28.[581]

Lignin undergoes esterification to produce thermoplastic with flexural properties comparable to common plastics such as polypropylene and polyethyleneterephthlate.[582-583]A cross-linked polymer network based on lignin and a highly branched poly(ester-amine) obtained by melt polycondensation of 1,1,1-triethanolamine and adipic acid showed similar tensile strength, flexibility and elongation at break as commercial polymers.[584]

ATRP and click chemistry have been used to develop lignin-based hybrid copolymers with lignin centre and poly (*n*-butyl acrylate) or polystyrene grafts using "graft from" and "graft onto" methods. While in the former method ATRP was employed to polymerize vinyl monomers from a lignin based macroinitiator, backbone lignin was linked to polystyrene graft via click chemistry in the case of latter. Hence, obtained lignin-based graft copolymers are expected to show high flexibility in processing as a thermoplastic polymer.[585]

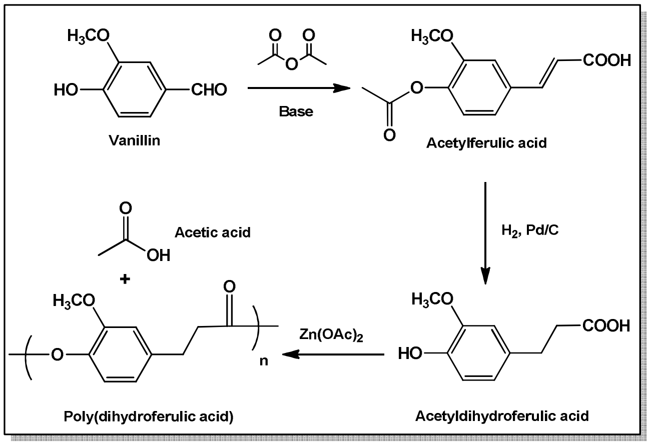

Fig. 28 Synthesis of biorenewable polyester from vanillin and acetic anhydride[581]

Lignin-*g*-polyNIPAM (*N*-isopropylacrylamide) copolymers prepared via atom transfer radical polymerization (ATRP) showed a thermoresponsive and ionic responsive.[586]The graft copolymer showed a LCST (lower critical solution temperature) at 32°C, Fig. 29.[587] Lignin-containing poly(BMA) graft copolymers formed by reaction of acryloyl modified lignin-based macromonomer with butyl methacrylate (BMA) showed higher thermal stability and also increased the glass-transition temperature of poly(BMA) due to presence of bulky aromatic group of lignin.[588] Grafting polymerization of lactide onto lignin utilizes more of aliphatic than phenolic hydroxyl groups. These polymers besides being green also showed the possibility of usage as dispersion modifiers in PLA based materials.[589]

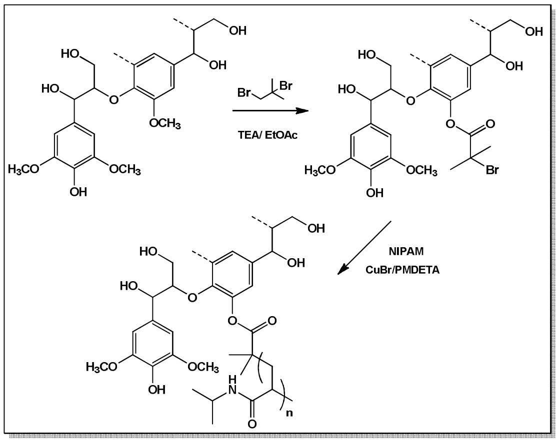

Fig. 30 Synthesis of Lignin-g-polyNIPAM copolymers

Vinyl acetate (VAc) have also been grafted on lignin using potassium persulfate as an initiator and ammonium iron (II) sulphate as a catalyst in aqueous reaction medium paving way for value-added greener products.[590]

Studies carried out to understand the influence of lignin on the grafting mechanism of lignosulphonate with acrylic acid (AA) indicate the dependence of product yield, monomer conversion and grafting efficiency on phenolic group's content.[591]

The graft copolymerization of eucalyptus lignosulphonate calcium from hardwood and AA using Fenton agent as a co-initiator also confirmed the involvement of phenolic group in the grafting reaction as an active centre.[592]

