Derivatives and Applications of Lignin – An Insight

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Abstract

Lignin, a component of plants, has great potential for its conversion into value-added products that could significantly improve the economics of a biorefinery. The derivatives from lignin assume importance towards an effective & efficient utilization of biomass. It is a non-toxic and renewable raw material contributing ~30% of the weight and ~40% of the energy content of lignocellulosic biomass. Due to complex nature of lignin, this highly abundant biomass product is undervalued and it is mainly used as boiler fuel for paper & pulp industry. The increasing fuel prices with changing fuel specifications are some of the key drivers, which lead to development of new technologies. The polymeric lignin can be converted into low molecular weight and monomeric aromatic forms, that serve as the building block for chemical syntheses of high-value products. This paper covers in detail the utilization of lignin to derive value-added products, their applications and business opportunities. It also contains various other applications for lignin, their production and current market potential.

Keywords: Lignocellulosic biomass, lignin, monolignols, lignosulfonates, aromatic, biopolymer, biorefinery

Introduction

Biomass including forest, agricultural waste, crop residues, yard clippings, wood chips and municipal solid waste etc. remains the largest renewable energy sources. Biomass derived from plant materials comprises of carbohydrate polymers, cellulose, hemicellulose and an aromatic polymer called lignin. It contains different sugar monomers tightly bound to lignin. While cellulose & hemicelluloses are of carbohydrate category, the lignin fraction is a non-sugar molecule. Biomass consists of cellulose (40 to 43%), hemicelluloses (28 to 35%) and lignin (22 to 29%) depending on type of lignocellulosic material. Cellulose, a polysaccharide, is the most abundant organic polymer on earth. It consists of a linear chain of several hundred to over ten thousand β (1→4) linked D-glucose units. Hemicelluloses are polysaccharides containing various monosaccharide subunits. They can be extracted with different concentrations of alkali, acid and other chemicals (Xu N. et al., May 2012). Lignocellulosic materials consist of ~30% lignin by weight and 40% by energy (Perlack R D., Stokes B J. et al., 2005 & Beauchet R. et al., 2012).

Lignin, derived from the Latin term lignum meaning wood, is an integral part of the secondary cell walls of plants. With its cross-linked macromolecules (molecular masses > 10,000 u), lignin fills the gap in the cell walls among cellulose, hemicelluloses and pectin components imparting mechanical strength to the cell wall. Wood containing high amount of lignin can be used as an excellent raw material with good durability. Lignin, used as fuel yields more energy when burnt compared to cellulose. It is estimated that 50 MMT of lignin is produced annually from pulp and paper industries worldwide. This is mostly used by the paper mills to produce waste heat and/or electricity. Lignin has the combustion heat of 26.6 KJ/g, and has high energy content among all natural polymeric compounds. As lignin is derived from biomass combustion it results in zero net carbon dioxide release (Dr. Qin C., 2009).

Chemistry of Lignin

Lignin has high energy content due to the presence of the reactive groups. These provide a significant opportunity for deriving a wide range of products having commercial potential. (Higson A., Smith C., 2011). Lignin with natural hydrophobicity has phenolic macromolecule, made up of three main phenylpropane units (monolignols) namely, coniferyl alcohol (G), sinapyl alcohol (S) and minor amounts of p-coumaryl alcohol (H) (Beauchet R. et al., 2012). The monolignol units when incorporated into the lignin polymer are called guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) units (Vanholme R. et al., 2010).
Lignin contains several functional groups like methoxyl, phenolic, hydroxyl and a few terminal aldehyde groups which have an impact on its reactivity. Lignin is classified into three major groups depending on its origin namely, softwood, hardwood and grass. While the hardwoods contain lower amount of lignin, softwoods have a larger proportion of lignin. In softwood lignin, termed as guaiacyl lignin, comprises of coniferyl alcohol and trace amounts of sinapyl alcohol-derived units. Hardwood lignin, termed as guaiacyl-syringyl lignin, comprises of coniferyl alcohol and sinapyl alcohol-derived units in different ratios. Grass lignin, termed as guaiacyl-syringyl lignin, contains significant amounts of structural elements derived from p-coumaryl alcohol (H) (Donostia S.S., 2012). The basic structure of lignin suggests that it could play a vital role mainly in the formation of supramolecular materials and aromatic chemicals.

Isolation of Lignin

Lignin can be isolated by different extraction methods (enzymatic, chemical and mechanical) resulting in intermediate products such as binders, carbon fibres, dispersants, phenols & plastic materials. Lignin could also be processed to obtain end products like activated carbon, motor fuel, sorbent, surfactant & vanillin, etc. Lignin is generally extracted from plants by using an organic solvent or high-pressure steam treatment. Different types of lignin obtained from various extraction methods along with their yields are mentioned in Table 1.

