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Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

A review on thermal chemical reactions of lignin model compounds

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ARTICLE INFO

Article history:

Received 22 June 2016

Received in revised form 1 October 2016

Accepted 14 November 2016

Available online xxx

Keywords:

Catalysis

Lignin

Monomer

Dimer

Review

ABSTRACT

Biomass-based energy fulfills the future need of sustainable humanity. The utilization of lignin which is a primary constituent of biomass still remains the world most difficult problem due to its highly aromatic polymeric structure. Investigations on lignin model compounds renew the knowledge on C–C and C–O bond cleavage chemistry and indicate directions for lignin deconstruction. This review is to present the state of the art of the chemical transformation of lignin model compounds including monomers and dimers based on catalyst classifications, with emphasis on the fundamental catalytic chemistry in different processes. Moreover, how ideas derived from concepts transform to strategies for controlling the reaction pathways is also discussed.

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1. Introduction

As a consequence of the gradual depletion of fossil resources and the increased awareness of the need for environmental protection, a renewable, clean and world-wide available alternative resource of fuels and chemicals is required. Biomass is one of such options and is predicted to be capable of providing for up to 20% of world energy demands by 2050 [1]. It represents an alternative to fossil resources with potentially enough amount and carbon neutral in nature for the production of chemicals and fuels [2]. A number of conversion processes allowing the utilization of biomass have been proposed, e.g., gasification [3,4], pyrolysis [5,6], liquefaction [7,8], hydrolysis [7], ethanolysis [9–11] and etc [12,13].

Biomass consists of 40–45 wt.% cellulose, 25–35 wt.% hemicellulose, 15–30 wt.% lignin and up to 10 wt.% inorganic components [14]. Their structural fragments are shown in Fig. 1. Cellulose is a homopolymer, in which 100–3000 glucose residues are linearly connected with each other at the β (1,4) position [15]. This structural feature implies that cellulose can be depolymerized into glucose, which can be converted further, e.g., to ethanol by enzymatic catalysis [12,16–20]. Hemicelluloses are heterogeneous polymers of pentoses (xylose, arabinose) and hexoses (mannose, glucose, galactose) [21]. Structures of pentoses allow hydrolysis to furfural and furfural-based derivatives, while hexoses hydrolysis to 5-hydroxy methyl furfural (5-HMF) is the most investigated

reaction [22–24]. Lignin is a high molecular mass biopolymer (600–15000 kDa) made up of three monomers based on phenolic backbone and connected by different chemical linkages, mainly C–O–C ether bond [25]. The three most important monomers (Fig. 2) are coumaryl- (a), coniferyl- (b) and sinapyl alcohol (c) [26], which are typically propyl-phenyl units with phenolic hydroxyl and alkoxy groups attached. The carbon on the benzene ring connected to the propyl group is denoted as position 1 and the carbons on the propyl group are denoted as positions α , β and γ . Normally these three monomers are partly methoxylated and vary in abundance in the polymer, depending on the plant species and the plant tissue where they are present [27]. Coniferyl alcohol dominates in softwood, while sinapyl alcohol together with coniferyl alcohol dominate in hardwood. All the three make up the grass plant species [28–32]. Theoretically, lignin conversion may end up with aromatics.

There is a great vision for lignin application, but currently, lignin is produced in a large quantity as a waste in pulp and paper production as well as in biofuel generation processes. The lignin is isolated in such processes, but so far has been used mainly as a low heating value boiler fuel via combustion. Only less than 5% of the world's supply is used for other purposes [33]. At least 40 and 50 MMT/year lignin is generated worldwide as a mostly uncommercialized waste product [27]. However, the need to evaporate a large amount of water present in the lignin feedstock makes the energy balance even less favorable for combustion. The application of lignin as the resource for chemical production has been extensively explored. Two major challenges have been encountered. First, the amorphous poly-phenolic structure of lignin is very

