



Heterogeneous Catalysis as a Tool for Production of Aromatic Compounds From Lignin

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Heterogeneous Catalysis as a Tool for Production of Aromatic Compounds From Lignin

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1 INTRODUCTION

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The perspective depletion of fossil fuels and the need to control emissions of greenhouse gases has provoked research in finding alternative renewable resources. Among them, lignocellulose is a largely underutilized form of natural biomass, not directly competing with food resources. However, the difference in structure, composition and complexity of biomass as compared with crude oil requires an extensive reevaluation and rethinking of feedstock processing strategies to render economically viable the proposed transition to a bio-based industry [1,2].

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Lignocellulosic biomass is essentially composed of three components: cellulose (38%–50%), hemicellulose (23%–32%), and lignin (15%–25%). Cellulose is currently hydrolyzed to glucose and converted into valuable products, such as ethanol biofuel, and platform chemicals, such as levulinic and formic acids, gamma-valerolactone, and derived products. Hemicellulose has potential applications for biofuel production, and for the generation of valuable chemicals intermediates, such as furfural. Lignin is the most underutilized fraction of lignocellulose. The total lignin availability in the biosphere exceeds 300 billion tons and annually increases by around 20 billion tons [3]. Annually, 40–50 million tons of roughly isolated lignin are available as waste of the pulp and paper industry and biorefineries. Only

approximately 2% of the lignin available is commercially exploited while the remainder is burnt as a low-value fuel in the lignocellulose fractionation units [4].

1.1 The Potential of Lignin

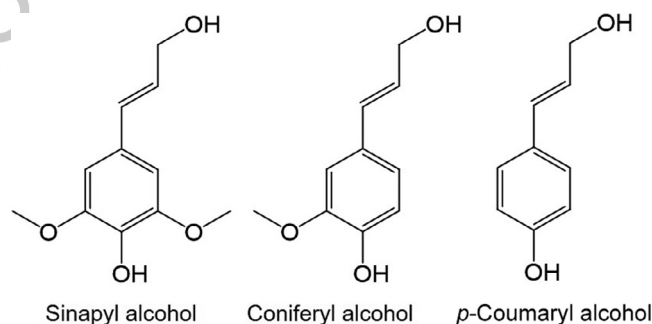
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Lignin is an important component of secondary cell wall of plants, which forms a matrix between cellulose fibrils and provides mechanical strength and chemical protection to the plant. Lignin is a tridimensional amorphous polymer composed of three types of propylphenyl monolignols (Fig. 13.1), differing by their degree of substitution: sinapyl alcohol (S), coniferyl alcohol (G), and *p*-coumaryl alcohol (H) units (see Fig. 13.1).

p0025

According to the source from which it derives, lignin presents a high diversity of chemical structure, not only in terms of percentage of each monolignol, but also from the different ways the building blocks are connected to each other through various crosslinked C—O and C—C bonds, including β -O-4, β -5, β - β , 4-O-5, 5-5, or β -1 to form a complex matrix (see Fig. 13.2) [5]. Generally softwood has 45–48 wt.% and hardwood has 60 wt.% of β -O-4 aryl glycerol ether bonds. Softwood has approximately 5 wt.% and hard wood has 0–2 wt.% of dibenzodioxocin 5-5'- α , β -O-4' bonds. In addition, softwood has 3.5–8 wt.% and hardwood has 6–9 wt.% of



f0010 FIG. 13.1 Monolignols, the building units of lignin.

2. BIO-BASED PROCESSES AND BEYOND

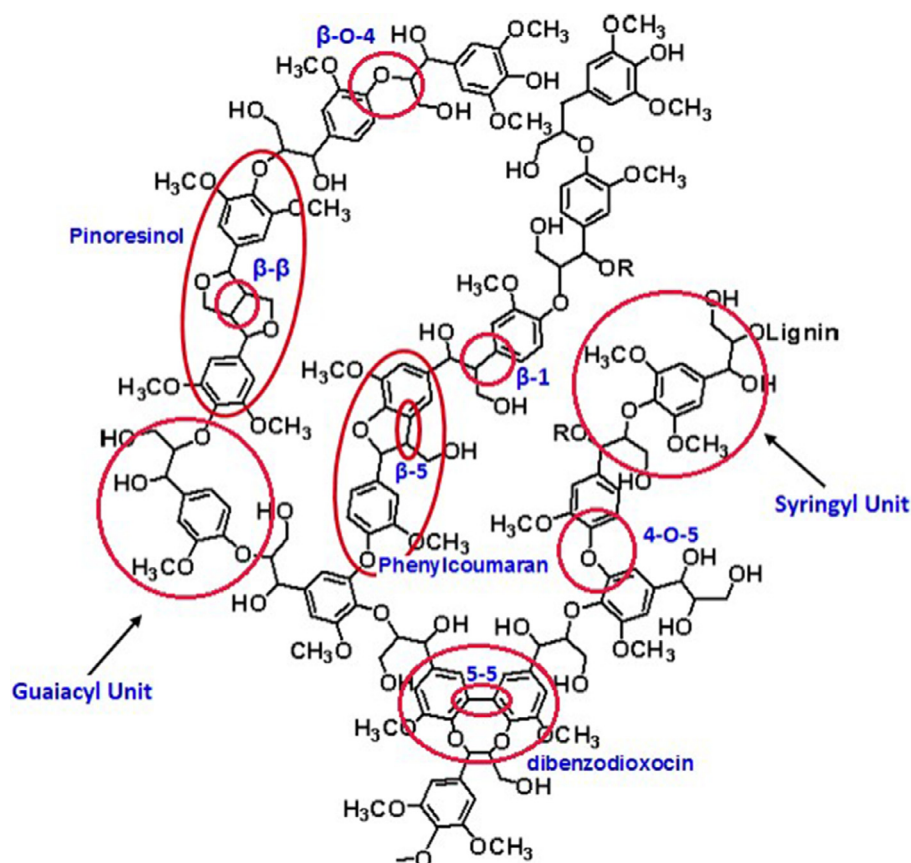


FIG. 13.2 Idealized structure of lignin with the most representative functional groups.

diphenyl ether 5-O-4' linkages [6,7]. The presence of these propylphenolic groups is at the basis of the interest for lignin, as a large reservoir of aromatic hydrocarbons and fine and specialty chemicals [8].