Lignin by Kraft Process

Lignin is most commonly obtained worldwide as a byproduct of Kraft-based pulping process in paper mills. This is mainly utilized as black liquor for generating power, process steam and also chemical recovery in the pulp mill. A few pulping mills divert lignin for value added products. Thermochemical techniques such as gasification of lignin to syngas or its pyrolysis to bio-oils can contribute to value-addition. Gasification of black liquor to bio-oils can contribute to value-addition. Gasification of black liquor to bio-oils can contribute to value-addition. Gasification of black liquor to bio-oils can contribute to value-addition. Lignin by Kraft Process

As technology barriers are addressed, lignin transitions from a mere fuel source into a key biorefinery process stream. This can be processed further to ethanol, mixed alcohols, green fuels or other syngas products. Potential of using lignin as a macromolecule for high-molecular weight applications also exists. Further, aromatic products with large market opportunities remain a possibility (TIFAC report, 2010).

Lignin as Lignosulfonate

Natural lignin is colourless or pale yellow but on treatment with acid or alkali, its color changes to brown or dark brown. The physical and chemical properties of lignin derivatives vary depending on the extraction method e.g. lignosulfonates are hydrophilic in nature obtained from sulfité pulping whereas Kraft lignins obtained from the Kraft pulping process are hydrophobic (TIFAC report, 2010).

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In pulp manufacturing by the sulphite method lignosulfonates are obtained as salts of lignosulfonic acid. The composition of lignosulfonates varies based on the extent of the lignin degradation and number of sulfonic groups present. 90-95 % of lignosulfonate is precipitated as calcium salts by the treatment of lime with spent process liquid and black liquid from sulphite plants.

The production of lignosulfonates and sulphonated lignin is estimated to be around 800,000 MT and 15,000 MT respectively. Lignosulfonates are sold as odourless and brown amorphous powder. They are not hygroscopic and insoluble in organic solvents but form colloidal solutions or dispersions with water. Lignosulfonates with complex properties are used in traces to prevent scaling in hot and cooling waters and also to dissolve micro-nutrients in liquid fertilizers (KEMI report, 2010).

### Lignin by Enzymatic Hydrolysis

Enzymatic hydrolysis technique for isolating residual lignin was first developed by Yamasaki et al. The process is based on selective hydrolysis and dissolution of carbohydrates by cellulolytic enzymes leaving lignin as an insoluble residue. Biomass is typically subjected to successive enzymatic treatments to ensure complete dissolution of the carbohydrates and to increase the amount of recovered insoluble lignin residue. The residual lignin samples contain 65-80% lignin, 7-8% carbohydrates, and the remaining impurities from proteins generated during the enzymatic treatment.

Lignin isolation by enzymatic hydrolysis suffers from several demerits, which include some carbohydrates that cannot be removed.
by prolonged and repetitive enzymatic treatments or by purification methods that are commonly employed for milled wood lignin.

**Lignin Derivatives**

Lignin, a phenyl propanoid-based biopolymer, could become the main renewable aromatic source for the chemical industry in the future and substitute phenol in most of its industrial applications such as phenolic resins, surfactants, epoxy resins, adhesives or polyester etc. (Frost & Sullivan, 2012).

**Phenolics**

Phenolics can be used to derive phenolic compounds. Phenols are reactive compounds and are acidic in nature due their -OH group. They form chelate complexes with metals and they are easily oxidized and, if so, form polymers. These substances and their derivatives are intermediates of the biosynthesis of lignin (Botany online 1996-2004).

Phenol is commonly (~95%) produced from petroleum-derived benzene by cumene process. It is a versatile precursor to a large array of drugs (mainly aspirin), many herbicides and pharmaceuticals. It is also used as an oral anesthetic/analgescic to treat pharyngitis. Two thirds of global phenol production is converted to precursors to plastics and it is an important building block for bioplastics, phenol-formaldehyde or epoxy- or polyurethane resins. (Kleinert M., Barth T., 2008).

The phenolic products have potential usage for tanning of animal hides and other industries, such as chemical, pharmaceutical, food and perfumery. The phenol derivatives are used in the preparation of cosmetics including sun screens, hair colorings and skin lightening preparations.

