The Depolymerization and Applications of Lignin

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Abstract. Apart from an energy crisis, concerns about climate change have grown as a result of reliance upon fuels of fossil, prompting research on renewable and clean energy alternatives. Lignin as the world's greatest renewable source of aromatic building blocks, is second most rich reproducible resource after cellulose for sustainable biofuels manufacture. It has three dominant harbingers, p-coumaryl, sinapyl and coniferyl alcohols. Besides, it is considered to be a promising material by virtue of its biocompatibility, abundance and low cost in nature. The current contribution serves to review recent progresses in electrochemical, thermochemical and biological tactics critically for depolymerizing lignin primarily concentrating upon microwave-assisted, base/acid/metal-catalyzed and enzymatic degradation methods. Then, this retrospection contains the current research advancement in lignin valorization, particularly concentrating upon electrochemical, medical and 3D printing utilization. In the domain of medicine, drug delivery stuffs, pharmaceuticals and wound dressings employ lignins. Therefore, 3D printing lignin–plastic materials and electrochemical energy devices are used.

Keywords: Lignin; Depolymerization; Application.

1. Introduction

Apart from an energy crisis, concerns about climate change have grown as a result of reliance upon fuels of fossil, prompting research on renewable and clean energy alternatives [1]. Consequently, employing lignocellulose, a natural resource of plant, to create energy and bioethanol has gained popularity in a number of sectors [2]. Lignin accounts for about 10–30% dry weight of lignocellulose biomass, serving as greatest globe reproducible source of aromatic blocks [3]. To provide viable substitutes to widely adopted petroleum-derived benzene, toluene, and xylene (BTX), lignin has tremendous tendency to be employed as a starting stuff for manufacturing bulk or functionalized aromatic composites. Moreover, the change from lignin to other value-added compounds is an active research subject. The lignin molecule owns a complex cross-linking construction and includes a number of functional groups, like aliphatic methoxyl, phenolic hydroxyl, and hydroxyl groups. To decide the polymer features, aside from hydroxyl groups, aromatic construction is most important function groups. These functional groups have an impact on lignin chemical properties and its reactivity [2].

P-coumaryl, coniferyl and sinapyl alcohols are three leading precursors of the lignin polymer [2]. Different plants build lignin using varying ratios of these precursors. The lignin polymer's dominant bond, accounting for at least 56% of all connections, is an ether linkage. The precise ratios of links also vary in different species as a result of the various rates of the monomers among distinct lignin sources. According to various typical links (β-5, β-O-4, α-O-4, β-1, β-β, 4-O-5, 5-5), β-aryl ether (β-O-4), accounting for > 50% of lignin construction (Figure 1), is most prominent relationship [3]. The β-O-4 cleavage is also viewed as one pivotal stage for depolymerizing lignin to use lignin as a raw material for making the other chemicals because aryl ether linkages are simpler to cleave than the enriched linkages in lignin conversion process and depolymerization process [2].

Lignin is second most rich reproducible resource after cellulose for sustainable manufacture of bulk chemicals and biofuels because it makes up about 25% of all land-based biomass [3]. Many natural resources, like energy crops, agricultural waste products and woody biomass, can be used to obtain lignin. There exist commonly two methods for valorizing lignin, regardless of kind of lignin. One method utilizes it as one macro-polymer with a view to making useful stuffs, while that

alternative method depolymerizes into the monomer with low molecular weight. Monomers of lignin are able to be derivatized using a variety of chemical techniques to create the intended products. In this article, the various depolymerization techniques as well as cutting-edge lignin uses in the polymer, electrochemical, and medicinal industries would be introduced.

