



Short Communication

Oxidative depolymerization potential of biorefinery lignin obtained by ionic liquid pretreatment and subsequent enzymatic saccharification of eucalyptus



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ABSTRACT

This study compared the oxidative depolymerization potential between ionic liquid (IL)-pretreated/enzyme lignin, diluted acid (DA)-pretreated/enzyme lignin, and soda lignin of eucalyptus, by means of alkaline nitrobenzene or cupric oxide (CuO) oxidation which depolymerize lignin into phenolic aldehydes such as vanillin and syringaldehyde. Here, the IL-pretreated/enzyme lignin was prepared by 1-ethyl-3-methylimidazolium acetate pretreatment and subsequent enzymatic saccharification. Upon the oxidative depolymerization of lignin sample by alkaline nitrobenzene oxidation, total yield of vanillin and syringaldehyde was 36.6% for untreated control eucalyptus. In contrast, the yield was enhanced upto 48.0% for IL-pretreated/enzyme lignin. As for the soda lignin prepared by alkali cooking, the yield was 29.0%. As for the DA-pretreated/enzyme lignin prepared by DA pretreatment and subsequent enzymatic saccharification, the yield was 39.5%. Therefore, it was found that the IL-pretreated/enzyme lignin showed the highest yield of phenolic aldehydes (vanillin and syringaldehyde) via alkaline oxidation, namely, highest oxidative depolymerization potential among the lignin tested.

1. Introduction

Lignin is a complex, amorphous, and aromatic polymer present in the cell walls that support cellulose structures together with hemicellulose, and is the second most abundant natural polymer after cellulose (10%–30% of the mass, depending on the botanical source) (Li et al., 2015). Lignin is biosynthesized by random polymerization of three different types of phenyl propane monomer units (called monolignols), namely, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, which comprise guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) residues. They are connected with various linkages of ether bonds (i.e., β -O-4 (45%–60%) and 4-O-5 (2%–10%)) and carbon–carbon bonds (i.e., 5–5 (5%–25%), β -5 (5%–25%), β -1 (2%–10%), dibenzodioxocin (0%–10%), and β - β (2%–10%)), depending on the botanical source (Zakzeski et al., 2010; Li et al., 2015).

The procedures for lignin preparation from lignocellulosic biomass are roughly classified into two types. One is lignin extraction by heating in alkali or organic solvent or by solvent extraction after ball milling,

which provides kraft lignin, lignosulfonate, soda lignin, organosolv lignin, or milled wood lignin. Another method is carbohydrate removal by enzymatic or concentrated acid hydrolysis, which provides enzyme lignin or klason lignin (Li et al., 2015). Especially, enzyme lignin obtained from the cellulosic ethanol production process is called as “biorefinery lignin”, which is distinguished from the “technical lignin” such as kraft lignin obtained from the papermaking process (Ma et al., 2015).

To date, lignin has been utilized for low value products, such as binding, dispersing, or emulsifying agents (Calvo-Flores and Dobado, 2010), and has been used as a component of synthetic polymers, such as phenol-formaldehyde resin, epoxy resin, or polyurethane resin (Sen et al., 2015). Chemically modified lignin was utilized as a reinforcing agent or filler for composites and polymer blends (Kai et al., 2016). Further, raw lignin also functions as an antioxidant or an antimicrobial agent, and provides ultraviolet protection (Kai et al., 2016). Besides the utilization as macromolecule, lignin can be also catalytically depolymerized into aromatic monomers via cracking, hydrolysis, reduction, or

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oxidation (Zakzeski et al., 2010; Li et al., 2015; Ma et al., 2015).

The lignin depolymerization via oxidation has been conducted in alkaline medium with using nitrobenzene, metal oxide (e.g. cupric oxide (CuO)), or oxygen as mild oxidants to preserve the lignin aromatic ring and produce phenolic aldehydes such as vanillin and syringaldehyde (Villar et al., 2001; Pandey and Kim, 2011). The alkaline nitrobenzene oxidation and alkaline CuO oxidation have been used to analyze the lignin structure for extracted lignin such as kraft lignin and milled wood lignin. There has not been any attempt to use alkaline CuO oxidation for conversion of biorefinery lignin to value-added products (Ma et al., 2015).

Ionic liquids (ILs) have received attention as green solvents, as ILs are thermally stable, nonvolatile, and can therefore be recycled. Some ILs can dissolve cellulose, lignin, and lignocellulosic materials (Swatoski et al., 2002; Kilpeläinen et al., 2007; Zakrzewska et al., 2010; Brandt et al., 2013). Recently, oxidative depolymerization of lignin into phenolic aldehydes was conducted using IL as the reaction medium instead of alkaline medium (see review by Chatel and Rogers, 2014; Gillet et al., 2017). In contrast, the lignocellulosic materials obtained by dissolution in IL and re-precipitation (i.e., IL pretreatment) showed lowered crystallinity and enhanced enzymatic saccharification (Kilpeläinen et al., 2007), producing sugar solution for cellulosic bioethanol and residual enzyme lignin. As far as we know, there is no report that the enzyme lignin obtained by IL pretreatment and subsequent saccharification is compared with other biorefinery lignin and technical lignin with regard to the oxidative depolymerization potential.

Therefore, this study examines an oxidative depolymerization potential of the enzyme lignin obtained by IL pretreatment and subsequent saccharification (hereafter, designated as IL-pretreated/enzyme lignin), by using alkaline nitrobenzene or CuO oxidation which depolymerize lignin into phenolic aldehydes such as vanillin and syringaldehyde. As a comparison, we also test the oxidative depolymerization of a soda lignin prepared by alkali cooling. Furthermore, as another control, we test the oxidative depolymerization of another enzyme lignin which is prepared with diluted acid (DA)-pretreatment and subsequent enzymatic saccharification (hereafter, designated as DA-pretreated/enzyme lignin), to highlight the uniqueness IL-pretreated/enzyme lignin obtained by IL pretreatment and subsequent enzymatic saccharification.