**Guaiacol**

Guaiacol, a naturally occurring organic compound, can be usually derived from guaiacum or wood creosote or can be synthesized by a variety of organisms. It is produced on dissolution of biomass and lignosulfonates. It is main product due to the cleavage of β-aryl ether linkages (Varanasi P. et al., 2). Guaiacol is used as precursor to various flavouring agents like vanilla, roasted coffee etc. Its derivatives are used as expectorant, antiseptic, local anesthetic and also as an indicator in chemical reactions that produce oxygen.

**Carbon Fibre**

Over 90 % of the global carbon fibre production uses petroleum derived polyacrylonitrile (PAN). Compared to PAN, lignin has more than 60% carbon content and is a renewable material, which is available in large quantities (Norberg I., 2012). Kayocarbon fibre produced by Nippon Kayaku Co., Japan has commercialized production of carbon fibre using lignosulfonate as a precursor derived from lignin and polyvinylalcohol as softening agent. Lignin-based carbon fibre promises high value addition potential for the biomass. It could increase gross revenue of the biomass by 30% to 300% and reduce CO₂ emissions (Baker, F. et al., 2014).

Carbon fibre composites provide high modulus coupled with high strength and reduced weight thus making it an ideal option as aerospace material to substitute aluminium and titanium alloys. Recreational sports and leisure market segment comprising tennis rackets, golf clubs, hockey sticks, archery arrows & bows, fishing rods uses carbon fiber composites. Formula 1, National Association for Stock Car Auto Racing (NASCAR), and high end cars also use carbon fiber for reduced weight (Johnson.T). The market for carbon fiber is also projected to grow exponentially to cater to the needs of clean energy technologies (Baker, F. et al., 2014).

**Activated Carbon**

Activated carbons are adsorbents that are industrially used in deodourization and purification for process streams and for the treatment of liquid and gaseous effluents. Lignin can be converted to activated carbon by physical or chemical activation. The chemical activation at high temperatures gives higher product yields (Mussattoa S. I. et al., 2010).

Activated carbon finds excellent in metal finishing for purification of electroplating solutions. The other applications include gas & water purification, decaffeination, gold purification, metal extraction, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air etc. The pharmaceutical industry would exploit activated carbon fibers, which can adsorb bacteria. In case of waste incineration, volatile heavy metals and combustion products such as dioxins and furans present in the post combustion areas can also be adsorbed by activated carbon (Concise Analysis of the International Activated Carbon Market - Forecasts to 2016, March 2014).

**Vanillin**

Vanillin (3-methoxy-4-hydroxybenzaldehyde) extracted naturally from the dried pods of vanilla plant, is the most widely used flavouring agents in the world. The commercial vanillin market is served by three major sources namely, natural vanilla from beans, vanillin produced from chemical/petrochemical sources (over 90%) and vanillin produced from lignin derived from the wood pulping process. Lignosulfonate obtained from the sulphite pulping process is used for industrial vanillin production. The major products obtained are vanillin, vanillic acid, and acetovanillone along with some other aromatic compounds. Lignin-derived vanillin, which is marketed as a premium product, is priced at $100-200 per kilogram (Wong J.T., 2012). Currently, Borregaard, Norway is the only company, which produces vanillin from lignin via sulphite pulping method. Approximately 60% of industrial vanillin is used in the food industry; 33% as fragrances in perfumes and cosmetics; and 7% in pharmaceuticals (Wong J.T, 2012).

**Bio-plastics**

Thermoplastic compounds based on renewable resources are compostable and biodegradable and thus offer environment friendly alternatives to synthetic petrochemical plastics. To synthesize bioplastics, lignin is mixed with natural fibres like cellulose, flax, hemp and additives resulting in a material that can be processed at elevated temperatures. The mechanical properties of bioplastics such as strength, rigidity, dimensional stability etc. can be varied by adjusting their composition. Bioplastics find wide applications in jewelry, musical instruments, furniture, automotive interiors, garden supplies etc. (Bogomolova A., 2013). Globally, bio-plastics industry is expected to grow significantly and it is estimated to reach US$7.02 billion by 2018 (Bioplastics News, January, 2014).

**Lignin Applications**

Lignin has effective and economical adhesive properties, which can be improved through phenol and aldehyde or by modification of lignin itself. It can be used as rubber intensifier, polyolefin, rubber packing,
used in composite materials and also in the unsaturated polyester and vinyl ester as filler and co-monomer. Kraft lignin products are generally used in high end applications such as in foam fire extinguishers to stabilize the foam and in printing inks for high speed rotary presses, extender/modifier, and as reinforcement pigment in rubber compounding etc (John Wiley & Sons, Inc). After modifying base lignin, it can be used as emulsifying agents/emulsion stabilizers, as sequestering agents like pesticide & dye dispersants, additives in alkaline cleaning formulations, complexing agents in micronutrient formulations, flocculants, and extenders for phenolic adhesives. Lignosulfonates used on unpaved roads reduce environmental concerns from airborne dust particles and stabilize the road surface.

