

Structural changes in lignin during integrated process of steam explosion followed by alkaline hydrogen peroxide of *Eucommia ulmoides* Oliver and its effect on enzymatic hydrolysis



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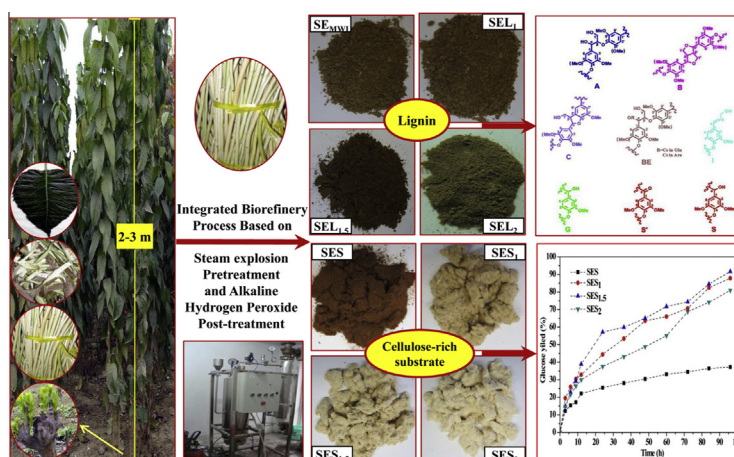
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HIGHLIGHTS

- EU was subjected to steam explosion followed by alkaline delignification process.
- Lignin and cellulose-rich substrates were obtained from the integrated process.
- The structural characteristic of the lignin was comprehensively elucidated.
- The maximum enzymatic hydrolysis of the treated EU wood reached 91.69%.
- Removal of hemicelluloses and lignin facilitated subsequent enzymatic hydrolysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Eucommia ulmoides Oliver (EU) wood was successively treated by a combined system based on steam explosion pretreatment (SEP) and alkaline hydrogen peroxide post-treatment (AHPP). In this case, SEP was to disrupt the lignocellulosic structure, and the subsequent AHPP process was to isolate the high-purity lignin and cellulose-rich substrates. Results showed that the lignin fractions obtained during the AHPP exhibited smaller molecular weights, narrow polydispersity, less phenolic OH groups and lower syringyl/guaiacyl ratios (S/G) than those of the milled wood lignin (SE_{MWL}) obtained from the only steam exploded EU. NMR characterization of lignin revealed that the AHPP process has a slight effect on the composition and molecular characteristic of lignin, and the lignin isolated had lower amounts of substructures (aryl- β -ether, resinol, and phenylcoumaran linkages) as compared to those in SE_{MWL} . Moreover, the subsequent SEP followed by AHPP process enhanced the enzymatic hydrolysis of cellulose-rich substrates to a maximum value of 91.69%. It was found that the synergistic treatment removed most of lignin, degraded hemicelluloses, and incurred a higher crystalline index and surface area of the cellulose-rich substrates as compared to the only steam explosion pretreatment. The combination

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of the SEP and AHPP processes is an environmentally benign and advantageous scheme for the production of high-purity lignin and cellulose-rich substrates, which will be further transformed into the value-added biomaterials and bioethanol.

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1. Introduction

The non-renewability of fossil resources (coal, crude oil, and natural gas) are indispensable resources for hundreds of years [1]. As the increasing energy demand, the growing concerns on development sustainability have been promoting great interest in finding renewable and clean energy sources (e.g., solar energy, wind energy, hydroenergy, and biomass) [2]. Recently, the utilization of lignocellulosic biomass for energy production is increasing due to its environmental friendliness [3]. Lignocellulosic materials are the most abundant, sustainable, and cost-effective biomass, which are primarily composed of cellulose, hemicelluloses, and lignin [4,5]. The three polymers together form complicated and rigid cross-linking structures [6], which is beneficial to enhance the plant recalcitrance to physical attack, biological and chemical degradation [7], however, the recalcitrance limits the value-added applications of plant cell wall in a biorefinery process. Currently, most integrated biologically based biorefinery process comprise five major sections: feedstocks harvest and storage, pretreatment, enzymatic hydrolysis, sugar fermentation, and distillation/rectification to meet requirements as fuels [2]. Generally, the pretreatment step is critical in bioconversion of lignocellulosic biomass, which deconstructs the cross-linking structures of plant cell wall and makes cellulose more digestible by the enzymes, and further facilitates the subsequent enzymatic hydrolysis process [8,9]. In light of this, several kinds of pretreatment technologies have been developed for decades (e.g., physical pretreatment, physic-chemical pretreatment, chemical pretreatment and biological pretreatment) [1,8,10–12].