1.2 The Challenges of Lignin

Ultrasformed lignin finds property-based applications as components of epoxy glues for wood and packages, as fillers for bitumen and oil drilling fluids, or as a precursor of carbon fibers [9]. Considering the rich chemical functionalities of lignin, it is really promising to develop methods of depolymerization for the

production of phenolic monomers for the polymer, flavor, and pharmaceutical industries [10]. Development of effective catalytic processes is badly needed in lignin depolymerization to orient the selectivity toward well-defined monomers, in order to minimize the separation costs, which can nullify the economic viability of depolymerization.

In order to tailor processes for the chemical valorization of lignin, a considerable challenge is to interpret the exact structural arrangement in the macromolecule. The structure of native lignin is only accessible by analysis of its hydrolysis products, which nature depends on the separation process used. Moreover, the

variability of lignin coming from different plant species hinders the developments of set protocols for lignin depolymerization. To cope with lignin's chemical complexity, a multifaceted, translational approach is required, which includes new analytical tools for structure characterization of substrates and products. The lignin depolymerization technology is still in the early phases of R&D. Taking advantage of lignin as a reliable alternate source to fossil resources relies on the interest from game-changing investors, which will provide funding options when the depolymerization technology will reach a sufficient level of maturity [5].

2 LIGNIN MODEL MOLECULES

The complexity and variability of the structure of lignin has complicated the study of industrial lignin as a substrate. This fact has prompted the reliance on simplified, low molecular weight lignin model compounds to study lignin depolymerization. The basic advantage of these models is that they mimic the linkages present in the real lignin polymer, which helps in a better understanding of the breaking mechanisms of specific bonds. Furthermore, similar molecules are often present in the lignin degradation streams, after the depolymerization of lignin itself. The small compounds generated by fragmentation of lignin model compounds could be separated by chromatographic techniques, and further identification is possible using conventional analytical methods like GC-MS and NMR. Therefore, better and reliable characterization can be done because often only one type of linkage is present in the model molecule, which helps in understanding the reaction paths and the catalytic performance.

Catalytic systems can be studied in detail on oligomers and dimers aiming to understand the reactivity and selectivity of multifunctional group models. This is often the first step of

research in lignin valorization. Considering the solubility and polyfunctionality of native lignin, as well as the repolymerization with an intermediate, demand a further step in the research planning. Different molecules are used as model compounds for different bonds of native lignin (see Fig. 13.3).

2.1 β -O-4 Model Molecules

It is the most abundant linkage found in lignin. The ether bond is readily cleaved; indeed, the cleavage of these bonds during alkaline pulping constitutes the principle pathways in which the lignin is depolymerized and generates monomers with a phenyl propane structure.

The fragmentation of these linkages tends to lead to the generation of water-soluble oligomers containing phenolic hydroxyl groups [11]. The disruption of β -O-4-containing model molecules results in simpler analogs of the coumaryl, coniferyl, and sinapyl alcohols of monolignols (see Fig. 13.1). Secondary products obtained during the fragmentation include 3-hydroxypropaldehyde and arenes, with various aldehyde or alkyl side chains [12]. Successive oxidation reactions of coniferyl alcohol form vanillin, or lead to oxidation of the aromatic ring and form quinones (see Fig. 13.4 for possible lignin depolymerization products).

2.2 C—C Linkage Model Molecules

The C—C linkage in the lignin/model molecules are the hardest to break. Although carbon-carbon linkages are present in the native lignin polymer, additional carbon-carbon bonds can be formed during lignin pretreatment, such as in alkali-promoted condensation reactions during kraft pulping [11]. The development of catalysts capable of performing these disruptions (particularly the aryl-aryl linkages) is therefore a considerable challenge that has not yet been adequately addressed. Model compounds with

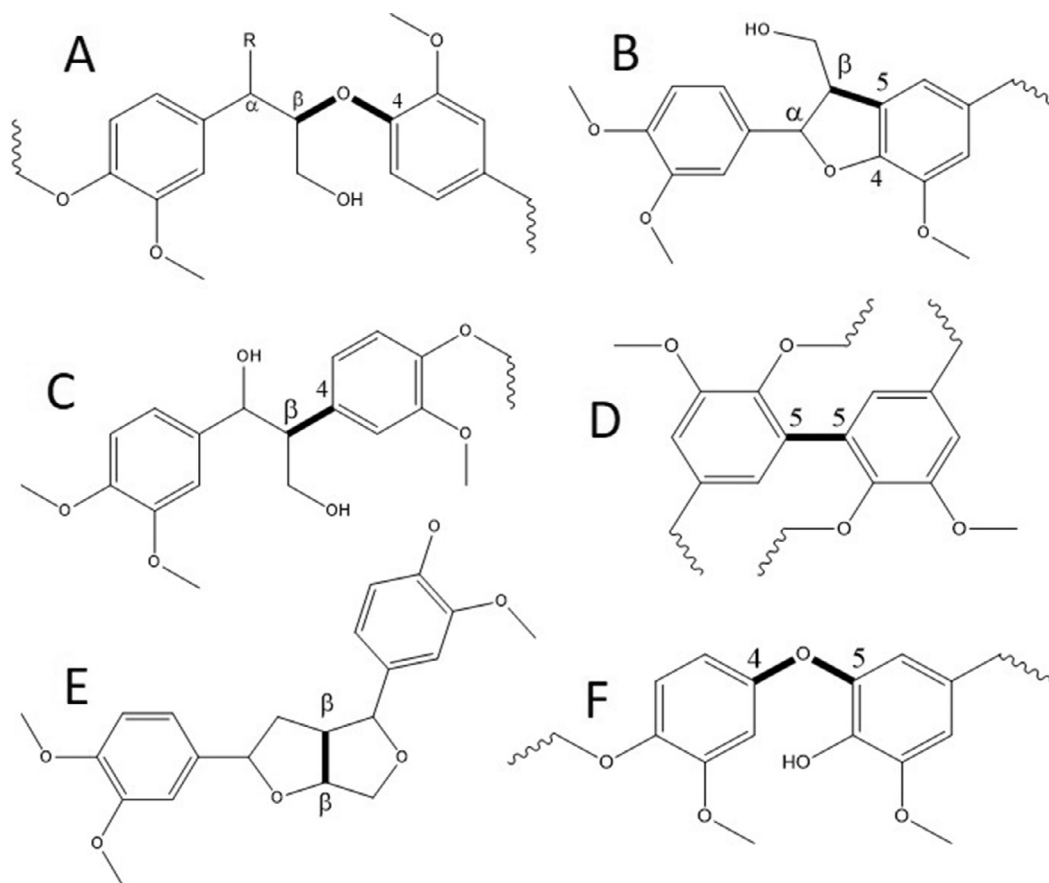


FIG. 13.3 The main linkages in the lignin structure: β -O-4 (A), β -5 and α -O-4 (B), β -4 (C), 5-5 (D), β - β (E), 4-O-5 (F).

