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Review on Lignin, Its Derivatives and Their Applications

Akshita Rai[1], Ioan Barabulica[2], Sandeep Rai[3,*]

Abstract

Due to the excessive use of fossil fuels day by day everywhere, several severe problems on the globe and related to environmental issues like environmental problems and heating are cropping up and posing a big problem. Due to this reason, several attempts are being made to develop other sustainable alternate energy sources which are based on plant biomass. However, those materials contain lignin, which makes up approximately 18-30% of the total content. Lignin is used as fuel but has many potential and valuable applications, including nanoparticles synthesis, poly-carboxylic acid production, supercapacitor electrode fabrication, and use as a photocatalyst and photovoltaic material. Recently, researchers have been working to develop more sustainable bioenergy production technologies. This review paper focuses on lignin and its derivatives for different industrial applications, including sustainable energy conversion.

Keywords: Lignin, Lignin Derivatives, Lignin Isolation, Lignin Extraction, Lignin Applications

INTRODUCTION

Lignin is a natural aromatic polymer class of natural organic complex compounds, that was mentioned first by a botanist, A.P. de Candolle in 1813 who manage to experiment the property of lignin of being solved in alkaline solution, from which can be separated by the use of acidic reagent [1]. In later years (1923) the Swedish chemist Peter Klason design a method for lignin quantification based on lignin hydrolysis in H2SO4 61-68% that opens the research about this natural compound linked to wood and cellulose processing in that time [2].

The importance of lignin comes from its abundance as the second most abundant bioorganic polymer on earth after cellulose and the most abundant aromatic bioorganic polymer with most significant contribution to soil organic matter [3]. The abundance of an ingredient is the key parameter for sustainability together with regeneration capacities for environmental conservation issue. In this case, with lignin as an aromatic natural polymer widely distributed on earth, sustainability and the environmental conservation issues are very well covered as the primary challenges for human civilization [4] development.

Chemically Lignin contains methoxylates of phenylpropane units & derivatives. Lignin is a three-dimensional amorphous polymer. Lignin is a naturally occurring amorphous polymer and has great potential to be used as a building block. Lignin accounts for around 15–35% by wt. for lignocellulosic biomass. It can be used in the production of fuels & valuable chemicals as renewable resources [5–9]. Huge quantities of lignin are commercially produced & processed in the pulp and paper industries. Millions of tons of lignin are produced from the paper industry. A limited quantity of lignin is also extracted annually directly from plants [10]. Several review articles

***Author for Correspondence**
Sandeep Rai
E-mail: sadeep1964@yahoo.co.in

[1]Executive, Zentiva Private Limited, GIDC, Ankleshwar, Bharuch, India
[2]Research Scientist, Gheorghe Asachi Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Romania
[3]General Manager R&D, Dyne Chemicals LLP, Chatral, Gandhinagar, Gujarat, India

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reported and summarized various processes for converting lignin which include gasification, pyrolysis, and de- polymerization [11–20]. Lignin is present as a significant biomass, along with cellulose & hemicellulose. The use of industrial lignin finds very limited usage, which leads to waste of resources and increasing pollution [21].

Lignin utilization in different industrial applications is therefore a worldwide activity, its utilization in developing value- added materials. The amorphous lignin biopolymer is consists of mainly three monolignols:a) *p*-coumaryl (P), b) coniferyl (C), and c) sinapyl (S) spirits having varying ratio of ether and carbonic bonds [22]. Lignin obtained from plant biomass is different from natural lignin as by-products. The aromatic chemical structure of lignin with large amounts (phenolic, aliphatic and carboxylic) of OH groups, it is possible to alter technical lignin's via reaction to the epichlorohydrin reaction of OH groups [23].

Lignin can be used for the processing of numerous products such as, petroleum- based syngasses, phenolic compounds, multifunctional hydrocarbons, oxidized products, and carbon fiber etc. As compared to its oil-derived counterparts, lignin-based materials, and fuels are better environmentally friendly, having lower weight, more fuel efficient, and more importantly can reduce costs substantially. Lignin can be potentially used in different types of application such as the adsorption of heavy metal ions in effluent water, in synthesis of nanoparticle, in super capacitor electrode, as a photo-catalyst, in photovoltaic, as water flocculants, etc. Here, lignin derivatives show better properties [24, 25].

