

Conversion of lignin into chemicals with heterogeneous catalysis – Current and future technologies

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Introduction

The research interests in biomass conversion to fuels and chemicals has increased significantly in the last decade in view of current problems such as global warming, high oil prices, food crisis and other geopolitical scenarios. Many different reactions and processes to convert biomass into high-value products and fuels have been proposed in the literature, giving special attention to the conversion of lignocellulosic biomass, which does not compete with food resources and is widely available as a low cost feedstock. [1]

Lignocellulose biomass is a complex material composed of three main fractions: cellulose (40-50%), hemicellulose (25-35%) and lignin (20-30%). [2]

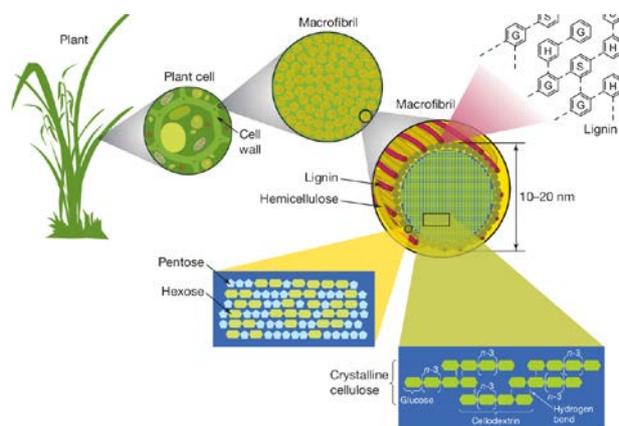


Fig. 1. View of the role of lignin, cellulose and hemicellulose in a typical plant.

Lignin constitutes up to 30% of the weight and 40% of the heating value of lignocellulosic biomass. It is the most complex fraction and is harder to process compared to the sugar fractions [2]. The complexity has led lignin to be treated as a waste stream, and typically burned to produce energy. However, lignin is a significant portion of the total carbon in biomass, and better use of this fraction is a requirement to improve the economic balance of any bio-refinery. For this reason, research on upgrading lignin has become of recent interest, as many interesting products, mainly aromatics, can potentially be produced from lignin [3]. Here we therefore present an overview conversion of lignin into chemicals with heterogeneous catalysis.

Lignin structure

Lignin is a three-dimensional amorphous polymer consisting of methoxylated and phenylpropane moieties.

The exact structure of the lignin found in plants is variable but the biosynthesis of lignin is thought to involve the polymerization of three monomers: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Fig. 2) [4].

Lignin structure and composition are different from plant to plant, so lignin obtained from one source may need to be handled differently than lignin from another source. However, lignins have different structural linkages in common such as, e.g. β -0-4, 5-5, β -5, 4-0-5, β -1, dibenzodioxocin and β - β of which the β -0-4 linkages are the most dominants. The linkages and monomers are shown in Fig. 2 in an example of softwood lignin structure [2].

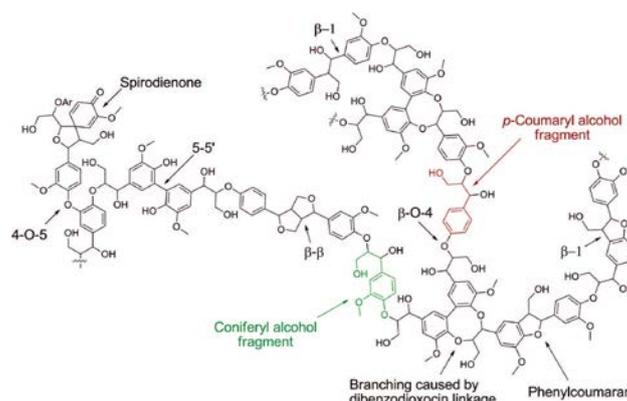


Fig. 2. Structure of softwood lignin with linkages and monomer fragments.

Methods of lignin upgrading

Due to the complex structure of lignin, most upgrading studies use model compounds, such as phenol, cresol, guaiacol, and anisole (Fig. 3) instead of real lignin [5].

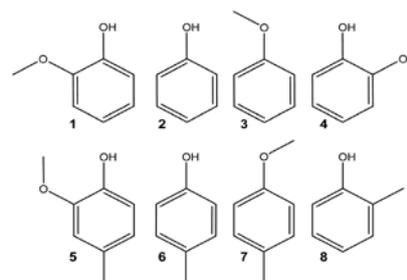


Fig. 3. Model compounds used instead of lignin. Guaiacol (1), phenol (2), anisole (3), catechol (4), 4-methylguaiacol (5), *p*-cresol (6), 4-methylanisole (7) and *o*-cresol (8).