Steam explosion pretreatment (SEP) is a promising approach among the available pretreatments because it combines the chemical modification of the chemical compositions and physical fracture of the plant cell wall [5,10,13,14]. In this case, the lignocelluloses were exposed to saturated steam with high-pressure, and followed by a quick decompression, forcing the fibrous material to “explode” into separated fibers and fiber bundles [10]. The main advantages of SEP include the low energy requirement, no recycling or environmental costs as compared to other pretreatments [8]. During this process, the high temperature causes hemicelluloses degradation and lignin transformation, thus improving the part hydrolysis of cellulose. Hemicellulosic polymers are degraded and hydrolyzed by released organic acids (mainly acetic acid) during SEP process. The SEP process was achieved by the exposing the surface of cellulose and increase the accessibility of cellulase to the microfibrils of cellulose by removing the hemicelluloses [15]. However, lignin was removed slightly during the SEP process, and most of the lignin is redistributed on the surfaces of pretreated fiber due to the migrating and melting of the depolymerized/repolymerized lignin [16]. The removal of hemicelluloses and the redistribution of lignin during SEP are unavoidable, releasing some degraded products, which can be a hindrance to following enzymatic hydrolysis process [8]. Therefore, it is necessary to employ a further post-treatment to remove the redistributed lignin and the degraded hemicelluloses in the SEP substrates before enzymatic hydrolysis.

Alkaline hydrogen peroxide post-treatment (AHPP) has shown effective delignification on several lignocellulosic substrates [17].

Basically, the main advantage of AHPP of lignocellulosic substrates is the utilization of simple and clean chemicals at mild conditions (low concentration and temperature). Furthermore, the operation of AHPP is generally at atmospheric pressure and low temperatures, thus specialized expensive reactors are not needed in an industrial scale. Besides, low cost makes it to be a promising pretreatment process than other effective process, for example, ionic liquids pretreatment [18] and organic solvents pretreatment [19]. Moreover, the addition of oxidant agent (hydrogen peroxide) to alkaline pretreatment can enhance the reactivity of the substrates by removing the degraded lignin [17]. Therefore, the AHPP process can enhance enzymatic hydrolysis by removing of lignin and hemicelluloses from the lignocellulosic substrates [20].

Lignin, accounting for 15–40% dry weight in lignocellulosic biomass, is the second most dominant naturally synthesized aromatic polymer [2], which can be utilized to produce chemical products and others valuable materials [21]. It is an amorphous and thermoplastic three-dimensional polymer with different linkages (e.g., β -O-4, α -O-4, β - β , β -5, 4-O-5, 5-5, β -1, and dibenzodioxocin structures), depending on the different terrestrial plants [22]. In plant cell wall, lignin plays a vital role in providing structural supports, forming impermeable capacities, and resisting against microbial attacks [23]. In fact, the presence of lignin in lignocellulosic biomass limits the cellulose accessibility and further influences the bioconversion of the biomass [24–26]. Moreover, the high content of lignin in the substrates after pretreatment can adversely affect enzymatic hydrolysis through physical inhibition and non-special adsorption on enzyme [27,28]. From this perspective, it is significant to remove and investigate the molecular characteristic of lignin from the AHPP process based on the SEP substrates, and then identify their future applications.

Eucommia ulmoides Oliver (EU) was named as Dù-zhòng (in Chinese), Tuchong (in Japanese), Gutta-percha tree, Chinese rubber tree, Sixian, Sizhong, and Yusipi [29]. The traditional arbor forest model of *Eucommia* planting (Fig. S1b) is quantitatively limited. Since it usually is a kind of tall tree, its seeds, leaves, barks or woods are not easy to be collected. For utilizing some of its useful parts, the traditional way is to chop down the whole tree. To overcome these shortcomings, our group has succeeded in cultivating EU tree to a small height of 2–3 m named using leaf model of *Eucommia* planting (ULMEP, Fig. S1a), ULMEP is based on its strong sprouting characteristic. After planting, the trunks were stubbed at the level close to the ground in every spring before the sap flow. Only three to six evenly sprouts, at different directions, were kept on the trunk to constitute an open canopy. After three years' planting, the annual production of leaves, barks and branches or stems can reach about 10.0–15.0 tons/hectare, 5.0–7.5 tons/hectare and 18.0–22.5 tons/hectare, respectively [30]. Up to now, the secondary metabolites in the leaves and barks in ULMEP have been used for many years. However, the research on ULMEP branch wood has rarely been reported. It is true that the economic value of ULMEP will be increased significantly, if the huge amount of wood could be developed as useful biomaterials and chemicals.

In this study, EU wood from ULMEP was fractionated by applying an integrated process: (1) steam explosion pretreatment to disrupt the lignocellulosic structure; (2) AHPP process to isolate high-

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