these linkages usually involve dimeric arenes, with varying methoxy and hydroxyl substituents on the arene, which resemble dimers of *p*-coumaryl or coniferyl alcohols.

resulting from the disruption of only one bond (i.e., the R-O-4 ether linkage) leaves compounds containing isolated β -5 linkages. In some instances, the β -5 bond remains intact and products resulting from the oxidation of the arene ring are observed [7].

2.3 Phenylcoumaran Model Molecules

The β -5 linkage is often located in a five-membered oxygenated ring fused with an aromatic ring in a coumaryl structure. In the model molecules, the rupture of both of these bonds often yields monomers such as vanillin and vanillic acid. Because of the inherent complexity in selectively disrupting both bonds, products

2.4 α -O-4 and 4-O-5 Linkages Model Compounds

Compounds containing α -O-4 have also been observed in the lignin network, however, modern NMR experiments do not confirm the presence of noncyclic α -O-4 moieties [7].

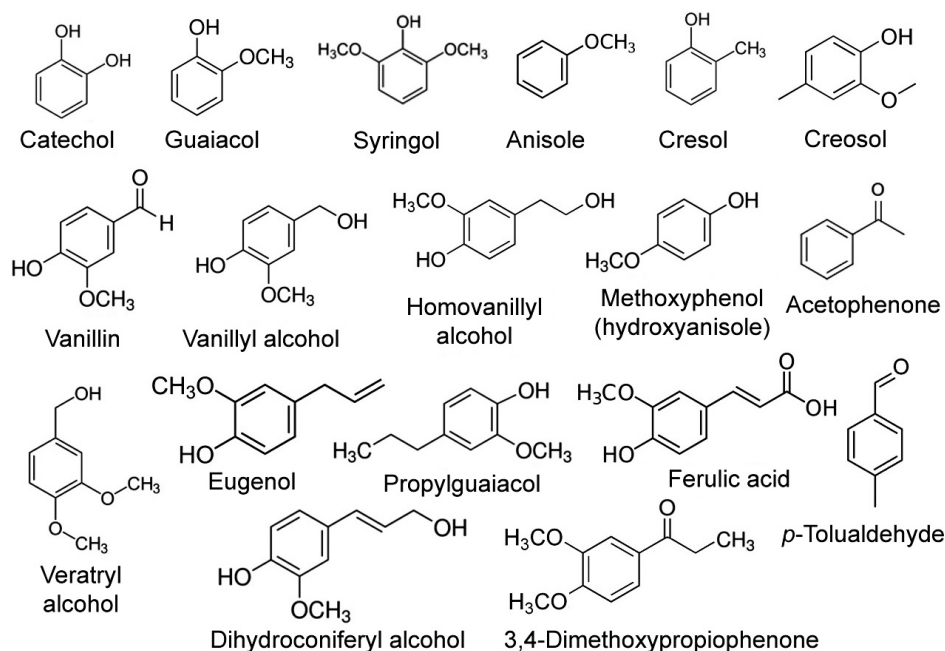


FIG. 13.4 Common monomers to be familiar with in lignin chemistry.

The 4-O-5 aryl-aryl ether linkage is, however, present in lignin mainly as the result of demethoxylating oligomer-oligomer couplings and leads to branching of the polymer. Some model compounds have been studied in order to understand the chemistry of this particular linkage as well.

3 LIGNIN DEPOLYMERIZATION STRATEGIES

Catalysts are essential to facilitate energy and atom-efficient lignin depolymerization and to selectively deoxygenate the products for further applications. Considerable efforts have been devoted to this field, but current methodologies are not satisfactory from the economical or environmental viewpoint. There are generally three main approaches for depolymerization: thermochemical (pyrolysis), biochemical, and chemical processes. In this chapter, we will deal

essentially with the latter class of processes, under the aspects of hydrolysis, oxidation, and reduction. Pyrolysis refers to the thermal treatment of biomass/lignin in the absence of oxygen, with or without any catalysts at temperature between 300°C and 600°C [3,13]. The cleavage of OH functional group linked to the aliphatic side chain, the breaking of alkyl side chain, aryl ether bonds, and linkage between aromatic ring occur when the temperature increases, forming a mixture of phenol, guaiacol, syringol, and catechols. Cracking of the aromatic ring occurs at temperatures above 500°C [13,14]. The process is poorly selective and is affected by several factors including feedstock type, heating rate, and reaction temperature [15]. Biochemical methods have also been employed for the depolymerization but, despite interesting selectivities and mild conditions required, the time to grow the microorganisms/fungi and dilution of the system can make the process slow and less efficient [16]. In the chemical conversion, ether bonds C-O-C

are targeted. Compared with thermochemical and biochemical processes, the chemical treatment of lignin has shown reliable results in terms of high selectivity and reaction control, with efficient valorization of lignin into functionalized aromatics.

p0085 The development of selective and robust catalysts must be a core effort in a biorefinery program. While selecting the catalytic route, there are two main considerations:

- o0010 1. Maximization of activity and selectivity of the catalyst under the chosen conditions (as mild as possible), bearing in mind the bulky nature of biomass source and the reaction conditions
- o0015 2. Repolymerization and self-condensation capability of lignin under processing conditions, due to the formation of radicals and/or C—C bonds through self-condensation reactions, which eventually leads to a complex pool of re-condensed aromatics [1].

p0100 The accountability of successful industrial scale production of chemicals is based on the selection of optimized reaction conditions. These include the chemical, engineering, and financial aspects of a feasible reaction. This chapter outlines the major pathways of lignin depolymerization, which can directly affect the reaction mechanisms controlling the nature and yield of valuable products. For the chemical depolymerization of lignin, a choice to be made among homogeneous and heterogeneous catalysis is on the top of the list.