Acetone-fractionated SKL with protected phenolic hydroxyl groups have been utilised for the synthesis of poly(arylene ether) sulphones, demonstrating the use of technical kraft lignin as a phenolic precursor for the creation of heat stable thermoplastic materials.[593]Lignin exhibits strong ultraviolet (UV) absorbing properties which were explored by the copolymerization of acryloyl chloride modified biobutanol lignin with n-butyl acrylate and MMA by free-radical polymerization to yield potential UV-absorbent films.[594] Utility of lignin as a biomaterial gets hampered due to its non-uniform structure and low thermal stability. Application of low dosage of γ-irradiation has come up as a promising technique to modify its thermal properties and to attach requisite functional groups onto lignin.[595]

The graft copolymerization of lignin and 1-ethenylbenzene co-initiated by lignin, calcium chloride, and hydrogen peroxide in dimethyl sulphoxide solution lead to a change in the surface properties of lignin from hydrophilic to hydrophobic. Thermoplastic material hence obtained showed biodegradability where rate of degradation was found to increase with an increase in lignin content of copolymer sample.[596]

Star-shaped polymers (SPCs) containing PEG with cardanol side groups synthesized by ATRP undergo self-cross-linking reaction between unsaturated hydrocarbon chains of cardanol moieties upon UV irradiation imparting water-insoluble properties to SPC thereby exhibiting antifoulant applications.[597] Cardanol has also been used to prepare trithiocarbonate RAFT agent and a reactive anionic surfactant, which were combined to prepare a cardanol-PMMA polymer resulting in high stability latex.[598]

5. Properties of Polymers Derived from Naturally Occurring Phenolic Derivatives

5.1 Thermal stability

CNSL showed a higher thermal stability when heated for a longer duration at 140 °C due to thermal oligomerisation.[599]

The thermal stability of CF resins is lower than the PF resins due to the presence of *m*-alkylene side chains. The poorer thermal stability of the CPF and CF resins cannot be explained only by the low temperature stability of the alkyl group of cardanol but also by the negative influence of the long alkyl chain (because of its steric effect) on the cross-linking of the resins. Therefore, the addition of CF resins to the PF resins results in a decrease in thermal stability of the blends. A cardanol content within 15 wt% in CPF resins does not seriously affect the thermostability of the resin blend at temperatures below 400°C, which is of most practical importance.[465]

The thermal stability of CF resin is found to be less than cardanol-furfural-hydroxy compound based resin and can be explained on the basis that the furfural moiety in the resin backbone imparts a higher stability than the methylene bridge present in CF resin.[469]

CF resin containing boron-nitrogen co-ordinate bond (CFBN) has higher thermal stability than CF resin. The temperature of maximum rate of weight loss was 394 °C in CF resins but it increased to 437 °C in CFBN.[600]

Our group has studied thermal behaviour of benzoxazine monomer blends based on cardanol (Bz-c), bisphenol-A (Bz-A), and *p*-hydroxybenzoic acid (Bz-pA). The curing characteristics[onset of curing (T_o), peak curing temperature (T_p) and heat of curing (ΔH)] and thermal properties [$T_{5\%}$, $T_{10\%}$ and Char yield (Y_c)]of monomer blends Bz-C:Bz-A with and without Bz-pA was studied by DSC analysis (Table 3). The T_o of Bz-C reduced from 242 to 211°C by addition of Bz-A (1:3 ratio). Addition of Bz-pA further reduced the onset temperature of curing. The catalytic effect of carboxyl acid in opening of benzoxazine ring is well documented in the literature.[601-602] Incorporation of Bz-pA however, lowers the thermal stability of the tri-copolymer due to decarboxylation of carboxylic group. Neat cardanol based polymer (PBz-C) and copolymers were found to be more thermally stable and flexible than neat bisphenol-A based benzoxazine polymer (PBz-A). This behaviour is different from CF resins, where incorporation of cardanol resulted in lowering of thermal stability of the resin.

Tannin based foams also exhibit physical properties which are at par with the existing commercial phenolic foams. Of note is their property of fire resistance which is even higher than that of other phenolic foams, as the latter have ignition time of around 2 min when submitted to a heat flux as high as 50 kW m^{-2}. The released heat, 12 kW m^{-2}, is much lower than what was required for burning them under the same radiant energy. Therefore, tannin foams slowly consume without flame if the heat flux is maintained and spontaneously self-extinguish as soon as the heat source is removed.[604]

5.2 Chemical resistance

Chemical resistance of the samples was determined after immersing the cured PF/CF samples in standard reagents such as water, acid, alkali, organic solvent for 7 days. Phenolic resole resins based on phenol and cardanol (<15%) showed higher chemical resistance than the PF resins.[465] In general a 20wt% of phenol replacement by cardanol in CPF resins showed no weight loss indicating sample were well cured. It was also found that with increase in cardanol content in the resin, a reduction of the weight gain in aqueous solvents took place. This is largely due to the fact that the cardanol molecule contains a long alkyl group which is hydrophobic in nature. However in acetone, weight gain is more in CF and accounted by lower cross-linking because of steric reasons of long alkyl chain and hence favours the higher reagent absorption.