This article briefly presents various types of application of lignin and its derivatives. It is believed that by developing new applications of Lignin will be helpful in developing new environmentally friendly range of lignin and modified compounds that will greatly contribute to energy and industrial sectors.

LITERATURE REVIEW

Chemical Structure of Lignin

Lignin, is referred to as nature's glue, stands as second of the most abundant organic polymers after cellulose on Earth. Normally Lignin is considered as a waste product in the pulp and paper industry, but now emerges as a promising natural resource in various industrial sectors due to its unique chemical structure & properties. Being a biodegradable material, lignin is getting more attention for its possible applications in different industrial segments [26, 27]. This review article explores briefly the vast potential of lignin, its derivatives and their potential applications across various industries. Lignin is a natural polymer present in the cell walls of plants and provides structural support and rigidity. Lignin is primarily composed of three phenylpropane and these units form a network of inter-connected units by chemical bonds. Lignin chemical structure is highly branched & irregular unlike Cellulose & Hemicellulose, this makes it resistant against degradation by enzymes.

Major Sources of Lignin

Lignin is present in abundance and is a naturally occurring polymer present in all vascular plants. Biochemistry that takes place in plants [28] begin with photosynthesis process followed by the C4 carbon fixation and Hatch-Slack pathway reaching to phosphoenolpyruvate (PEP) and then through Shikimate pathway leading to tyrosine, phenilalanine and tryptophan, and from here with the aid of enzymatic oxidase or peroxidase the monolignols are formed. This is synthesised in Figure 1 where it is illustrated the general pathway of chemical transformations that occur in plants that leads to lignin monomers and complex enzymatic ways for polymerising to lignin [29–31].

Isolation and Derivatization

Lignin is isolated from biomass which involves various methods, like Kraft pulping, organosolv extraction, & steamexplosion. After Lignin is isolated, it undergoes several chemical modification steps to produce a wide variety of value- added derivatives with customized properties. Derivatization methods ofLignin are sulfonation, esterification,oxidation, and depolymerization, toprepare derivatives with tailor made properties suitable for specific industrialapplications (Figure 2).

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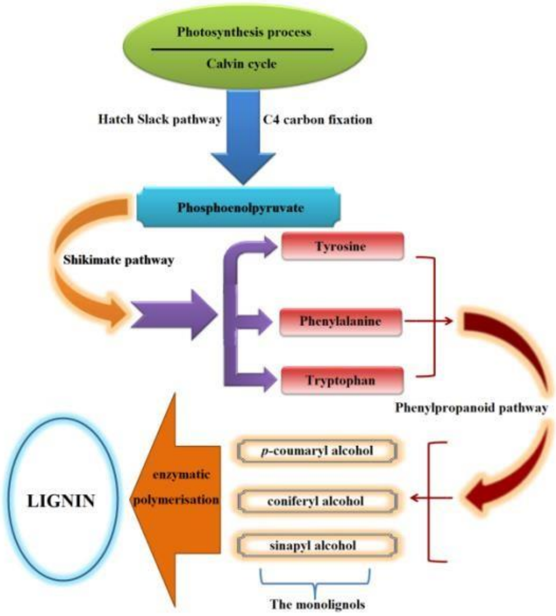

Figure 1. Biosynthesis of Lignin.