s0055 4 HOMOGENEOUS CATALYSIS FOR LIGNIN DEPOLYMERIZATION

s0060 4.1 Base-Catalyzed Depolymerization

p0105 Lignin depolymerization through base-catalyzed hydrolysis is a well-known and straightforward route for the production of monomeric substituted phenols. The mineral bases used as

catalysts, such as NaOH, KOH, and sometimes LiOH, are cheap and commercially available but require corrosion-resistant materials and treatment of waste sewage. Typically, reflux boiling of lignosulfonates in 12% NaOH solutions in nitrogen atmosphere provided up to 7% yields of high-value added vanillin [17]. The reaction proceeds with cleavage of alkyl-aryl ether bonds, including (β -O-4), which is considered to be the weakest bond in the lignin structure [13,18]. However, in the base-catalyzed lignin hydrolysis reactions, the selectivity and yield are chiefly dependent on temperature, concentration and nature of the base, time, pressure, and the lignin/solvent ratio [19]. Beauchet et al. worked on base-catalyzed depolymerization reactions on less reactive Kraft lignin using NaOH as a base catalyst [20]. Total yield of identified monomers reached a maximum of 8.4 wt.% at 315°C. Although the base-catalyzed process was simple, it needed to be carried out at a high temperature, and the control of selectivity was still difficult. The production of monomers is favored by high temperature and longer reaction time. The final yield is effectively decreased due to the formation of solid residues by the condensation reaction of intermediates and products. In base-catalyzed reactions, control of the rate of re-polymerization and condensation is the key challenge [3]. This fact is supported by the studies of Lercher and coworkers who carried out base-catalyzed liquid-phase hydrolysis of organosolv lignin at 300°C and 25 MPa using NaOH as a catalyst [21]. Syringol (4.1 wt.%), hydroxyacetophenone (1.6 wt.%), and guaiacol (1.1 wt.%) were the major products of base-catalyzed hydrolysis and that oligomers form as secondary products. Oligomerization and polymerization of these highly reactive products, however, limit the amount of obtainable low-molecular-weight phenolic products. The inhibition of parasite oligomerization reactions is crucial to ensure a high yield of monomeric products. For analytical purposes this can be achieved by using a capping agent, such as boric acid, to suppress addition and condensation reactions of initially formed products [21].

s0065 4.2 Acid-Catalyzed Lignin Depolymerization

p0110 Early attempts of acid-catalyzed lignin hydrolysis dates back to the 1920s when Hagglund and Bjorkman distilled lignin with 12% HCl and observed severe repolymerization of the products [22]. The hydrolytic cleavage of α - and β -aryl ether linkages plays a main role in the acid-catalyzed hydrolysis because aryl-aryl ether bonds, phenolic C—O bonds, and C—C bonds between aromatic lignin units are relatively more stable and difficult to break.

p0115 Better stabilization of depolymerization products were later obtained in aqueous solutions of organic solvents, where acid-catalyzed hydrolysis was combined with hydrodeoxygenation of the products by hydrogen transfer from hydroxyl-bearing solvents. Hewson and Hibbert studied an acid-catalyzed treatment on maple wood meal by combinations of various acids and alcohols including HCl/ethanol and formic acid/ethylene glycol systems, with the purpose of separating the lignin into water-soluble and water-insoluble components [23]. The low range of temperature (78–200°C) was moderately effective for the degradation of complex lignin into monomers. Later, high temperature conditions were studied on acid-catalyzed reactions. For example, Barth and coworkers studied the effect of 13 wt.% formic acid in ethanol [17]. At temperatures above 360°C the major products were methoxyphenol, catechol, and phenol [17,24]. The optimum reaction time was below 200 min. Formic acid/ethanol solutions in the presence of Pt/C catalyst allowed for the reduction of all carbonyl groups of the products and provided yields up to 7% propylguaiacol, 5% methylguaiacol, and 3% homovanillyl alcohol [25]. In general, acid-catalyzed depolymerization required harsh reaction conditions, which could affect the cost and economic feasibility of the reaction [13].

4.3 Oxidative Lignin Depolymerization

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Oxidative depolymerization to vanillin has been the main historical industrial process of valorization of vanillin, justified by the high added value of vanillin as a flavor molecule [26].

The cheap and effective oxidizing agent used is molecular oxygen, bubbled through basic solutions to couple oxidation reactions with alkaline hydrolysis.

Mathias and Rodrigues in 1995 described the classical state of the art, explaining that 60 g/L solution of softwood Kraft lignin, treated at 120–130°C for 4–6 h in the presence of 2 N NaOH, could yield a maximum 13% (w/w) of vanillin [27]. In the same year, the Monsanto process at 160°C in 10% NaOH solution claimed a yield of vanillin of 19% when softwood sulfite liquor was oxidized through carefully controlled oxygen pressure [28]. It is interesting to observe that these yields were normalized on the assumed lignin content in the sulfite liquor. When the vanillin yield in the same commercial process was expressed on the basis of the lignosulfonate mass, the yield value was not higher than 7% [29,30].

The original patent of Monsanto cited the optional use of Cu(II) salts as oxidants and catalysts. Copper salts were used when the Monsanto process was bought by Borregaard. and cobalt and cerium salts were also tested [29]. Pacek et al. studied the Borregaard process under highly alkaline conditions, catalyzed by Cu^{2+} at 120°C, 140°C, and 160°C and pressures up to 10 bars in flow reactors [30]. They were able to determine that nearly 55% of the vanillin formed was issued from hydrolysis and 45% from oxidation [6]. Yamamoto et al. found that the use of $\text{Bu}_4\text{NOH}\cdot 30\text{H}_2\text{O}$ (tetrabutylammonium hydroxide 30-hydrate) as reaction medium—instead of the commonly used aqueous NaOH solution—in aerobic oxidative degradation of lignin improved the yield of aromatic monomers [31]. At 120°C, total monomer yield of 6.5%–22.5% was obtained with vanillin and vanillic acid as the main products.