Several industrial applications of lignin are mentioned in the following sections:

Lignin as Binder
Lignin is used as the binder for glass wool building insulation. It is applied to hot glass as the ammonium salt solid recovered from the Kraft paper production process and allows the glass fibers to bind when the fiber pads are formed (Meister J. J., 2007).

Lignin improves the performance range of the asphalt binders (McCready N. S., Williams R. C., 2007). The binding ability of lignosulfonates makes it a useful component of biodegradable plastics, coal briquettes, plywood & particle board, ceramics, animal feed pellets, carbon black, fiberglass insulation, fertilizers & herbicides, linoleum paste, soil stabilizers etc.

Binder yields low cost composite materials with a reasonable wet strength. A lignin based modifier added to formaldehyde based binder systems namely, phenol formaldehyde (PF), urea formaldehyde (UF), melamine formaldehyde (MF), resorcinol formaldehyde (RF) and/or tannin formaldehyde resins etc. is used for panel boards such as plywood, hard board, medium density fiberboard or particle boards (Lignin Applications: Brief Overview).

Lignin as Dispersant
Chemically modified lignin has been used as a dispersing agents, flocculent, thickener or auxiliary agents for coatings, paints etc. Lignosulfonates prevent the clumping and settling of undissolved particles in suspensions. A lignin derived material has been used as a dispersant for soils, cleaning and/or laundry detergent compounds, cement mixes, leather tanning, oil drilling muds, pesticides & insecticides (TIFAC report, 2010).

A mixture of polyacrylic acid & lignin sulfonic acid has been used for cleaning aluminum plates to prevent calcium scaling. Lignosulfonates are used as biodegradable and non-toxic emulsifiers/dispersants for emulsion or dispersion polymerization. (Lignin Applications: Brief Overview)

Lignin in Battery
Lignin enhances performance of energy storage devices. It forms a thin layer on the graphite powder surface thus preventing the graphite powder from decreasing overvoltage without affecting its condition

Lignin as Dust Suppressant
Lignosulfonate acts as a dust suppressant by its affinity for binding with other polar and non-polar compounds. The smaller dust compounds adsorb lignosulfonate and form a larger, heavier complex which settles the dust (CWPA, 2005). It is also used for dust control in ceramic manufacture, synthetic fertilizer production and application, cement clinker milling, and concrete mixing (Harkin J. M., 1969).

Lignin as Sequestering Agents
Lignosulfonates are strong sequestering agents and readily form soluble complexes with iron, calcium, copper, nickel, tin, aluminum, and zinc. Hence they are used in treatment of poor soils either to add deficient minerals or to remove harmful ones. They are also used in industrial cleaning for hard water treatment and in boiler for scale control (Harkin J. M., 1969).

Lignin as Food Additives
Additions of alkali lignins to pet and human food as a roughage or fibre source are potential uses of lignin. An extensive research in this area has shown that high dietary fibre correlates with low incidents of colon cancer. (Meister J. J., 2007).

Lignin in Cement
Low levels of lignin and modified lignin can yield high performance concrete strength and grinding and reduces damage of external wall due to moisture and acid rain. Some selective lignin can improve the compressive strength of cement pastes.

Lignin Blends
Thermoplastic materials comprising lignin and protein blended with natural rubber exhibit improved impact resistance compared to lignin-free formulations. Blending soy protein with hydroxyl-propylated soda lignin results in increased tensile strength of the blended material. Lignin-polyolefin blends act as a stabilizer against oxidation under UV radiation or at elevated temperatures, to enable the biodegradation of the material.

Polybutylene adipate and polytrimethylene succinate with acylated, methylated and ethylated Kraft lignin can yield effective polymer blends. Kraft lignin can also form homogeneous blends with polybutylene terephthalate (PBT) and polyethylene terephthalate (PET)(William O.S., Doherty A.C. et al., 2011).

Lignin has been applied to hard glass as the ammonium salt solid recovered from the Kraft process until recently. However, the current focus on greater utilization of waste products has been driving research in the isolation, structural modification and utilization of lignin. Frost & Sullivan, a market research company published a market report in 2012 highlighting that lignin is the only renewable source for industrial aromatics production and is not linked with the fluctuating oil prices.