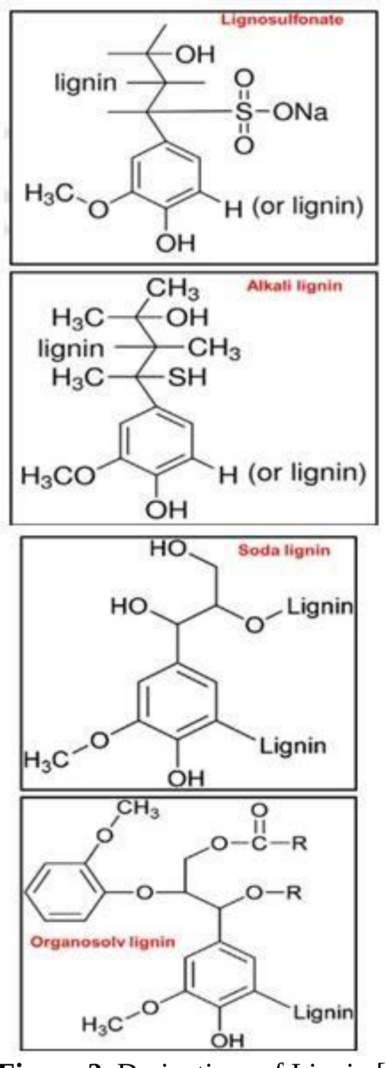

Figure 2. Derivatives of Lignin [32].

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Applications in Various Industries

Lignin is a complex organic polymer found in the cell walls of plants, particularly in wood and bark. It serves as a structural material, providing rigidity and strength to plant cells. Lignin is the second most abundant organic material on Earth, surpassed only by cellulose.

Despite its abundance and importance in plants, lignin has historically been seen as a waste product in various industries, such as paper and pulp production. Even in the present lignin base waste from the paper industry represents an environmental problem and efforts are made to reuse this kind of materials. However, in recent years, there has been growing interest in utilizing lignin and its derivatives for various applications due to its unique properties.

One significant application of lignin derivatives is in the production of biofuels and renewable chemicals such as bio- aromatic products. Lignin can be depolymerized and converted into valuable chemicals such as vanillin, phenols, and aromatic compounds. These chemicals can serve as alternatives to petroleum-derived products, contributing to the development of a more sustainable and environmentally friendly economy.

Moreover, lignin derivatives are used as additives in a wide range of industrial products, including adhesives, coatings, and resins. Due to their adhesive properties and ability to enhance the mechanical strength of materials, lignin-based additives are increasingly being incorporated into products like concrete, asphalt, and plastics.

Additionally, lignin derivatives have potential applications in the pharmaceutical and biomedical industries. Research is ongoing to explore their use as drug delivery systems, antioxidants, and therapeutic agents due to their biocompatibility and ability to interact with biological systems.

Overall, lignin and its derivatives offer promising opportunities for sustainable innovation across various industries. As research continues to advance, their versatility and unique properties are likely to lead to further developments and applications in the future.

1. *Polymer Industry:* Lignin-based polymers are emerging as a sustainable alternative/substitute to petroleum-based materials as replacement of bioplastics, adhesives, and composites. Lignin is being incorporated into various polymer matrices to enhance mechanical properties and biodegradability, UV resistance, and thermal stability, to make it suitable for critical and important applications like automotive, construction and packaging etc.
2. *Agriculture:* Lignin-based bio stimulants and soil conditioners are under development for their use in agriculture to enhance plant growth, improve soil structure, and minimize environmental stress. Lignin- derived products are found to promote microbial activity, increasing nutrient availability. The use of lignin and its derivatives are found to reduce soil erosion and lead to sustainable farming practices.
3. *The Energy Sector:* Lignin serves as a biodegradable and renewable feedstock for the production of biofuels and bioenergy via thermo- chemical & bio-chemical conversion processes. Lignin-based biofuels, like lignin-derived ethanol and biodiesel, are offering carbon-neutral alternatives to fossil fuels, minimizing and reducing greenhouse harmful gas emissions and significantly reducing dependence on non- renewable depleting resources.
4. *Chemical Industry:* Lignin-derived chemicals, i.e. vanillin, phenol, and aromatic compounds, can be used in the commercial production of flavours, fragrances, resins, and pharmaceuticals. By value added by derivatization, lignin can be used as a feedstock and thus chemical industry can reduce dependability on petrochemicals and minimize environmental pollution during commercial production scale.
5. *Biological Application:* Lignin and its derivatives are being considered for various biological applications like Hydrogel, Antioxidants and Anti-bacterial and Biochemical etc. An efficient process for extraction of phenolic compounds from bio-oils produced by lignin pyrolysis is

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reported [33] High pH alkaline solution was used for the partial extraction of phenolic compounds from crude bio-oils. Improvement can be achieved by increasing the number of stages of extraction or by using alkaline solution with higher concentration.