5 HETEROGENEOUS CATALYSIS FOR LIGNIN DEPOLYMERIZATION

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Homogeneous catalysis for the depolymerization of lignin presents several drawbacks, notably in separation of catalyst from the reaction mixture and corrosiveness when strong mineral acid and bases are used [32]. Depolymerization by heterogeneous catalysis offers promising strategies in spite of mass transfer limitations from bulk lignin to catalyst surface [1]. Heterogeneous catalysis means that catalysts and reagents form different physical phases. This type of catalysis is usually favored because it can be carried out over a wide range of operating conditions and offers easy separation and recyclability of the catalyst. The product recovery and purification are significant industrial facets of catalysis, on which the advantages of heterogeneous catalysis are based. As David Parker (ICI) said on April 24, 1988, during the 21st Irvine lectures at the University of St. Andrews in Scotland, "At the molecular level, there is a little to distinguish between homogeneous and heterogeneous catalysis, but there are clear distinctions at the industrial level." This chapter discusses the heterogeneous forms of catalysts applied to the fragmentation of lignin via pyrolysis, reduction, and oxidation pathways.

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5.1 Catalytic Pyrolysis

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Liquefaction by pyrolysis has been developed to convert lignocellulosic biomass to bio-oil. It involves a rapid heating of biomass at high temperatures (450–650°C) in the absence of oxygen to generate a mixture of noncondensable liquid, gas, and oil mixtures [33]. The main target of biomass pyrolysis is the reduction of the oxygen content of biomass to make it suitable as a fuel component. Lignin, as the biomass component with the lowest O/C ratio, has been extensively

studied as a bio-oil precursor. Indeed, the activation energy of lignin pyrolysis is lower than the activation energy of cellulose pyrolysis [34].

The requirement for high temperatures of the pyrolysis processes is energy intensive and the final product is a mixture of a large number of components, mainly substituted aromatics. It is considered that the product distribution is the result of a number of reactions where non-volatile compounds are broken down into heavy volatile compounds at first, and finally cracked into volatile alkyl aromatics and ultimately to coke and gas [33].

The addition of a catalyst to the pyrolysis reactor introduces some selectivity and directs the distribution of the product stream toward higher-value desired products. The proportion of each pyrolysis product is dependent on the process variables, particularly temperature and heating rate [34]. At lower temperatures the first bonds cleaved are hydroxyl and ether groups attached to alpha or beta carbons to form condensable volatile products and water. Large fractions of methoxyphenols, such as substituted syringol and guaiacol, are present in the condensable volatile products as the methoxyl groups show more resistance than the ether linkages against thermal degradation. C—C bond is the strongest bond in many transformations, its breaking only occurring at very high temperatures [35].

Several kinds of catalysts have been tested for lignin pyrolysis. Zhan et al. studied the product distribution obtained from lignin at 400°C, 500°C, and 600°C on several catalysts with different pore structures and acidity—HZSM-5, MCM-41, TiO₂, ZrO₂, and Mg(Al)O [36]. It was concluded that HZSM-5 was the best catalyst for fast pyrolysis whereas the basic catalysts trigger reduction of the liquid, leading to oligomers and coke formation. Ohra-aho and Linnekoski studied the activity of HZSM-5, zeolite Y, and Pd/C on Kraft lignin and pine wood

lignin at 600°C. The catalyst with the larger influence on product distribution was the zeolite Y, which increased the extent of demethylation and demethoxylation of the monoaromatic products [37]. The yield of liquid and the selectivity of products can be monitored by tuning acidity and pore size of zeolites. Ma et al. compared the activity of several zeolites with micro-pore size from 0.5 to 0.7 nm, and the Si/Al ratio from 7 to all silica [38]. Zeolite US-Y, the catalyst with the largest pores and the highest density of acid sites, allowed for an increase of the yield of liquid to 75% from 40% without a catalyst. Zeolite H-ZSM5 with smaller pores and a smaller number of stronger acid sites was able to increase the selectivity of phenol alkoxy species. The small size of pores is expected to prevent repolymerization and coke formation reactions.

p0165 Studies on model molecules have contributed to a better understanding of the mechanisms of lignin pyrolysis. For instance, Zhang et al. have recently investigated the catalytic pyrolysis products of guaiacol over ZSM-5 between 400°C and 650°C, showing that the mechanisms of pyrolysis are similar to the dehydration, decarbonylation, and hydrogen transfer pattern of the geological formation of coal and hydrocarbons from lignocellulosic biomass [39,40].

s0085 5.2 Reductive Transformations

p0170 The idea of reductive depolymerization of lignin began in the late 1930s when the insoluble biomass isolated from tree sawdust was hydrogenated. The selective catalytic reduction of lignin has attained great attraction for the improvement of bio-oil over the past few years. For lignin reductions, typical reactions involve the removal of the extensive functionalities of the lignin subunits to form less substituted monomeric compounds, such as phenols, benzene, toluene, or xylene (BTX). These simple aromatic compounds can then be hydrogenated to alkanes for fuel applications or used as

platform chemicals for the synthesis of bulk and fine chemicals using technology already developed by the petrochemical industry. The biomass or lignin model molecules are subjected to hydrogenating conditions for the production of high yield phenols and aromatics. Oxygen is generally removed in the form of H₂O and CO/CO₂ by means of different catalytic processes such as hydrogenation, C—O bond hydrogenolysis, dehydration, decarboxylation, and decarbonylation [1]. Bifunctional catalysts having both acid and noble metal can give interesting results where they can simultaneously break ether bonds and deoxygenate the resulting monomers in the presence of H-donor solvent or H₂.

In 1938, Harris et al. studied the catalytic p0175 hydrogenation of hardwood lignin at 260°C for 18 h in the presence of a copper-chromium oxide catalyst and successfully achieved 70% conversion [41].

Pepper et al. extended comparative studies p0180 on the effectiveness of different metal catalysts (Raney Ni, Pd/C, Rh/C, Rh/Al₂O₃, Ru/C, Ru/Al₂O₃) for the hydrogenolysis of spruce wood lignin in dioxane/water at 195°C under 3.3 MPa H₂ pressure [42]. The best results were obtained on Rh/C, with a yield of identified monomers of 33%, the main products being 4-propylguaiacol and dihydroconiferyl alcohol [43]. The distribution of products was greatly influenced by catalyst loading and pH variations resulting in over-hydrogenated or degraded products.