The pulp and paper industry is interested in improving its production of lignosulfonate, a key component in papermaking processes.
industry related developments:

- Alberta-Pacific (Alpac), Ontario, a large forestry-products company in collaboration with the Lignoworks Network (Ilderton, Ontario) aim to explore technology development for lignin based novel materials and chemicals to substitute fossil-fuel derived chemicals and products. Alpac is specially interested in developing value-added products from lignin to diversify their product base from bleached Kraft pulp process.

- Invetnia, Sweden, a research company has developed carbon-fiber production technology using lignin. They have also developed LignoBoost technology in partnership with Chalmers University of Technology (Gothenburg, Sweden) for the production of high-quality lignin from the paper pulping process.

- Domtar Corp, Canada, in early 2013, installed a 75 TPD lignin separation plant using Invetnia’s LignoBoost technology catering to bio-fuels and bioplastics production.

- The natural fibres (hemp, flax or similar plants, and natural additives) are mixed with lignin and processed at raised temperatures by Tecnano GmbH, Germany to produce thermoplastics that can be incinerated for disposal. The automotive interior panels, casings for electronics and the construction industry have used this novel material (Arboform). Arboform has been found to be an excellent substitution for wood in the construction industry for its uniform structure (no grain) and ability to withstand loads (Evans D, 2013).

- Green Value, a Swiss company, has been producing and marketing high purity sulfur-free lignin and its derivatives. The products find applications as plywood adhesives, high pressure laminates, foundry core binders, brake pad binders, molding compounds, dispersants, antioxiants etc. (Lora J.H. et al.,).

- The binding and dispersing agents, derived from lignin and lignosulfonate are manufactured and marketed by LignoTech, USA. The applications include animal nutrition (pellet binders, bypass proteins), additives for ceramics, concrete and gypsum board, dispersing agents for agro chemicals, battery expanders, carbon black, dye baths, dyestuffs and water treatment, dust control for roads and industrial dusts, binders for carbon black, fertilizers, limestone and mud dispersants and plant nutrition etc.

- Tembec with their plants in Europe and North America produces 5,70,000 MT/yr of lignosulfonates with application in dispersants, binders and chelators etc.

- Non-sulfonated Kraft lignin, aromatic ring sulfonated and hydroxyl methylated lignin are manufactured by MeadWestvaco, USA. They have capacity to produce other specialty products like propoxylated lignin polyols, which find application as dispersants for cements and animal feeds, particle board, wax emulsions, dyes and pigments, lead acid batteries, ceramics, concrete and refractory etc.

- Specialty binders manufactured by Northway Lignin Chemical, Ontario, include sulfur-free Kraft lignin, stabilizers, emulsifiers, organic binders, dispersants and liquid/powder agglomeration.

- KMT Lignin Chemicals, U.K., manufactures lignosulfonates for binding and dispersing applications in concrete admixtures, oil well drilling muds, dust abatement, dyestuffs, leather tanning, ceramics, insecticide sprays etc.

- Lignosulfonates manufactured using pinewood by Melbar, Brazil, find application as agglomerants, dispersants, emulsifiers and wetting agents, chelating agents, and animal hide treatments.

- Lennox Polymers Ltd., USA, have developed technology related to formaldehyde-free resins and adhesives based on lignin from black liquor (Holladay J.E. et al., 2007).

There is an increasing demand for lignin in countries (like China, India etc) due to their expanding industrial base (Lignin Market - Global Industry Analysis, Size, Share, Growth, Trends and Forecast, 2013 – 2019, March 2014). Globally, ~40 MMT of lignin is produced annually out of which ~1 MMT of lignin is sold each year for low volume and niche applications. The market for lignosulfonates is growing at a slow rate due to limited development in this area (NNFCC Report, October 2009).

**Conclusion**

Depolymerization of lignin provides environmental benefits. It is a valuable by-product of industries which can improve the economics of lignocellulosic biorefinery. Genetic modification of the lignin content and its composition in biomass would improve the utilization of lignin in several industries including paper and pulp, biofibre, forage, bioenergy, food processing etc. These transgenic varieties produced by expression of antisense RNA, sense suppression, ribozyme, RNA, etc. should not contaminate the food chain in order to avoid the public health concerns. Proper understanding of lignin biosynthetic pathway & metabolic pathways should also be taken into account.

Focused efforts are warranted to develop the technology for isolation, extraction & derivation of value-added products from lignin in the next five years. This may call for a mission mode programme with the deployment of adequate resources, multi-disciplinary research teams with the primary objective of developing cost competitive derivatives of lignin. The networking among the industry and research institutes would go a long way in increasing the application scope and awareness in the market for lignin based products.

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