Pre-treatments of Lignin with ammonia have been extensively studied in the last decade and considered as one of the leading pre-treatments [34] for biorefining of lignocellulose biorefining. Reported work described key features and comparative performances of several leading ammonia-based pre-treatments technologies (e.g., soaking in aqueous ammonia or SAA, ammonia recycled percolation or ARP, ammonia fiber expansion or AFEX, and extractive ammonia or EA).

A new process for efficient oxidation of lignin by chlorine dioxide was reported [30] the effect of substituent localization on lignin oxidation was discussed and explained. High purity pulp fibres can be prepared & it was observed that chlorination was inhibited during the oxidation of lignin by chlorine dioxide.

CHALLENGES AND FUTURE DIRECTIONS

The use of ethanol fuel produced by biomass is expected to increase significantly [35] several countries of the world are focusing on ethanol production from food grains and unused biomass. The proper utilization of biomass is possible through ethanol production by producing lignocellulosic waste. Ethanol can be produced by lignocellulosic biomass at relatively lower cost through new innovative technology. The application of lignin in industrial applications should be increased by extensive research & development and the addition of some modified lignin derivatives that could lead to newer biological applications.

D-lightment [36] is one of the innovative technologies which is being developed for bioethanol production. The proper use of lignocellulose and appropriate catalysts can be successfully scaled up to commercial level. There is currently a lot of research work under way on lignin and its derivatives on how to increase their proper use. Lignin and its derivatives can be used for adsorption of heavy metal ions in effluent water.

Some parameters such as temperature, pressure and condition need to be optimized for the development of lignocellulose application technology. Research should be focused on reducing fuel consumption and minimizing pollution caused by this technology. Lignin can be modified to different types of derivatives and showed better properties for acting active sector [37, 38]. This is projected that in future, lignin will make a significant contribution to various industrial and energy fields. Research efforts need to be directed towards developing new applications and the government should supports & encourage these through the necessary steps. Biomass is going to play a key role in demonstrating the sustainability of usage of Lignin and its derivatives. Using the right energy & creating a helping environment will lead to major changes in existing technology & industry in the future. Below (Figure 3) the current and future applications for processing Lignin to produce various value-added compounds are shown into a diagram.

Lignin and its derivatives have exhibited their vast potential as biodegradable feedstock in various industrial applications. However, to achieve applications and widespread usage on commercial scale, lignin and its derivatives still faces several technological hurdles, including cost effectiveness/ competitiveness, scale up for industrial production, and technological limitations. Research efforts are now under way on developing cost-effective isolation & extraction methods, optimizing processing parameters for chemical conversion processes, and exploring newer and novel industrial applications to fully utilize the value of lignin as a bio-degradable renewable natural resource.

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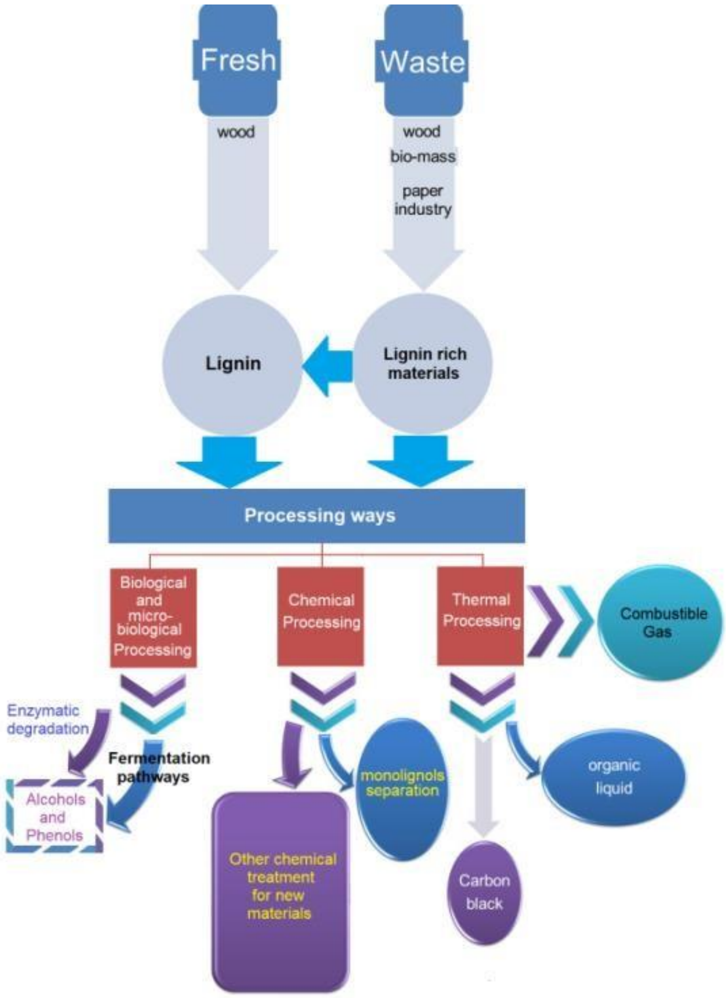