In previous years, many types of metal cata- p0185 lysts have been tested for hydrogenation of model molecules, commercial lignin or lignin-issued bio-oil (see Table 13.1). Metal catalysts are very effective in the improvement of the fuel properties of bio-oil, by decreasing its O/C ratio. Hydrodeoxygenation of substituted guaiacols and syringols, among the main components of bio-oil, was achieved on a variety of metal catalysts at 250–300°C under 40–50 bar H₂ with high yields of cycloalkanes, provided an

TABLE 13.1 Some Recent Literature on the Heterogeneous Catalysis of Hydrogenation of Lignin and Model Molecules

Catalyst	Solvent	Experimental Conditions	Substrate	Major Products	Ref.
Pd/C, H ₃ PO ₄	H ₂ O	250°C, 50 bars H ₂	Phenolic monomers	79% cycloalkanes	[44]
Ni/SiO ₂ -ZrO ₂	Dodecane	300°C, 50 bars H ₂	Guaiacol	97% cyclohexane	[45]
Raney Ni + Nafion/SiO ₂	H ₂ O	300°C, 40 bars H ₂	4-Propylguaiacol	74% alkylcyclohexane	[46]
RhPt/ZrO ₂	Tetradecane	400°C, 50 bars H ₂	Guaiacol	43% cyclohexane	[47]
Rh/Ru nanoparticles	[bmim][TF ₂ N]	130°C, 40 bars H ₂	4-Ethylphenol	99% ethylcyclohexane	[48]
Ru/Nb ₂ O ₅	H ₂ O	250°C, 7 bars H ₂	Birch lignin	21% arenes, 8% cycloalkanes	[49]
Ru/C	THF	250°C, 40 bars H ₂	Formaldehyde-treated beech lignin	77% phenolic monomers	[50]
Ni/C	THFA, dioxane	220°C, 20 bars H ₂	Beech lignin	14% phenolic monomers	[51]
Ni ₇ Au ₃ , NaOH	H ₂ O	160°C, 10 bars H ₂	Birch lignin	11% phenolic monomers	[52]
Zn/Pd/C	Methanol	150°C, 20 bars H ₂	Vanillin	81% cresol	[53]
Ni/TiN	Ethanol	150°C, 12 bars H ₂	Diphenyl ether	49% cyclohexanol, 46% benzene	[54]
Ni/SiO ₂	Decalin	130°C, 30 bars H ₂	Dihydrobenzofuran	95% 2-ethylphenol	[55]
Pt/SiO ₂	Gas phase	400°C, flowing H ₂	Anisole	42% phenol, 33% cresols	[56]
Pt/HBeta	Gas phase	400°C, flowing H ₂	Anisole	52% benzene, 28% toluene	[56]
Pd/C	Dioxane	200°C, 1 bars H ₂	Miscanthus lignin	15% phenolic monomers	[57]
Raney Ni-H-USY	Aqueous methanol	270°C, N ₂	Bamboo lignin	28% phenolic monomers	[58]
Ni/C	Methanol	200°C, Ar	Birch lignin	49% phenolic monomers	[59]
CoMo/Al ₂ O ₃	Hexadecane	300°C, 69 bars H ₂	4-Methylcatechol	25% methylcyclohexane, 20% cresol	[60]
Cu-Mg-Al mixed oxides	Methanol	180°C, 40 bars H ₂	Organosolv lignin	63% phenolic monomers	[61]
MoOx/CNT	Methanol	260°C, 30 bars H ₂	Birch lignin	47% phenolic monomers	[62]
CoMo, NiMo	Tetradecane	400°C, 50 bars H ₂	Guaiacol	46% phenolic monomers	[47]
Mo ₂ N	Decalin	300°C, 50 bars H ₂	Guaiacol	47% phenol	[63]
FeS ₂ /C	Cyclohexane	300°C, 100 bars H ₂	Dibenzyl ether	98% toluene	[64]
MoO ₃	Gas phase	320°C, flowing H ₂	Guaiacol	31% phenol	[65]
MoO ₃	Gas phase	320°C, flowing H ₂	Anisole	44% benzene	[65]
Ni ₂ P/SiO ₂ or Co ₂ P/SiO ₂	Gas phase	300°C, flowing 20% H ₂ in N ₂	Guaiacol	48% benzene	[66]
WP/SiO ₂	Gas phase	300°C, flowing 20% H ₂ in N ₂	Guaiacol	60% phenol	[66]

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acid function was also present [44–46]. The nature of the metal catalysts used spanned from noble metal palladium to Raney nickel and the acid function could be provided by the addition of an inorganic acid, such as H_3PO_4 [44], or by a heterogeneous co-catalyst, such as silica-zirconia or Nafion [45,46]. At such high temperatures, water has proven to be a good solvent for the reaction, allowing easy separation of the less polar hydrocarbon products at the end of the process [44,46,49]. The use of Rh/Ru nanoparticles and a Brønsted-acid ionic liquid ([bmim][TF2N], 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) as the solvent allowed for still higher yields of cycloalkanes at a much lower temperature of 130°C [48], while a lower hydrogen pressure of 7 bar allowed only partial depolymerization and hydrogenation of lignin, giving a low yield of arenes and cyclohexanes [49].

p0190 In the absence of an acid function, metal catalysts allowed effective depolymerization of lignin at 250°C under 40 bar H_2 but the product was mainly a phenolic bio-oil with no significant hydrogenation of the aromatic rings [50]. Metal catalysts as different as Ru, Ni, Zn, Pd, Ni_7Au_3 have been used with yields of phenolic monomers mainly depending on temperature and H_2 pressure [50–53]. Lin et al. studied the mechanism of hydrodeoxygenation of guaiacol, using mono and bimetallic Rh-based catalysts on zirconia and showed that RhPt significantly accelerated the hydrogenation to cycloalkanes by comparison to plain Rh or RhPd [47]. Studies on model molecules showed that ether bonds were easily cleaved also in mild hydrogenation conditions [54,55].

p0195 The difference between simple metal catalysts and bifunctional metal-acid catalysts was highlighted by Zhu et al. in a mechanistic study of the hydrogenation of anisole (methoxybenzene) over a bifunctional metal-zeolite catalyst Pt/HBeta or a monofunctional catalyst Pt/SiO₂ [56]. Anisole fed in gas phase at 400°C in flowing

H_2 at atmospheric pressure was converted to phenolic monomers by demethylation and transalkylation on the metal catalyst and was hydrogenated to BTX (benzene, toluene, xylene) on the bifunctional catalyst.