2. Materials and methods

2.1. Materials

Cedar, eucalyptus, and bagasse powder (c.a. 3 mm), purchased from Toyota Motor Corporation (Miyoshi, Japan), were used as lignocellulosic biomass. The powder was pulverized using a mill and then sieved to gain a powder with a particle size less than 250 μm . The biomass was dried in an oven at 90 °C for 24 h before use. 1-ethyl-3-methylimidazolium acetate (EmimOAc) purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) was used as IL. The water content for IL was below 0.5% wt by Karl–Fischer titration (AQ-2200, Hiranuma Sangyo Co., Ltd, Mito, Japan). All other chemicals purchased were of reagent grade. Commercial cellulase (Cellic[®] CTec2) (batch number VCNI 0008, 106 filter paper units (FPU) per milliliter) was obtained from Novozymes Japan, Ltd. (Chiba, Japan). The FPU of the cellulase was determined using the method reported by National Renewable Energy Laboratory (NREL) (Adney and Baker, 2008).

2.2. IL pretreatment of biomass

Biomass pretreatment by IL was conducted as described previously (Ninomiya et al., 2013), with minor modification. Specifically, 2 g of biomass powder was mixed with 20 g of EmimOAc (9.1% solid loading) in a 100-mL glass beaker. The resulting biomass/EmimOAc slurry was

heated on a mantle heater at 110 °C with stirring. After heating for 16 h, the biomass/EmimOAc slurry was suspended with 200 mL of deionized water in centrifugation bottles. After mixing, the suspension was centrifuged at 10,000g for 10 min at 25 °C and the supernatant was removed to obtain the IL-pretreated biomass as precipitate. Washing with deionized water was repeated three times to remove the EmimOAc solution from the biomass. The recovered biomass was dried in an oven at 90 °C for 24 h and ground into a powder using a mill.

2.3. DA pretreatment of biomass

Biomass pretreatment by DA was conducted as described elsewhere (Li et al., 2013), with minor modification. Specifically, 2 g of biomass powder was mixed with 33.3 g of 1.2% sulfuric acid (5.7% solid loading) in a 100 mL pressure-proof autoclave reactor (RDV-100, SAN-AI Kagaku Co. Ltd., Nagoya, Japan). The autoclave reactor was heated in a rotary oven (RDV-TM2, SAN-AI Kagaku Co. Ltd.) to 160 °C with stirring. After heating for 20 min, the suspension was centrifuged at 10,000g for 10 min at 25 °C and the supernatant was removed to obtain the DA-pretreated biomass as precipitate. Washing with deionized water was repeated until the pH of the wastewater was 5. The recovered biomass was dried in an oven at 90 °C for 24 h and ground into a powder using a mill.

2.4. Preparation of enzyme lignin

Enzyme lignin was prepared as described previously (Ninomiya et al., 2013), with minor modification. Specifically, 1 g of biomass powder was mixed with 33 mL of a CTec2 cellulase solution (10 FPU/g-dry biomass) in 50 mM phosphate buffer (pH = 5.0) (ca. 3% solid loading) in a 250 mL centrifugation bottle. The bottle was incubated at 50 °C on a rotary shaker at 130 rpm. After incubation for 96 h, the reaction mixture was centrifuged at 10,000 g for 10 min at 25 °C and the supernatant was removed to obtain enzyme lignin as precipitate. Washing with deionized water was repeated three times. The recovered enzyme lignin was dried in an oven at 90 °C for 24 h and ground into a powder using a mill.

2.5. Preparation of soda lignin

Soda lignin was prepared as described elsewhere (Mousavioun and Doherty, 2010), with minor modification. Specifically, 5 g of biomass powder was mixed with 52.5 mL of 1 M sodium hydroxide solution (8.7% solid loading) in a 100 mL pressure-proof autoclave reactor (RDV-100, SAN-AI Kagaku Co. Ltd.). The autoclave reactor was heated in a rotary oven (RDV-TM2, SAN-AI Kagaku Co. Ltd.) at 170 °C with stirring. After heating for 1.5 h, the reaction mixture was vacuum-filtered to obtain black liquor as flow through. To the black liquor, 5 M HCl was slowly added with stirring until the pH became 2, followed by incubation at 65 °C for 45 min. The suspension was centrifuged at 10,000 g for 10 min at 25 °C and the supernatant was removed to obtain the soda lignin as precipitate. Washing with deionized water was repeated three times. The recovered soda lignin was dried at room temperature and ground into a powder using a mill.

2.6. Alkaline nitrobenzene or CuO oxidation

Alkaline nitrobenzene oxidation was conducted as described elsewhere (Iiyama and Lam, 1990), with minor modification. Specifically, 25 mg of biomass powder and 0.125 mL of nitrobenzene or 125 mg of CuO was mixed with 2 mL of 2 M sodium hydroxide solution (1.2% solid loading) in a 4 mL pressure-proof autoclave reactor (MH-100-4, SAN-AI Kagaku Co. Ltd.). The autoclave reactor was heated in a rotary oven (RDV-TM2, SAN-AI Kagaku Co. Ltd.) at 170 °C with stirring. After heating for 4 h, the reaction mixture was transferred to a beaker by rinsing the vessel with approximately 5 mL of deionized water. HCl

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