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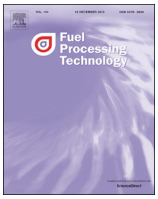

Review

# Advancement in technologies for the depolymerization of lignin

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ABSTRACT

Lignin is one of the largest sources of naturally occurring aromatic building blocks that possess immense potential to be employed as starting material for the production of value-added chemicals involving biofuels. Despite various challenges associated with lignin valorization, several strategies have emerged that could deliver value-added products in good yields. The present contribution aims to critically review recent advancements in biological, thermochemical and electrochemical strategies for lignin depolymerization mainly focusing on enzymatic, acid/base/metal-catalyzed, and microwave-assisted degradation approaches. All lignin degradation strategies result in the production of an arsenal of several monomeric, oligomeric and polymeric compounds, with no single molecule being produced in significant amount. For large-scale production of biofuels and other value-added chemicals via lignin depolymerization, the combination of two or more technologies with low cost and recyclable catalysts operating at mild reaction conditions needs to be explored.

## 1. Introduction

The gradual depletion of fossil fuels along with the need to diminish global greenhouse gas emissions has triggered interest in the utilization of renewable resources, such as plant biomass, not only for the production of second generation biofuels, but also for the synthesis of several value-added commodity chemicals [1,2]. The dry weight of lignocellulose plant biomass consists of approximately $(10-30)$ % lignin, which forms a large-volume renewable feedstock of aromatic compounds [2]. Architecturally, lignin is chemically intermeshed with cellulose and hemicellulose through both covalent and non-covalent bonds, forming a complex 3D heterogeneous network (Fig. 1) [3]. Due to the irregular heterogeneous structure of lignin, the production of value-added commodity chemicals, such as vanillin (widely used flavor compound in food), ferulic acid, cinnamic acid, vanillic acid etc., via lignin depolymerization, remains a big challenge. Although vanillin is obtained in small amounts, its production via lignin depolymerization has recently attracted great attention due to the low cost, high reserve and unique aromatic structure of lignin. Since the yield of vanillin obtained from natural vanilla is limited by the production of vanilla beans, the vast majority of vanillin is currently synthesized from guaiacol (a raw material from petrochemical industry) [4]. The amount of vanillin produced via lignin depolymerization solely depends upon the source of lignin and its isolation process. Inter unit linkages of lignin plays vital role in influencing vanillin yield, for instance, lignin with high content of β-O-4 linkages significantly improves the yield of vanillin [5]. Lignin is derived from lignocellulose biomass, either by the dissolution of lignin while leaving behind cellulose and hemicellulose as insoluble residues, or vice versa. The extracted lignin from lignocellulose biomass retains high calorific value, due to the lower oxygen-to-carbon (O/C) ratio than both cellulose and hemicellulose [6]. Being lower in O/C ratio (Table 1), lignin is preferred over wood as a fuel source. In spite of its high calorific content, lignin is the most recalcitrant component of plant cell wall, due to the diversity of linkages between monomeric units, which renders it invulnerable to hydrolytic cleavage [7,8]. Out of several typical linkages (β-O-4, β-5, β-1, 5-5, α-O-4, 4-O-5, β-β) (Fig. 2), β-aryl ether (β-O-4), constituting > 50% of lignin structure, is the most dominant linkage [9,10]. Since lignin constitutes almost 25% of the total land-based biomass, it is considered as the second most abundant renewable resource after cellulose for the sustainable production of biofuels and bulk chemicals [11]. The paper and pulp industry produce > 50 million tons of extracted lignin, out of which almost 98% is burned out as low-value fuel, emitting tons of greenhouse gases [12]. Industrial cellulosic bioethanol production also generates several million tons of lignin as low-value by-product. By the end of 2022, the US bioethanol industry alone is expected to generate lignin up to 60 Mt./yr [13].

Lignin is an aromatic and optically inactive amorphous heteropolymer, which is often synthesized by free radical assisted peroxidase-mediated dehydrogenation of phenylpropanoid precursors, namely