Molecular hydrogen was not the only possible agent of hydrodeoxygenation of lignin. Internal hydrogen transfer from alcohol groups has been suggested by Hartwig and co-workers to be active in breaking ether bonds of lignin [57]. They found that H_2 pressure of 1 atm was used to reduce the weak amount of olefinic bonds present in the miscanthus lignin used. Hydrogen transfer from a hydrogen-donor solvent has been shown to be effective in the hydrodeoxygenation of lignin, 49% yield of phenolic monomers having been attained by treatment of birch lignin in methanol on a Ni/C catalyst at 200°C in an inert atmosphere [58,59].

Nonmetal catalysts were also tested in lignin hydrogenation, looking for a parallel with the highly stable classical sulfided CoMo and NiMo hydrotreatment catalysts of oil refineries. In a seminal study, Petrocelli and Klein investigated the hydrodeoxygenation of several model compounds over a sulfided $\text{CoOMoO}_3/\gamma\text{-Al}_2\text{O}_3$ commercial catalyst at 300°C and 69 bars of hydrogen pressure [60]. Compounds with aromatic methoxyl groups (4-methylguaiacol, eugenol, vanillin) underwent primary demethylation as their major reaction. Hydroxyl groups were removed readily at temperatures well below those required for thermal dehydroxylation. Catalytic cleavage of the inter-aromatic unit linkages of *o*-hydroxydiphenylmethane and phenyl ether was facile, while *o,o'*-biphenol was converted to single-ring products through dibenzofuran and 2-phenylphenol intermediates. Previously, yields of phenolic monomers as high as 47%–63% were obtained by lignin depolymerization at $180\text{--}260^\circ\text{C}$ under 30–50 bar H_2 on catalysts as different as Cu-bearing basic mixed oxides issued from hydrotalcite decomposition or on molybdenum oxides on carbon nanotubes [61,62]. Molybdenum oxides and nitrides, as well

as sulfides and phosphides of different metals, were tested in mechanistic studies of hydrodeoxygenation of model molecules at temperatures as high as 400°C and under H₂ pressure up to 100bars or in a flowing hydrogen atmosphere [47,63–66]. The main results of these studies were the suggestion of a scale of reactivity of the functional group of phenolic molecules, with ether bonds being more easily hydrogenated than methoxy groups, phenolic OH being the more resistant to hydrodeoxygenation. The interest of flow processes for the depolymerization of lignin is evident, albeit the results on model molecules in the gas phase at high temperatures are surely difficult to transpose to the reactivity of lignin of higher molecular weight.

5.3 Oxidative Transformations

Oxidative treatments of lignin are aimed to the production of high added-value aromatics, especially aromatic aldehyde flavors. The increase of the O/C ratio in oxidative treatments render them inappropriate for the production of fuels but justifies some interest in total oxidation of lignin-containing paper mill wastes or selective oxidation of lignin-derived alcohols to aldehydes [12,67–69]. In this chapter, we will only examine applications of heterogeneous catalysis to selective oxidative fractionation of lignin or model oligomers (Table 13.2).

The formation of aromatic aldehydes by oxidative cleavage of model molecules containing β-O-4 bonds was studied on supported homogeneous catalysts using hydrogen peroxide as the oxidant. Crestini et al. used methyltrioxorhenium immobilized on poly(4-vinyl pyridine) or polystyrene at room temperature in acetic acid whereas Badamali et al. used Co(salen) complexes in SBA-15 mesoporous silica in acetonitrile with microwave heating, obtaining 21%–28% yields of guaiacol [70,71]. Mottweiler et al. inspected Cu-V hydrotalcites for catalytic activity in the cleavage of the lignin model compound erythro-

1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol with molecular oxygen as the oxidant [72]. High yield of veratrylaldehyde was observed at 130°C but pyridine had to be used as a solvent of the reaction.

Nitrogen-containing graphene materials were also tested for the oxidative cleavage of β-O-4 bonds by using tert-butyl hydroperoxide as the oxidant [73]. Also at the mild temperature of 120°C, overoxidation to benzylic acid was observed. Deng et al. tested several nonnoble metal oxides as catalysts and reported that cerium oxide can efficiently catalyze the one-pot oxidative conversion of 2-phenoxy-1-phenylethanol in methanol under 10bars of molecular oxygen [74]. The presence of a noble metal in CeO₂-supported palladium nanoparticles (Pd/CeO₂) allowed them to be reduced by a factor of 10, the oxygen pressure needed for the reaction. With both catalytic systems, overoxidation of tolualdehyde to methyl benzoate was observed. The same Pd/CeO₂ catalyst was used in the same reaction conditions—not on a model system but on organosolv lignin. On such a more demanding substrate, high yields of syringaldehyde and vanillin were obtained [74].

Indeed, several heterogeneous catalysts have been successfully used in oxidative depolymerization of several kinds of lignin in conditions similar to the ones of the Monsanto-Borregaard process for the synthesis of vanillin. Sales et al. employed Pd/γ-Al₂O₃ catalysts for the oxidative conversion of alkaline lignin extracted from sugar cane bagasse in both batch slurry and continuous fluidized-bed reactors [75]. Good yields of syringaldehyde and vanillin were obtained in 2M aqueous NaOH solution at 120–140°C. The use of the perovskite-type mixed oxides LaM_{1-x}Cu_xO₃ (M = Co or Fe) has been proposed for the wet aerobic oxidation of cornstalk enzymatic lignin in 2M NaOH under 5bars O₂. Yields of aromatic aldehydes comparable to the Monsanto process were reported and the catalysts were stable after a series of successive

TABLE 13.2 Some Literature on the Oxidation of Lignin and Lignin Model Oligomers by Heterogeneous Catalysis