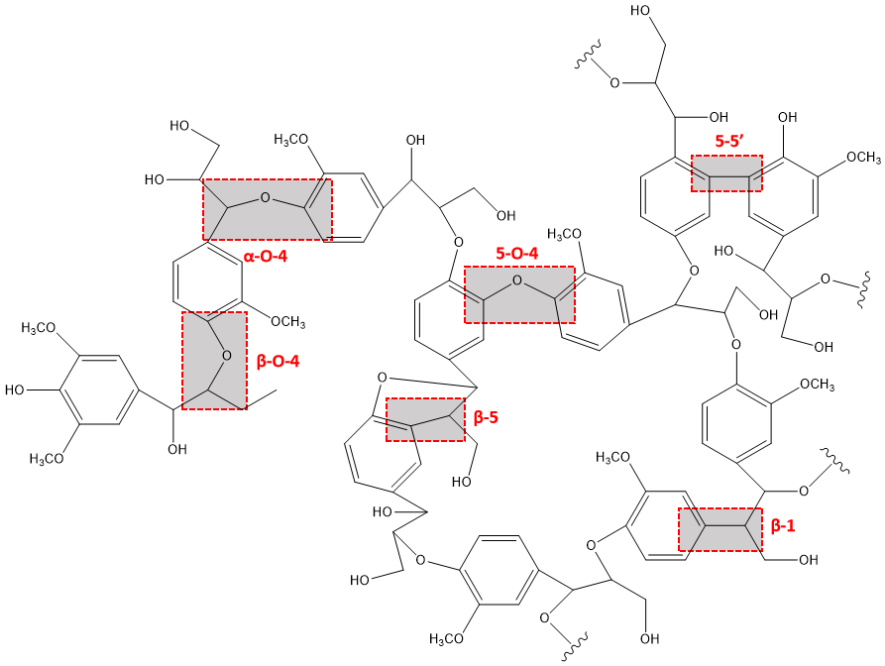

Fig 1. Some representative linkages inside the molecule of lignin. Those linkages labeled by the solid squares are just the linkage of ether. Those linkages labeled by dot squares are just enriched linkages.

2. Depolymerization Methods

2.1. Thermochemical Methods

2.1.1. Pyrolysis

Pyrolysis is one of the most extensive approaches for biomass or lignin to be degraded as well as converted into other biomaterials. Pyrolysis of lignin is divided into primary (200~400 °C) and secondary (>400 °C) pyrolysis, depending on range of temperature. During initial phase, the condensed linkage and aromatic methylated groups are steady. Thereby, depolymerized lignin fragments are typically the foundational lignin unit, including 4-methylguaiacol, coniferyl alcohol, syringol as well as a few lignin derivatives.

The response enters a secondary pyrolysis phase when temperature of the pyrolysis exceeds 400–450 °C; during this stage, researchers break down most linkages, and the more severe gasification begins. At about 450 °C, the group of aromatic methoxyl turns extremely reactive; additionally, O-CH3 bonds are homolyzed. Further raising temperature to 550 °C causes pyrogallols and catechols to vanish as well as generally generate coke, but it also considerably increases the output of non-condensable gases, especially CO. Lignin can be effectively converted and liquefied to bio-oil for use in other applications by the process of pyrolysis. However, methoxyl groups and lignin's low melting point, which support polymerization process as well as agglomeration process, separately, reduce bio-oil generation and cause char to form. Its use in the manufacture of certain compounds was restricted by the reaction's low selectivity.

Therefore, pyrolysis is frequently coupled with different solvents and catalysts to enhance its efficacy. Because of the enclosed environment in the course of pyrolysis, solvents or catalysts could provide a number of helpful accompanying molecules, such as hydrogen donors or oxidants, to enhance the pyrolysis efficiency through aiding demethylation or demethoxylation and offering

enough hydroxyl or hydrogen groups to prevent condensation and repolymerization. For example, Sirous-Rezaei et al. investigated catalytic outcomes of $PdReO_x/ZrO_2$, $NiReO_x/ZrO_2$, $FeReO_x/ZrO_2$, Fe/HBeta, ReO_x/ZrO_2, Fe/ZrO_2, and $FeReO_x$/MCM-41 for ex-situ catalytic hydrodeoxygenation of phenolic composites generated in one authentic sample [4]. This study demonstrated that zeolite-supported catalysts including Fe/HBeta produced the higher coke yields than Fe/ZrO_2, $FeReO_x/ZrO_2$ and $FeReO_x$/MCM-41 [4].

2.1.2. Microwave-assisted depolymerization

In the recent years, it has become recognized that microwave heating technology can speed up chemical responds through lessening their energy of activation while also improving the effectiveness of the heat energy through a special inner non-thermal heating phenomena [3]. The thermochemical conversion of lignin and biomass has extensively used the microwave as a heating method in substitute of the normal bath heating [2]. Muley et al. proved that microwave heating can reduce the processing time significantly and promote selective bond cleavage when depolymerizing lignin [5]. Compared to conventional heating techniques, microwave heating owns an allocation of narrow molecular weight. Besides, microwaves can also assist lignin liquefy or dissolve by accelerating the heating process. A variety of industry applications are available for lignin biopolymer liquefaction by microwave heating.

