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Research review paper

Biological valorization of low molecular weight lignin

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ABSTRACT

Lignin is a major component of lignocellulosic biomass and as such, it is processed in enormous amounts in the pulp and paper industry worldwide. In such industry it mainly serves the purpose of a fuel to provide process steam and electricity, and to a minor extent to provide low grade heat for external purposes. Also from other biorefinery concepts, including 2nd generation ethanol, increasing amounts of lignin will be generated. Other uses for lignin – apart from fuel production – are of increasing interest not least in these new biorefinery concepts. These new uses can broadly be divided into application of the polymer as such, native or modified, or the use of lignin as a feedstock for the production of chemicals. The present review focuses on the latter and in particular the advances in the biological routes for chemicals production from lignin. Such a biological route will likely involve an initial depolymerization, which is followed by biological conversion of the obtained smaller lignin fragments. The conversion can be either a short catalytic conversion into desired chemicals, or a longer metabolic conversion. In this review, we give a brief summary of sources of lignin, methods of depolymerization, biological pathways for conversion of the lignin monomers and the analytical tools necessary for characterizing and evaluating key lignin attributes.

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1. Lignin — An introduction

1.1. Lignin in nature

Lignin is one of the main constituents of terrestrial plant biomass together with the carbohydrate polymers cellulose and hemicellulose. It is stated to be the second most abundant naturally occurring polymer on the planet, and it is by far the most important renewable source of aromatic compounds (Bozell et al., 2007). The amount of lignin formed annually in nature has been estimated to be in the range 5 to 36×10^8 tons (Gellerstedt and Henriksson, 2008). The lignin polymer is not found isolated in nature, but is strongly physically associated with hemicellulose and cellulose. The exact linkage structures in native biomass are not fully known. In technical processing of biomass, such as pulping, linkages are, however, formed between the lignin and carbohydrates giving rise to a lignin carbohydrate complex (LCC) (Lawoko et al., 2005). The fraction of lignin varies widely between different types of biomass. The highest lignin fraction is typically found in softwood with a range of 25–32 wt% of dry matter, whereas the lignin content in hardwoods is slightly lower (18–25%) (Mutturi et al., 2014). The lignin content is even lower for straw and grasses, and lignin is almost completely missing in mosses and green algae (Vanholme et al., 2010). From an evolutionary perspective, the incorporation of lignin into the plant structure enabled development of the tracheid cell type, and thereby a better transportation of water in the plant (Gellerstedt and Henriksson, 2008). This in turn made expansion of plants into dryer land possible. Lignin also has an important function as a protectant of the polysaccharides, since it is difficult to degrade.

Out of the three main polymers in plant, lignin has the most complex and heterogeneous composition and structure. The tridimensional polymer is built up from phenyl propanoid units which are substituted at various positions, linked by ether and C—C bonds. There are three basic building block structures abbreviated H (*p*-hydroxyphenyl), G (guaiacyl) and S (syringyl), differing in the number of methoxy groups on the aromatic ring; 0, 1 or 2, respectively. These structures can be represented in their alcohol form; namely as *p*-coumaryl, coniferyl, and sinapyl alcohols (Fig. 1). The primary lignin building blocks originate from the shikimate pathway (Higuchi, 1990). The initial step is the formation of cinnamic acid from phenylalanine, through the action of the enzyme phenylalanine lyase (PAL). Cinnamic acid is then further converted in a multistep process to the three basic structures. The polymer, in turn, is formed by radical coupling of the basic building blocks in a process involving enzymatically catalyzed oxidation. The initial step of this process is an oxidation of the phenol group of the monolignols, which gives rise to reactive radicals (Ralph et al., 2004). Since the monolignols are conjugated systems, mesomeric effects will give several ways of linking the building blocks together, gradually forming a lignin polymer. The relative proportions of the building blocks vary depending on the type of biomass. For instance, the coniferyl part (G) is completely dominant in softwoods (90–95%), whereas the proportion of sinapyl (S) (45–75%) is larger than the coniferyl part (25–50%) in hardwoods (Gellerstedt and Henriksson, 2008). Lignin in grasses contains significant amount of coumaryl (H) (5–35%), which is low in both softwoods and hardwoods. Lignin degradation in nature is slower than degradation of the carbohydrates, and lignin consequently constitutes a large part of the humic acid – the organic part of soil.

1.2. Technical lignin

Huge amounts of lignin are produced yearly in the pulp and paper industry as a co-product in the cooking process. Lignin is insoluble in water in its native state, and the purpose of the cooking process is to solubilize lignin and thereby separate it from the fiber fraction. The yearly amount of lignin produced in this manner can be estimated to be around 130 million tons (Rinaldi et al., 2016), most of which is directly used on-site. The Kraft cooking method is today by far the most common pulping method followed by sulfite-cooking (Sjöstrom, 1993). In particular for non-woody biomass, alkaline cooking with anthraquinone added, that is more selective towards lignin removal, is used to some extent (Hedjazi et al., 2009), and lignin may furthermore be removed using organic solvents, e.g. ethanol or methanol. A few different organosolv process concepts have been developed but these are of limited commercial significance for pulping at present (Viell et al., 2013), and the economic viability of the process needs to be clearly proven at pilot and demo scale (Michels and Wagemann, 2010).

The structure of the technical lignin is different from the native lignin and is furthermore dependent on the cooking method applied (Constant et al., 2016). As a result of the method used to obtain lignin, the abundances of different C—O and C—C linkages present in lignin will be substantially different from those existing for the native lignin (Abdelaziz and Hulteberg, 2016). This in turn affects the choices for further depolymerization. In the Kraft process, wood (normally softwood) is treated with an aqueous solution of NaOH and Na_2S (white liquor) at a temperature range of 155–175 °C for several hours, giving OH^- and HS^- ions as active reactants. Aromatic ether bonds in the lignin structure are broken by the hydroxide and hydrosulfide anions resulting in smaller water/alkali-soluble lignin fragments. These fragments, having a lower molecular mass, diffuse more rapidly into the cooking liquor – the black liquor. The mode of lignin removal is different in the sulfite-cooking process, which can take place under acidic, neutral, or even alkaline cooking conditions. Ether bonds are hydrolytically cleaved, after which sulfonations by the sulfite ions occur. The resulting lignosulfonates are highly water-soluble and dissolve in the cooking liquid (Adler, 1977). The sulfite process dominated the industry in the beginning of the 20th century, but has gradually been out-phased by the Kraft process, which gives stronger fibers and a more efficient recovery of

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