



## Research review paper

## Lignin-enzyme interaction: Mechanism, mitigation approach, modeling, and research prospects



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## ARTICLE INFO

## Article history:

Received 1 December 2016

Received in revised form 19 February 2017

Accepted 23 March 2017

Available online 25 March 2017

## Keywords:

Lignocellulosic biomass

Biofuel

Enzymatic hydrolysis

Lignin

Interaction mechanism

Non-productive adsorption

Hydrophobic interaction

Hydrogen bonding

Steric hindrance

## ABSTRACT

The adverse environmental impacts of the fossil fuel and the concerns of energy security necessitate the development of alternative clean energy sources from renewable feedstocks. Lignocellulosic biomass is a 2nd generation feedstock used in the production of biofuels and bio-based products that are conventionally derived from fossil resources. The biochemical conversion, which entails biomass pretreatment, enzymatic hydrolysis and fermentation, is one major platform used to transform lignocelluloses into biofuels. However, lignin presents many challenges to enzymatic hydrolysis leading to the need of high enzyme dose, low hydrolysis yield, low level of recyclability, high cost of enzymatic hydrolysis (because of the high cost of enzymes), and so on. Therefore, enzymatic hydrolysis, which is not cost effective, becomes one of major cost contributors. To mitigate the negative effects of lignin, extensive research has been conducted to explore the fundamental mechanisms of lignin-enzyme interactions to develop technologies to overcome the negative effects of lignin on enzymatic hydrolysis. Non-productive adsorption, which is characterized by hydrophobic, electrostatic and/or hydrogen bonding interactions, is widely known as the primary mechanism governing lignin-enzyme interactions. In addition, lignin-enzyme interaction is also influenced by steric hindrance (i.e., the physical blocking of enzyme access to carbohydrates by lignin). However, the mechanisms underlying the lignin-enzyme interactions remain unclear. This article aims to present a comprehensive review on the lignin-enzyme interactions (i.e. the mechanism, governing driving forces, modeling, and technologies for mitigating the negative effect of lignin). The current challenges inherent in this process and possible avenues of research in cellulosic biorefinery conclude this article.

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**Abbreviations:** AA, aqueous ammonia; AFEX, ammonia fiber expansion; ARP, ammonia recycled percolation; BSA, bovine serum albumin; CBH, cellobiohydrolase; CBM, cellulose binding module; CEL, cellulolytic enzyme lignin; CEPL, cellulolytic enzyme-protease isolated lignin; CS, corn stover; DA, dilute acid; EG, endoglucanase; FT, flow through; GHG, greenhouse gas; IL, ionic liquid; LCA, life cycle analysis; LCC, lignosulfonate-cellulase complex; LDP, lodgepole pine; LLP, loblolly pine; LHW, liquid hot water;  $M_w$ , molecular weight; MWL, milled wood lignin; OL, organosolv lignin; PEG, polyethylene glycol; PDI, polydispersity index; SE, steam explosion; SW, sweetgum.

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## 1. Introduction

The adverse environmental impacts of the continued use of fossil fuels have necessitated the development of alternative sustainable energy resources to respond to climate change and ensure energy security (Pragya et al., 2013; Rocha et al., 2014). The development and implementation of biorefineries to produce biofuels and chemicals is one of the most feasible methods for creating renewable clean energy resources in that lignocellulose is one of the most abundant biomasses (Maurya et al., 2015; Sanchez and Cardona, 2008) and it is produced through photosynthesis using sunlight and carbon dioxide (CO<sub>2</sub>) as energy and carbon sources, respectively. The consumption of biofuels and biomass-derived chemicals can diversify energy supply, reduce the dependence on fossil fuel and result in less adverse environmental impacts (Gnansounou et al., 2009; Halleux et al., 2008). Research into the life cycle analysis (LCA) of lignocellulosic biofuels undertaken to assess the environmental impact, energy efficiency and cost, has determined that the potential benefits (e.g., carbon emission reduction) of biofuels should be evaluated in the entire production chain, which is characterized by feedstock, land use, transportation, biofuel production process, waste treatment, etc. (Stoeglehner and Narodoslawsky, 2009). In their evaluation of biofuel production from various biomass feedstocks (e.g., wheat, wheat straw, rapeseed, maize, willow), Börjesson and Tufvesson (2011) found that the use of biofuels reduced the greenhouse gas (GHG) emissions to below 40 kg CO<sub>2</sub> eq/GJ (compared to 80 kg CO<sub>2</sub> eq/GJ of gasoline consumption) and even exhibited a negative carbon emission when perennial crops were used as feedstocks. Although only a partial substitution of fossil fuel is achievable given the current technology and actual availability of lignocellulosic biomass, the biofuel from biomass remains a promising alternative to fossil fuel and has been the subject of extensive research (Mabee et al., 2011). However, many technical challenges, such as lignin utilization and its adverse influence on the biochemical conversion of biomass, makes biofuel production not commercially viable.