Figure 3. Lignin Circuit in Current Development and Future Directions.

Few salient features regarding Lignin are as follows [39]:
Recovery of Kraft lignin in pulp mills globally was 265,000 MT in 2018.

Modification of Lignin is key for making superior substitution for enhancement & stability.

De-polymerization under mild conditions may lead to lignin upgrading.

Potential value-added products from Lignin are phenols & polyols which may be commercially available in short time.

As a long-term product are thermoplastics & carbon based on Lignin and its derivatives due to fast-growing demand.

Estimated global market of lignin at USD 1.08 billion in 2023 and is expected to grow with 4.5% CAGR from 2024 to 2030 [40]. Growing demand for lignin and derivatives in animal feed and natural products is expected to be driver for market growth. Lignin and derivatives are widely utilized in the production of polymers, also used in the bitumen, catalysts for bio-refinery and biofuels etc.

CONCLUSIONS

Lignin and its derivatives are class of a valuable resource with numerous commercial applications in various industries, like polymers, agriculture, energy & chemicals etc. As sustainable alternatives to

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fossil-based materials is need of the hour, lignin stands out as a potential naturally occurring renewable and abundant feedstock having various properties of driving innovation and promoting development environmentally friendly materials. For example, it would be interesting to research and study the replacement of Styrene based products with Phenyl propylene ones from p- Coumaryl Alcohol which is Lignin Model and precursor and can be prepared from Lignin as shown in Figure 4. If this way of research is successful, then will generate the needs of higher amounts to be produced and proposed path shown in Figure 4 may become main route for processing of lignin to produce value added products. The path depicted in Figure 4 could become the main route for processing Lignin to produce value added products.

By advancements in lignin chemistry through dedicated R&D efforts and engineering, we can develop new opportunities, products and applications for economic growth, environmental sustainability, and well-being of society.

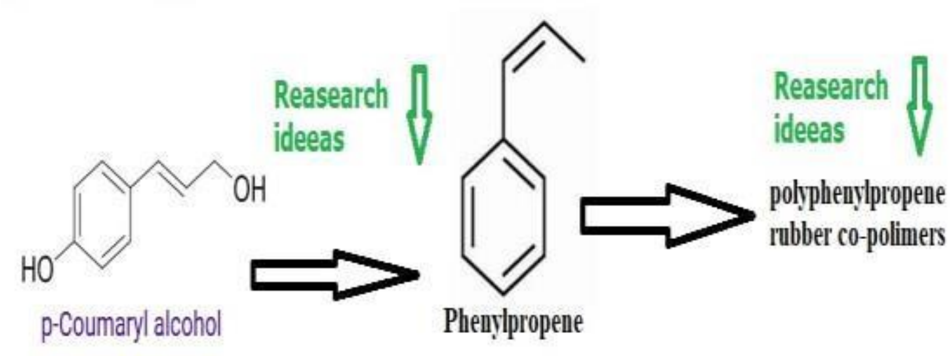

Figure 4. Proposed Path of Processing of Lignin to Poly phenylpropene

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