The Bergius Process

Based on the liquefaction of coal to synthetic oil, where brown coal, also known as lignite, is converted to synthetic oil by hydroliquefaction in the presence of a catalyst under high hydrogen pressure [5].

Pyrolysis

High temperature reaction performed in the absence of oxygen. It is a thermochemical decomposition of organic compounds, and might therefore be useful to break down lignin to low molecular weight compounds [6].

Solvent

The dissolution of lignin is critically important for efficient valorization of biomass but remains a challenge because of the particular properties of the lignin structure. Several solvents such as water, alcohols, oils or ionic liquids have been recently explored to dissolve biomass and separate it into its components [4].

Catalysts in lignin conversion

Catalysis has been considered an important technology in biomass and lignin conversion. Catalysts usually are required to assist selective bond cleavage, leading to high selectivity values for a particular compound in the product stream. Various catalysts have been tested for different processes and substrates including both model compounds and lignin extracts [6].

Zeolites and amorphous silica-alumina catalysts have been used to disrupt the lignin polymer by cracking and upgrading of lignin pyrolysis oils [4]. Aromatics hydrocarbons are mostly produced by zeolite H-ZSM-5 and aliphatic hydrocarbons are most favored by amorphous silica-alumina [7].

In hydrotreatment the use of catalysts, such as cobalt, tungsten, palladium or nickel increases the yield and promotes hydrodeoxygenation. Cobalt- and nickel-promoted molybdenum catalysts have been the ones most studied [6]. High yields have been reported by Oasmaa and Johansson in hydrotreatment of kraft lignin in the presence of water-soluble molybdenum catalyst [8]. Other catalysts that work in the hydrotreatment of lignin includes Ni-W, carbon-supported Pd and Ru catalysts, and the homogeneous hydrogenation catalyst Ru(PPh₃)₃Cl₂ [6].

Base-catalyzed depolymerization is another useful technology where lignin is dissolved in an aqueous base. This works as a solvolysis, where the solvent is also a catalyst. Base catalysts such as KOH and NaOH have been found effective in this process [9].

Catalysts have been used in both acidic and alkaline oxidation to increase the yield of aldehydes. Catalysts used in lignin oxidation range from metal supported alumina catalysts with Pd or Ni-Cu as active phase. Furthermore, metal salt-based catalyst such as CuO, CuSO₄, FeCl₃ and MnSO₄ are most frequently worn in lignin oxidation, usually using molecular oxygen as oxidant [6].

Future of lignin utilization

Lignin valorization constitutes an important component of the modern biorefinery scheme, and the

structure and composition of lignin offer unique routes to produce several fine and bulk chemicals.

Macromolecular lignin is utilized as raw materials in many industrial processes as a substitute for phenol in phenol-formaldehyde resins and fillers in polymers, carbon fibers, binders, polyurethane foams, epoxy resins and biodispersants [1]. However, the most prominent lignin utilization so far appears to be its depolymerization into lower molecular weight compound [6]. Lignin can be gasified to produce H₂ and CO (syngas), which in turn can be synthesized into methanol and various other chemicals through known technologies.

Considerable effort has already been devoted to developing a wide variety of catalytic routes specifically for lignin oxidation and reduction, yet several issues are apparent after review of these processes. Hence, it is necessary to further develop catalytic processes to allow transformation of lignin from a low quality, low-price waste product into a high-quality, high-value feedstock for bulk and specialty chemicals by the development of the appropriate catalytic technology.

Keep in mind that this transformation is critical because lignin represents the only viable source to produce the renewable aromatic compounds on which society currently depends [4].

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References

- [1] D. Martin, S.G. Wettstein et al., *Chem. Soc. Rev.*, 41 (2012) 8075.
- [2] P.T. Patil, u. Armbruster et al., *Energy Fuels*, 25 (2011) 4713.
- [3] J.H. Lora and W.G. Glasser, *J. Polym. Environ.*, 10 (2002) 39.
- [4] J. Zakzeski et al., *Chem. Rev.*, 110 (2010) 3552.
- [5] A. L. Jongerius, R. Jastrzebski et al., *J. Catal.* 285 (2012) 315.
- [6] M.P. Pandey and C.S. Kim, *Chem. Eng. Technol.*, 34 (2011) 29
- [7] J.D. Adjaye, N.N. Bakhshi, *Fuel Process. Technol.* 45 (1995) 161
- [8] A. Oasmaa and A. Johansson, *Energy Fuels*, 7 (1993) 426
- [9] V.M. Roberts et al., *Chem. Eur. J.*, 34 (2011) 29