2.2. Chemical Catalysis

2.2.1. Acid catalysts

Linked to the β-ether α-carbon, hydroxyl group is proposed to undergo protonation during the general depolymerization of lignin inside the surroundings of acid, subsequently dehydration for the sake of producing a stable benzylic carbocation. Next, the carbocation is capable of proceeding by means of a medium of the enol ether type, subsequently hydrolysis for the sake of producing Hibbert ketone–type constructions as well as oligomeric/monomeric phenols. In order to catalyze the lignin valorization effectively, a range of catalysts of solid acid, including metal salts, immobilized liquid acids, heteropoly acids, zeolites, and metal oxides have been created and put to use. Liquid acid catalysts include things like organic acids, mineral acids and acidic ion liquids. Sulfuric acid is a typical type of catalysts among the liquid acid. For example, Imman et al. explored a sulfuric methanol/MIBK/water (25%: 35%: 40% v/v) with diverse concentrations of H_2SO_4 catalyst (0.01~0.02 M) co-solvent mechanism to boost hydrolysis lignin hydrolytic depolymerization [6]. Accordingly, lignin removal and restoration after the course of solvothermal fractionation changed within ranges of 72.7–87.2% and 71.5–86.2%, respectively [6].

2.2.2. Base catalysts

For the lignin base-catalyzed depolymerization, inexpensive inorganic bases that are readily accessible on the market, including the alkali metal hydroxides, have been utilized extensively to be the catalysts. The α-aryl ether bonds are broken in the course of the base-catalyzed delignification, converting phenolate units into the intermediate quinone methide. Finally, this intermediate becomes guaiacol and coniferyl alcohol. In contrast, non-phenolic units undergo β-aryl ether (β-O-4) bond fragmentation by substituting the closest aroxy substituent. That procedure contains the oxirane ring formation, eventually undergoing ring opening with the aim of creating a glycol group with the addition of a hydroxide ion. Because NaOH is inexpensive and is often used in industry, earlier investigations concentrated on employing it as a catalyst for lignin depolymerization [3]. Zhong et al. developed one alkaline-catalyzed water/sulfolane solvent mechanism for isolating antioxidative and elevated-purity lignin from willow [7]. For efficient willow lignin extraction, optimization of pretreatment conditions including sulfolane/water proportion, alkaline catalyst (NaOH) dose and temperature were thoroughly explored. The delignification product grew to ninety-four percent with roughly seventy percent of lignin restoration product as alkaline catalyst (NaOH) was added at a rate of 4% [7].

2.2.3. Metallic catalysts

However, concentrating upon the ether bonds cleavage is the major goal of utilizing an acid or base catalyst. It is challenging to make certain items using these strategies. Moreover, base or acid-catalyzed depolymerization typically demands for quite extreme reaction conditions, such as elevated pressure (from 5 to 10 MPa) and elevated temperature (250 °C to over 300 °C). Numerous researches are exploring for catalysts or strategies that is capable of catalyzing the depolymerization course in moderate circumstances with a great selectivity because these conditions make it expensive and challenging to handle [2]. One of the most broadly used approaches for turning the lignin into compounds with added value is metal-catalyzed lignin depolymerization [2].

(1) Reductive depolymerization

In the subject of lignin depolymerization, metal catalysts are utilized rather frequently, primarily in reductive or inert atmospheres. For the hydroprocessing-based depolymerization of lignin, transition metal (Ru, Pd, Pt, Ti), backed up on diverse carriers (TiO_2, C, ZrO_2, Al_2O_3, SiO_2) or economical Ni, Fe or Cu-based solids have been commonly utilized in the past few decades. Du et al. adopted lignin as one source of carbon with a view to producing inlaid-type Ni/LCNF catalysts to catalyze ethanol organosolv lignin hydrogenolysis in supercritical ethanol/water [8]. Generations of phenols (7%) and light lignin fragments (87%), which were generated by means of Ni/LCNF catalyst, were exceedingly elevated. There existed irrefutable evidence that lignin had already been depolymerized because the mean molecular weight (Mw) was much under that of untreated lignins [8].

