Biomass Conversion and Biorefinery
https://doi.org/10.1007/s13399-022-02701-z

REVIEW ARTICLE

An overview of lignin pathways of valorization: from isolation to refining and conversion into value-added products

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Received: 12 January 2022 / Revised: 11 April 2022 / Accepted: 19 April 2022

Abstract
The increasing demand for greener and sustainable alternatives to fossil-derived fuels, chemicals, and materials has attracted huge attention to lignin, the largest renewable source of aromatic building blocks on earth. This natural polymer accounts for 15 to 40% of all lignocellulosic biomass. As such, in the pulp and paper industries, for example, huge amounts of lignin are produced worldwide. However, most applications for these lignins are of low value, such as their burning for energy. Furthermore, with the introduction of second-generation ethanol biorefineries, the overall lignin production increased. To attain a circular bio-based economy, all side-streams of lignocellulosic biomass and, particularly, lignin should be valorized to as high of a value as possible. Lignin's rich structure has allowed achieving various high-value products over the years, not only in the production of biofuels but also regarding chemicals and materials. The present paper addresses a broad vision of the several stages of lignin valorization, from the isolation of lignin through pre-treatments of lignocellulosic biomass and the current industrial lignin production to fractionation methodologies that provide homogeneous lignins more adequate for valorization and the conversion of lignin into value-added products via chemical and biological routes.

Keywords Lignin valorization · Lignocellulosic biomass · Lignin fractionation · Chemical conversion · Biological conversion

1 Introduction

Lignocellulosic biomass is made up of three main components: hemicellulose, cellulose, and lignin, of which the lignin fraction can account for up to 40% of its dry weight. The chemical composition of biomass and the relative content of macromolecular components vary according to their biological origin. In general, polysaccharides are the major components, followed by lignin. Typically, herbaceous materials and hardwoods are the richest in hemicelluloses (12–38 and 14–37%, respectively), whereas hardwoods and softwoods can have quite similar content of cellulose, 39–54 and 41–50%, respectively. Softwoods are the richest in lignin (25–35%), followed by hardwoods (15–28%) and herbaceous materials (9–20%). In woody materials, the lignin content in the bark can reach much higher values than those of wood [1–3].

The complex structure of lignin, constituted by several phenolic monomers, such as syringyl, guaiacyl, and *p*-hydroxyphenyl alcohol (Fig. 1), makes it the most abundant renewable source of aromatic building blocks on earth [4]. With the aggravating situation of the unsustainability of fossil fuel reserves and the environmental impact of their use, the exploitation of lignin as a natural and renewable carbon source became a major window of opportunity for the development of sustainable and green alternatives to petroleum-based fuels, chemicals, and materials. In the context of biorefineries, the cellulose fraction has been efficiently valorized for some years now, for example, is hydrolyzed to glucose and fermented to produce bioethanol [5, 6]. Furthermore, feasible new advances for the hemicellulose fraction are being developed to address its conversion into platform chemicals, along with strategies to extract and purify hemicellulose from lignocellulosic biomass [7–9].

Lignin, however, presents an intricate structure, aggravated by the significant compositional variability that is observed for different sources of biomass and from the

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Published online: 02 May 2022