### 1.1. Overall compositional and structural features of lignocellulose

Lignocellulose is mainly composed of cellulose, hemicellulose and lignin, with the content of each polymer varying among the lignocellulosic materials of different origins (Singla et al., 2012). The general structure of lignocellulosic biomass is shown in Fig. 1. Cellulose has high-molecular-weight linear chains of glucose linked by  $\beta$ -glycosidic bonds that are extremely stable and resistant to chemical and biological attack. Hemicellulose consists of short, highly branched chains of multiple sugars (five-carbon sugars such as D-xylose and L-arabinose, and six-carbon sugars such as D-galactose, D-glucose and D-mannose) and uronic acid. It has a lower molecular weight and degrades easier compared to cellulose. Lignin, which is rich in three-dimensional and highly branched polyphenolic constituents, has an amorphous structure and links with hemicellulose. These links are created through covalent and

non-covalent bonds which forms a dense matrix surrounding cellulose microfibrils, providing structural integrity to plants (Zhang et al., 2010). Cellulose and hemicellulose can be hydrolyzed into fermentable sugars and thus be utilized for biofuel production, while lignin cannot be efficiently biodegraded or utilized in biorefinery (Maurya et al., 2015). Lignin also interacts with hydrolytic enzymes (e.g., cellulase and xylanase) and impairs the hydrolysis efficiency significantly, thus increasing the cost of both enzymatic hydrolysis and biofuels.

### 1.2. Biochemical conversion of lignocellulose

Various platforms such as thermochemical, biochemical and combined conversions are used to convert lignocellulosic biomass into biofuels and bioproducts. The thermochemical conversion entails direct combustion, pyrolysis, gasification, and liquefaction. The energy stored within biomass can be released directly as heat/electricity, or can be transformed into solid (e.g., biochar), liquid (e.g., bio-oils) and gaseous (e.g., synthetic gas) fuels for various uses (Zhang et al., 2010). Such processes can effectively decompose most of the carbohydrates and lignin rapidly under high temperature and pressure either with or without chemical catalysts (Bridgwater, 2001). In the biochemical pathway, biomass is initially subjected to pretreatment (e.g., physical, chemical, biochemical, or combined pretreatments) to improve its biodegradability followed by enzymatic hydrolysis to degrade cellulose and/or hemicellulose into monosaccharides and oligosaccharides which will be finally converted into biofuels and bioproducts through microbial fermentation. Within the biochemical conversion process, enzymatic hydrolysis is an important cost factor because high enzyme dose is usually needed to achieve high hydrolysis yield. To enhance the economic feasibility of large-scale production of biofuels, extensive research has been undertaken to improve the hydrolysis efficiency and reduce the cost.

#### 1.2.1. Characteristics of lignin

Lignin is an aromatic polymer that encrusts and glues the network of the cell wall. The biosynthesis of lignin occurs through the radical coupling of the lignin precursors, such as hydroxycinnamyl alcohol, coniferyl alcohol and sinapyl alcohol (Guo et al., 2014; Vanholme et al., 2010), generating three subunits including guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl (H). These three subunits differ in the substitution pattern of methoxy groups on the aromatic ring (Goundalkar et al., 2014; Haven and Jørgensen, 2013; Lin et al., 2015b), and are sequenced randomly in lignin macromolecules (Ralph et al., 2004) (Fig. 2A). The relative percentage of G, S and H units in lignin differs significantly from biomass to biomass, which are used to categorize three major types of biomass, i.e., softwood lignin mainly contains the G unit, both G and S units are abundant in hardwood lignin, and the lignin from grass and herbaceous origins is composed of G and S units as well as a small part of the H unit (Fig. 2B). Some common inter-unit linkages have been identified in lignin, such as  $\beta$ -O-4,  $\alpha$ -O-4/ $\beta$ -5 (phenylcoumaran),  $\beta$ - $\beta$  (pinosresinol), dibenzodioxocin, and 4-O-5

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