(2) Oxidative depolymerization

There are also a few reports concern oxidative depolymerization of metal catalyst. Honorato et al. applied non-noble trimetallic (Co, Fe and Ni) nano-alloy as a nucleus to one phosphidated nitrogen-doped carbon shell (P-NiFeCo/NC) to prepare a novel and efficient catalyst for the efficient kraft lignin electro-oxidation. With lignin, this catalyst theoretically generates hydrogen at a rate of roughly 0.37 mol/min, which can obviously exceed the ratio of 0.0078 mol/min in pure 1 M KOH [9]. This provides a pathway to developing an effective catalyst for the kraft lignin electro-oxidation. Besides, polyoxometallates (particularly those based upon vanadium or molybdenum metals), metal oxides and perovskites are more general oxidation catalysts.

2.2.4. Ionic liquid (IL)

ILs, which are salts with melting temperatures of less than 100 °C, are a special class of solvents with almost little vapor pressure and a wide range of solvent properties. Due to their potent capacities to dissolve this biopolymer, they have recently been proven as superior solvents for carrying out numerous organic processes. Due to its ability to adjust the degree of oxidation, the liquid of ion is frequently employed as the solvent; also, it works in conjunction with the other catalysts for the sake of depolymerizing lignin [2]. Tolesa et al. suggested the approach for lignin in NH_4^+-based IL to selectively fractionate into phenolic composites or pivotal poly-hydroxy [10]. Di-isopropylethylammoniumbenzoate and di-isopropylethylammonium chloride ([DIPEA] [Cl]) are chosen ionic liquids (ILs) ([DIPEA] [Bn]). The findings demonstrated that lignin's polymeric structure is broken down into its monomers and oligomers. This study demonstrates the selected ILs' dual functionality (solvation medium and catalytic agent) in the depolymerization of lignin. The current work is highly helpful in developing a different source for the environmentally friendly manufacture of valuable compounds [10].

2.3. Biological Methods

Lignin is capable of being depolymerized by diverse chemical catalysts and thermochemical treatments. However, masses of the approaches need severe conditions, elevated energy input, and high cost. Biological courses are regarded as a perfect method for lignin transformation on account of its cost-effectiveness and specificity. Therefore, biological courses, particularly the microorganism-mediated bio-catalytic courses commonly requests the moderate conditions. That

lessens the investment of the energy and offers a more effective and specific alternative for adopting lignin.

2.3.1. Fungi

One of the microbes with the most research on lignin depolymerization and degradation is the fungus. White-rot fungi, the only class of microorganisms known to be capable of entirely converting lignin into H_2O and CO_2 at standard temperature and pressure, are the most promising. White-rot fungi own an elevated capability of degrading lignin, on account of their special extracellular lignin lowering the enzymes system, which includes manganese peroxidases, lignin peroxidases and laccase [11]. Among a variety of lignocellulosic biomass sources, several white-rot fungi have been found for their effective lignin degradation, including *Irpex lacteus, Phanerochaete chrysosporium* and *Pleurotus ostreatus* [11]. Nevertheless, since there are just a few different kinds of lignin degrading enzymes produced by fungal monocultures, the lignin treatment procedure has poor outcomes and is inefficient [11]. The lignin breakdown process by the fungal coculture, in contrast, has demonstrated some superiority on the part of enhanced enzyme activity, new secondary metabolites, and increased substrate application. Cui et al. used one consortium of white rot fungi comprised of *Trametes versicolor* as well as *Lenzites* betulina with an aim of increasing activities of manganese peroxidase and ligninolytic enzymes laccase (Lac) in microbial cooperation. The ratio of lignin degradation rose to 50%, which exceed that of fungal monocultures [12].

However, on account of their flaws, like poor adaptabilities to oxygen limits, temperature, pH and simple pollution by spores, few fungus-mediated courses have restricted usage in industries. It`s indispensable to investigate more efficient biological approaches for lignin conversion [13].

2.3.2. Bacteria

Bacteria are much more resistant of temperature, pH, and oxygen restrictions than fungus are. Some bacteria strains are confirmed applicable to lignin conversion and depolymerization [13]. However, the research concerning novel viable strains is necessary as ever, because most bacteria have a lesser capacity to degrade lignin than do fungi. As an illustration, Mei et al. extracted a strain from tobacco straw and recognized it to be *Bacillus* amyloliquefaciens SL-7. The lignin breakdown ratio in the Bacillus amyloliquefaciens SL-7 group grew by 22.26% as well as 11.70% during forty-one days of tobacco straw compost fermentation, compared to the control team and efficient microorganism group, demonstrating strain's potent lignin degradating ability. After 15 days of strawliquid fermentation degradation, the bacteria were able to break down 28.55 % of the straw's lignin, a level that was comparable to that of fungus [14]. In the future, bacteria may be a possible candidate in later lignin application and conversion.