Anticorrosive properties of epoxy–cardanol resin based paints are superior to that of the paints formulated with the unmodified epoxy resin.[419]

Table 3 Results of DSC analysis of blends of benzoxazine monomers (Bz-C, Bz-A and Bz-pA, static air, heating rate 10°C min^{-1})

Designation	**T_o (^{o}C)**	**T_p (^{o}C)**	**ΔH (J/g)**	**$T_{5\%}$ (^{o}C)**	**$T_{10\%}$ (^{o}C)**	**Char Yield/ % at 800 °C**
Bz-C	242	263	71	398	430,467	12
Bz-C:Bz-A (3:1)	235	255	74	394	430,465	14
Bz-C:Bz-A:Bz-pA (3:1:0.1)	201	235	129	346	421	10
Bz-C:Bz-A (1:1)	233	250	114	379	430,456	17
Bz-C:Bz-A:Bz-pA (1:1:0.1)	174	216	157	258	346	15
Bz-C:Bz-A (1:3)	211	231	223	377	447	20
Bz-C:Bz-A:Bz-pA (1:3:0.15)	436	483	200	277	343	26
Bz-C:Bz-A:Bz-pA (1:5.67:0.57)	161	209	190	288	339	29
Bz-A	187	219	64.8	274	310.450	39

5.3 Mechanical properties

It was found that with the increase in cardanol content in PF resin from 0-15wt%, an increase of the flexural, tensile and Izod impact strength and a decrease in tensile modulus was observed. The alkyl group of cardanol plays the role of an intramolecular plasticizer and, hence, the resins become more flexible and more elastic. The lower tensile strength of CF resins compared to PF resins may be understood on the basis of the structure of the C-15 side chain imparting steric hindrance and reduction in intermolecular interactions. Neat CF resin has low tensile strength, modulus and high flexural strength. However, there is no effect on compressive strength with increase in cardanol content was observed. A cardanol/phenol, 15/85wt./wt. was found to have a good chemical resistance as well as mechanical properties, whereas the thermal stability up to 250°C still remains on the level of a phenolic resin and suitable for commercial use.[249] Interpenetration of CF with PMMA increased the mechanical properties only marginally.[558]

A replacement of phenol by lignin (40% wt./wt.) extracted from sugarcane bagasse by the organosolv process, was used as a partial substitute in the preparation of resole type lignophenolic matrixes. A reinforced carbon material obtained by a controlled pyrolysis of lignophenolic matrix/sugarcane bagasse showed a flexural strength as high as 21 MPa and flexural modulus in the range of 11-13 GPa.[605]Also short bagasse fibers composites with resole phenolic matrixes prepared by partial substitution for phenol (40 w/w) with lignin were reported.[606]An improvement in the impact strength was observed by use of sugarcane bagasse. The inner part of the fractured samples was analyzed by SEM, and the results indicated adhesion between fibers and matrix, because the fibers are not set free, suggesting they suffered a break during the impact test. The results as a whole showed that it is feasible to replace some phenol by lignin in phenolic matrices without the loss of mechanical properties.

Phenolic closed cells foams based on neat phenolic and partial substitute of phenol with lignin showed similar thermal conductivity analyses while mechanical properties showed that the partial replacement of phenol by lignin was extremely advantageous, because, it increases the compression strength and inserted the lignophenolic foam in the structural foam class.[141]

Plywood samples glued with the Organosolv LPF and Degraded Organosolv LPF adhesives with a phenol replacement ratio up to 75 wt% showed higher dry and wet tensile strengths than those of PF adhesives.[180,607] The reason may be because of the higher phenolic content organosolv and degraded lignin.

Phenol substituted with 50 wt. % lignin showed comparable adhesive strength.[608-609]The tensile strengths of the dry plywood samples bonded with the bio-oil PF resole resin adhesives were comparable to that of the conventional pure PF resin adhesive.[610]Resin formulation of conventional PF when substituted with 30% of bagasse lignin PF as wood adhesive gave tensile strength of 1.2 and 1.8MPa respectively.[611]

5.4 Conductivity

Conductive composites based on LPs and PANI (emeraldine salts) showed conductivities in the range of 4.6×10^{-6} - 1.0×10^{-7} S/cm which is sufficient for removal of static electricity and also enables resistance against rust.[612] A dependence of nature of wood from where LPs are extracted and grafted and nature of monophenol dictates the conductivity values.