Catalyst	Oxidant	Solvent	Experimental Conditions	Substrate	Major Products Yield	Ref.
MeRhO ₃ /polyvinyl pyridine	H ₂ O ₂	CH ₃ COOH	Room T	β-O-4 phenolic dimer	28% guaiacol	[70]
Co-salen/SBA-15	H ₂ O ₂	acetonitrile	150°C, microwaves	β-O-4 phenolic dimer	21% guaiacol	[71]
Cu,V-hydrotalcite	O ₂ 6bars	Pyridine	135°C	β-O-4 phenolic dimer	38% veratrylaldehyde	[72]
Graphene nitride	tert-Butyl hydroperoxide	H ₂ O	120°C	β-O-4 phenolic dimer	45% benzylic acid	[73]
CeO ₂	O ₂ 10bar	Methanol	185°C	β-O-4 phenolic dimer	42% phenol, 40% methylbenzoate	[74]
Pd/CeO ₂	O ₂ 1bar	Methanol	185°C	β-O-4 phenolic dimer	41% phenol, 20% methylbenzoate	[74]
Pd/CeO ₂	O ₂ 1bar	Methanol	185°C	Organosolv lignin	5% vanillin, 2% hydroxybenzaldehyde	[52]
Pd/Al ₂ O ₃	O ₂ 5bars	Aqueous 2M NaOH	140°C, flow reactor	Alkaline bagasse lignin	7% hydroxybenzaldehyde, 5% vanillin	[75]
La(Co,Cu)O ₃ perovskite	O ₂ 5bars	Aqueous 2M NaOH	120°C	Steam-exploded cornstalk lignin	12% syringaldehyde, 5% vanillin	[76]
La(Fe, Cu)O ₃ perovskite	O ₂ 5bars	Aqueous 2M NaOH	120°C	Steam-exploded cornstalk lignin	12% syringaldehyde, 4% vanillin	[77]
La-SBA-15	H ₂ O ₂	Aqueous 2M NaOH	microwaves	Organosolv beech lignin	15% syringaldehyde, 9% vanillin	[78]

recycling [76,77]. The best yields in syringaldehyde and lignin from organosolv lignin were reported in a microwave-heated 2M NaOH solution by using hydrogen peroxide as the oxidant and La-SBA-15 as the catalyst [78].

Pineda and Lee reported that oxidative protocols could sometime result in undesirable products because of free radicals-driven recondensation [32]. More complex multistep reaction pathways have been proposed in order to use milder conditions for each step of the process. Samec and coworkers investigated a mild and chemoselective oxidation of α-alcohols β-O-4 glycerolaryl ethers at 80°C on Pd/C catalysts [79,80]. In this reaction, the benzylic alcohol

groups were selectively oxydehydrogenated to the corresponding ketones attaining 60%–93% of yield. Successive Pd-catalyzed β-O-4 bond cleavage of the obtained 2-aryloxy-1-arylethanols by hydrogen transfer from formic acid reached 92%–98% yields of 3,4-dimethoxypropiophenone proposed as a platform molecule.

6 ECONOMICAL ASPECTS OF LIGNIN VALORIZATION

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Virtually all lignin presently available is a coproduct of the pulp and paper industry. However, the development of second-generation

p0235

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biorefineries is providing new industrial sources of isolated lignin. The concept of lignocellulose biorefinery is born with the perceived need of second-generation biofuels to ensure sustainability while avoiding direct competition with food resources [81,82]. The installation of biorefinery plants based on new technologies of biomass fractionation opens the way to the integration of optimized lignin recovery in the plant design [83,84]. The introduction of more advanced plants is one of the aspects of the current trend of shifting the design of biorefineries away from the production of biofuels and toward the production of higher value-added chemicals able to replace present fossil-issued products [85,86].

p0240 A significant hurdle in the development of profitable biorefineries is the adaptation to variability and seasonality of the biomass supply. Wood-issued lignin from the different processes of the pulp and paper industry enjoys a constant supply and a stable price throughout the year, while other lignin sources, notably from cornstalks and wheat or rice straw, present a significant seasonal variability. In any case, the status of lignin as a coproduct of the profitable cellulose industry provides it with a reasonable entry price, at the basis of its possible competition with oil-derived raw materials for the production of chemicals (see Table 13.3).

Clearly lignin, with a higher heating value of 21 MJ kg⁻¹, is a very poor fuel when compared with liquid hydrocarbons with a heating value of 45 MJ kg⁻¹. The same oxygen content which lowers the fuel performance of lignin necessary decreases the atomic yield of the production of any hydrodeoxygenation products. Albeit lignin, with a lower oxygen content than cellulose, can improve the yields of bio-oil production from biomass. It seems clear that production of valuable chemicals from lignin has to be based on the retention of useful functional groups already present in the raw material.

The retention of the aromatic rings by lignin hydrogenation to BTX has been developed at the pilot scale, despite the development of the process be hampered by the formation of chars which decreases the yield and poison the catalyst, as well as by the high selectivity to meta-xylene, the less valuable fraction of BTX [92]. The heavy burden of the cost of hydrogen strongly suggests that lignin be used for the production of oxygen-rich products rather than for fuels or base hydrocarbon chemicals [93].

Indeed, the exploitation of substituted phenolics present in native lignin is at the basis of the production of high added-value flavors like vanillin and derivatives, a traditional staple of biorefinery [94]. Other functionalized phenolics can provide valuable market outlets but the

t0020 TABLE 13.3 Market Values of Medium-Grade Lignins Compared With Fossil Oil, Significant Reagents, and Potential Products [87–91]

Lignins, Competitor and Reagents	\$/ton	Products	\$/ton
Kraft lignin	260–500	Vanillin	15,000–40,000
Lignosulfonates	180–500	4-Hydroxybenzaldehyde	9500–11,100
Soda lignin	200–300	Phenol	1400–1620
Organosolv lignin	280–520	Benzene	830–1280
Brent crude oil	490	Toluene	690–980
Methanol	460–490	Xylenes	690–1000
Hydrogen	~3900		

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formation of many products, each with relatively low yields, made separation issues critical for the viability of biorefinery processes [95,96].

p0260 It is clear that better economic returns require the development of technologies integrating easier fractionation of lignocellulosic biomass and more selective depolymerization. A fuller exploitation of the lignin potential as a source of aromatics remains a worthy technological challenge.

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Non-Print Items

Abstract

Lignocellulosic biomass offers a unique resource for the sustainable production of bio-derived chemicals and fuels in replacement of the fossil products. Lignin, a major component of biomass is largely underexploited, mainly due to its recalcitrant molecular structure which hinders the development of depolymerization techniques. Considering its rich phenolic functionalities in lignin, catalytic transformations can render lignin a viable source of value-added chemicals. The present contribution aims to highlight the emerging heterogeneous depolymerization strategies, challenges and economic viability aspects of pyrolysis, reduction and oxidation processes.

Keywords: Biomass, Lignin, Heterogeneous catalysis, Depolymerization, Biorefinery

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