3. Application

3.1. Medical Materials

Due to its excellent antioxidant and antibacterial characteristics, lignin has been employed to create drug delivery polymers called hydrogels [1]. Morales et al. prepared hydrogels originating in modified lignins and their byproducts. Mechanical characteristics, glass transition, temperatures, morphology and swelling capabilities were investigated. Also, by examining release kinetics concerning self-extracted quercetin from these hydrogels, the potential for employing them as drug delivery systems was investigated. They showed promising outcomes during the drug loading and release researches [15].

Besides, there exist specific composites originating in lignin which is also capable of being employed to establish pharmaceuticals to ease diseases [1]. Filho et al. studied the immunomodulatory of lignins originating in Opuntia cochenillifera and Opuntia fícus-indica (two species of Cactaceae) against mice splenocytes. Apart from changes in the potential of the mitochondrial membrane, an increase in cytosolic calcium levels and ROS was detected as activation

signals for both lignins. Additionally, elevated productions of IL-10, IL-6 and TNF were induced by lignins, and NO release was decreased. As a result, these lignins have a lot of promise as possible therapeutic agents and molecules blessed with a proinflammatory profile [16].

3.2. Energy Materials

Recently, growing lignin is produced, it is attainable cheaply. The correspondingly low cost and the leading superiority of environmental friendliness get it to be one kind of absorbing ingredient for the manufacture of anode materials for supercapacitors and batteries.

For example, Li et al. devised one kind of carbon stuff with pores from the natural lignin sacrificing one metal–organic framework as this template. Carbon anode's as-prepared specific capacity was a high 420 $mAh \cdot g^{-1}$. With three hundred cycles at 0.2 $A \cdot g^{-1}$, its capacity retention is ninety-nine percent. What`s more, it maintained an efficiency of 85% even after a lengthy period of one thousand cycles, demonstrating the designed anode usefulness inside lithium-ion batteries [17]. This study offers a potential candidate anode for LIBs that is both affordable and renewable, as well as a workable design strategy [17].

3.3. 3D Printing Materials

Incorporating lignin into the conventional plastic 3D printing materials yields compounds which are able to be employed for one more cost-effective and ecologically friendly 3D printing procedure, which recently attract attention. Arias-Ferreiro et al. investigated the impact of unaltered lignin upon 3D printed light-curable acrylic compounds [18]. Contents with the low lignin result in 3D printed compounds blessed with higher smoothness, increased hardness (Shore A grown by 5%), and increased wettability (contact angles dropped by 19.5%). When compared to lignin-free polyaniline composites, the lignin/ p-toluensulfonic doped polyaniline/acrylic composite clearly improved in the conductive substance dispersion, lessening average surface roughness by sixty-one percent. Simultaneously, the conductivity was improved by one order of magnitude, achieving a high value of up to 10^{-6} $S \cdot cm^{-1}$ [18]. As a result, adding organosolv lignin in wastes from wood to 3D printed photocurable resins offers a convenient, affordable possible utilization for creation of new, highly valuable, bio-based commodities.

4. Conclusion

To control the depolymerization process to obtain desirable chemical components. This article introduces several depolymerization and conversion techniques for lignins. Different approaches each have their own advantages and disadvantages.

There exists the most efficient way, Pyrolysis. It is used for turning biomass and lignin into crude bio-oil for producing energy from the perspective of lignin valorization. Yet, on account of its elevated conversion rate and specificity, chemical catalysis should be regarded as the most suitable method when depolymerizing lignin for the creation of particular important chemicals. Also, the catalytic reaction conditions are less severe than those of pyrolysis, which makes it easier to manage the facility and reaction. Another method of increasing the lignin value is biological depolymerization. The research on depolymerization of biological lignin is still valuable and important even though the effectiveness of turning lignin polymer into monomers or other chemicals are low because these technologies can also offer one environmentally friendly alternative method in diverse therapies by chemicals.

Lignin is considered a potential material since it is biocompatible, affordable, and abundant in nature, despite some technical difficulties in lignin depolymerization. Lignins can be employed as drug delivery materials and medications in the domain of medicine. They are also capable of being utilized in energy storage and conversionas well as 3D printing. Innovation of lignins will be updated endlessly due to the rise in market demand for renewable resources.

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