Composites of lignin-based polymers and their derivatives were also used as photosensitizers for nano-porous TiO_2 electrodes.[613]This is probably due to higher absorbance of lignophenol/TiO_2 electrodes in the region of λ = 400-600 nm leading to η of 0.48% under 100.3 mW/cm^{-2} of visible light irradiation. The dye-sensitized solar cells using porous $TiO_2$with lignophenols have showed a stable and higher light-electricity conversions, η = 3.3%. The photo-electricity conversions would be caused by both complexation of phenolic hydroxyl groups with Ti^{4+} and stacking of 1,1-bis(aryl)propane units of LPs onto the higher surface area provided by porous titanium dioxide nanoparticles.

5.5 Biodegradability

The main attraction for replacement of petro-based phenol with bio-based phenols such as cardanol, lignin, and the lignin derived lower molecular weight phenols into the polymers is to explore the possibility of bio-degradation of polymers upon completion of their usage. It was found that degradation of lignin-based polymers namely lignocatechol and lignocresol occurred in presence of peroxidise and laccase enzymes. Although the degree of degradation was found to be lower in case of *Rhus vernicifera laccase* compared to *peroxidase*, which might be because of the low activity of *laccase* on the lignin moieties in lignophenols.[614] White rot fungi was found to degrade styrene graft lignin copolymers samples and rate of degradation was found to increase with increase in lignin content.[615]

Distilled CNSL has been shown to be biodegradable when tested using OECD Method 301D (96% degradation after 28 days) in a GLP study.[616]

Tannic acid (TA) or tannin is a biocompatible and biodegradable polyphenol due to the presence of a glucose core linked with phenolic moieties. A biodegradable miscible blend of poly(butylene adipate-*co*-butylene terephthalate)[P(BA-*co*-BT)][617-618] or poly(ε-caprolactone) (PCL) with TA was prepared. The blends acid showed miscibility due to hydrogen bonding between phenolic hydroxyl in latter with carbonyl groups of the polymer.PCL and TA were found to be miscible as indicated by the single T_g and depression of equilibrium melting point of PCL in the blends.[619]

6. Conclusions & Future Challenges

In the past decade, naturally occurring phenolic derivatives have come up as an attractive precursor for developing new materials from renewable bio-sources for use in eco-friendly processes. Resins have been prepared utilising either the whole liquid product, or a phenolics enriched fraction obtained after fractional condensation or further processing, such as solvent extraction or use of greener extraction methods.

However, till date none of the phenolics production and fractionation techniques have been utilized to allow substitution of 100% of the phenol content of the resin without impacting its effectiveness compared to commercial formulations based on petroleum derived phenol. The variable nature of percentage of phenolic compounds in terms of purity from different batches of crops from one season to other, geographical influence does not allow the reproducibility of phenolic compound and hence the polymer. Therefore, the direction that needs to be explored is to be oriented towards complete replacement of petro-based phenolics with bio-based ones in the face of urgent petroleum crisis. In addition, there is a necessity of materials showing enhanced applicability and improved performance. It is a beginning of the era of such a step which requires further exploration of natural phenolic sources aimed at their enhanced utilization.

Notes and references

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Abstract

Exploration of sustainable alternative to chemicals derived from petro-based industries is the current challenge for maintaining the balance between needs of changing world while preserving the nature. The major source for sustainable chemicals is either the natural existing plant sources or waste generated from agro-based industries. The utility of such resources will supplement new processed materials with different sets of properties, and environmental friendliness due to their biodegradability and low toxicity during preparation, usage and discard. Amongst other day to day use polymers, phenolic resins account for vast usage. Replacement of petro-based monomers such as phenol and its derivatives either partly or completely utilized for the synthesis of such resins is ongoing. Extraction of naturally phenolic components from cashew nut shell liquid (CNSL), lignin, tannin, palm oil, coconut shell tar (CST) or from agricultural and industrial waste, their utilization as a synthon for the preparation of a bio-based polymers and properties obtained is reviewed in this paper. This review article is designed to acknowledge efforts of researchers towards 3C motto - not only trying to Create but also adapting the principles to Conserve, and Care for a sustainable environment. This review paper describes how extraction, separation and recovery of desired phenolic compounds occur recently? How substituted phenol compounds unmodified/modified act as monomer for polymerization? How the presences of sustainable phenolic material affect properties of polymer? There are about 600 references cited and still there is lot to unfold in this research area.