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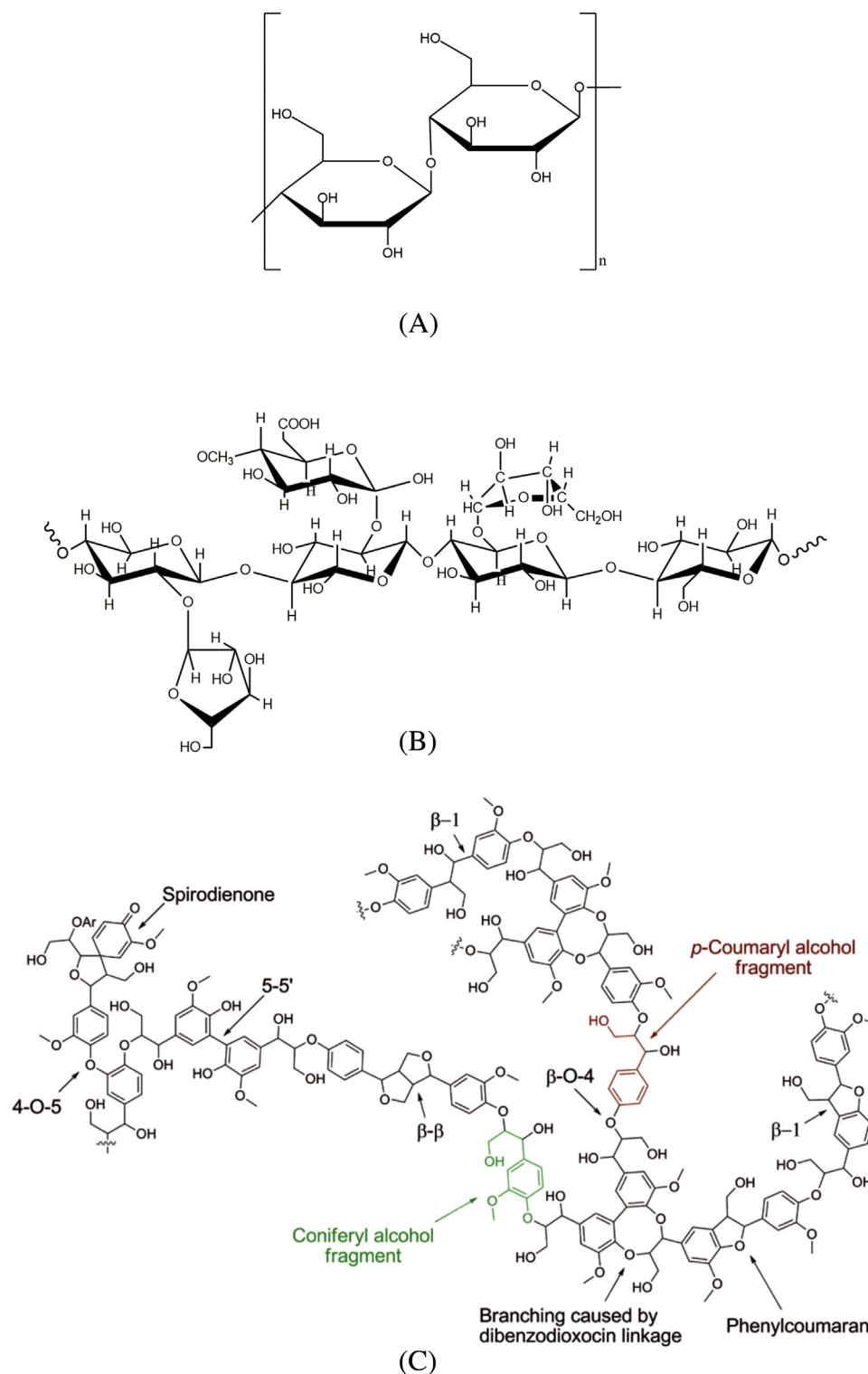


Fig. 1. Structural fragments of biomass components: (A) Cellulose fragment [15], (B) Hemicellulose fragment [21], (C) Softwood lignin fragment [25].

difficult to be decomposed to higher valued products [34]. Second, tar and char are often formed in the conversion processes [35]. Nevertheless, the chemical structure of lignin suggests that it can be a good source of valuable chemicals or intermediates, such as substituted phenols, which can be utilized in pharmaceutical synthesis or as the monomers of polymers [36]. Up to now, only the production of vanillin, as a food additive, through oxidation of softwood lignosulfonate, has been commercialized [37,38].

Thermal reactions of lignin are very complex. To understand it better, examination of the model compounds which are representatives for lignin is often practiced. The knowledge of the conversion of lignin model compounds is useful in designing the reaction system for the direct conversion of lignin and gives insight to the mechanism of lignin conversion. A large number of literatures on this topic have been published in recent years and a wide range of catalysts, solvents and reaction conditions have been investigated.

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