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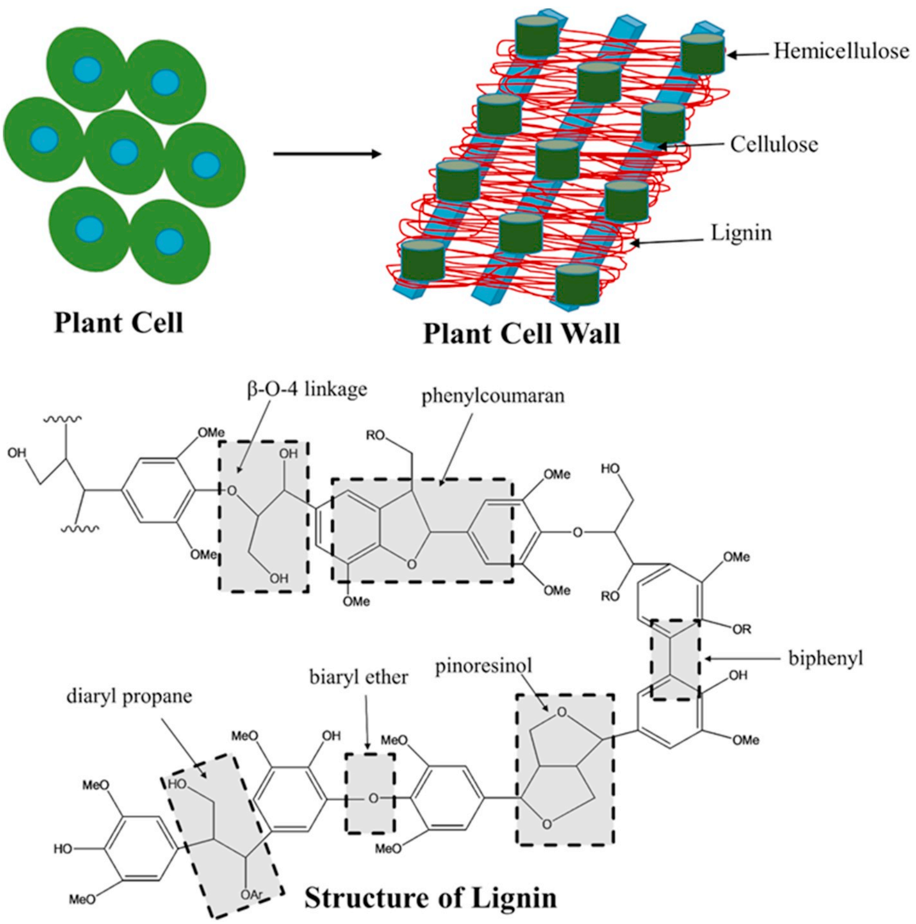

**Fig. 1.** Structure of lignin in lignocellulosic material.

**Table 1**
Comparison of the O/C and H/C ratios of various energy sources [14].

| | O/C ratio | H/C ratio |
|---|---|---|
| Crude oil | 0–0.03 | 1.60–2.10 |
| Lignin | 0.32–0.46 | 1.1–1.3 |
| Wood | > 0.61 | > 1.4 |

coniferyl alcohol, *p*-coumaryl alcohol, and sinapyl alcohol, joined altogether via non-hydrolysable linkages (Fig. 3). The ratios of these three monolignols vary significantly among different plant species. For example, coniferyl alcohol is abundant in soft wood lignin while hard wood lignin comprises both coniferyl and sinapyl alcohols; however, grass lignin contains all the three monolignols [15]. Depending upon the type of chemical pre-treatment method used, the extracted lignin has been classified into four main categories viz., kraft lignin, soda lignin, lignosulfonates and organosolv lignin. Kraft lignin is obtained upon treatment of biomass with sodium hydroxide and sodium sulphide while treatment with sodium hydroxide produces sulfur-free soda lignin. Pretreatment of biomass with aqueous sulfur dioxide and ethanol-water extraction method generates lignosulfonates and organosolv lignin, respectively. Besides four main types of lignin, ionic liquid lignin obtained by the treatment of biomass with ionic liquid has recently attracted interest, due to its low β-O-4 content and condensed structure [16]. Different types of lignin possess different chemical properties owing to structural changes that occur during lignin isolation from lignocellulose biomass. For example, organosolv lignin contains a large proportion of β-O-4 linkages, and is almost insoluble in water and organic solvents, in contrast with Kraft lignin and lignosulfonates [17]. This type of lignin is relatively the purest form of lignin, as its core structure remains unaltered, due to partial cleavage of β-aryl ether linkages. Kraft lignin is considered secondary to organosolv lignin, owing to its highly condensed structure. Kraft lignin is comprised of several C—C cross-linking bonds formed as a result of benzylic cation intermediate that develops upon the loss of benzylic hydroxyl groups in β-aryl ether units of lignin. As a result of structural condensation, Kraft lignin develops chemical inertness towards hydrolytic cleavage. During chemical pretreatment with sodium sulphide, sulfur gets incorporated into Kraft lignin in the form of the thiol group, which often poisons several chemical catalysts [18,19]. Additionally, biocatalysts, being highly substrate selective, are rendered inactive, due to the vast heterogeneous structure of lignin. Repolymerization of lignin fragments into higher molecular weight products is another limiting factor challenging lignin depolymerization [20]. Repolymerization generates large quantities of solid residue, while reducing the aromatic liquid content of the end product. Though lignin represents a cheaply available renewable resource of an arsenal of aromatic compounds (Fig. 4), biofuel production via lignin depolymerization has not been commercially viable. However, recently there has been considerable scientific interest in the development of the lignin-first biorefinery, based on fractionation strategies that aim to prevent structural lignin degradation by tandem depolymerization-stabilization of lignin, and active preservation of β-O-4 bonds [21]. The lignin-first biorefinery is expected to preserve the C9 basic structure of the original lignin, while possessing the potential to produce jet fuels comprised of C9 - C15 carbons [22]. This review article provides up-to-date information about recent developments in various thermochemical and biological techniques available for the degradation of lignin.