



Research paper

Alkaline oxidative cracking for effective depolymerization of biorefining lignin to mono-aromatic compounds and organic acids with molecular oxygen

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ABSTRACT

Alkaline oxidative cracking with molecular oxygen was demonstrated as an effective method to depolymerize lignin under moderate conditions. Ammonia-extracted lignin from corn stover was depolymerized to aromatics and organic acids by the alkaline oxidation. The identified products by GC-MS, NMR, and HPLC included mono-aromatic compounds (such as vanillin, *p*-coumaric acid, vanillic acid, acetovanillone etc.) and organic acids (such as oxalic, acetic, formic acids, etc.). The overall mass yield of quantified aromatics and organic acids varied from 24% to 58% under the investigated conditions. It was found that the yields and compositions of the products were determined by the reaction conditions (temperature, reaction time, and oxygen pressure). More vanillin and organic acids were produced with oxygen under high temperature and long time, while *p*-coumaric acid was the primary product under oxygen deficient condition.

1. Introduction

Lignin is a natural aromatic polymer of three phenylpropanoid monomers (coniferyl alcohol, coumaryl alcohol, and sinapyl alcohol) linked by a variety of C-O and C-C bonds, accounting for a mass fraction of 15–35% of plant cell wall. Lignin provides physical strength and protection from pathogens to plants; on the other hand, which forms the major recalcitrance of lignocelluloses toward bio-deconstruction and bioconversion of cell wall carbohydrates. Therefore, in the bio-conversion of lignocellulosic biomass, lignin is either removed (completely or partially) through pretreatment before cellulose and hemicelluloses can be efficiently used or left over as a residue after the carbohydrates are used for biofuels and chemicals. It is a consensus that valorization of the separated and residual lignin to value-added products is crucial to the commercial success of any bioconversion technology [1].

Because of its aromatic nature, lignin has been identified as a promising feedstock for producing aromatic chemicals [2]. Diverse technologies have been investigated for producing aromatics from lignin, such as pyrolysis, hydrogenolysis, and oxidation. Pyrolysis with or without catalyst decomposes lignin at elevated temperature (400–600 °C) within short time (≤ 2 s) in the absence of oxygen [3–6].

However, pyrolysis faces the issues like low yield and poor selectivity of aromatic products due to the formation of significant amount of char (more than 40%) [7–9]. Hydrogenolysis, a catalytic reducing process in the presence of hydrogen and metal catalysts, is another extensively investigated method to depolymerize lignin into aromatics [10–13]. In spite of high yield of phenolic compounds, the major issue of hydrogenolysis is high operational and capital cost due to the use of expensive catalysts, H₂, organic solvents, and harsh reaction conditions (high temperature and pressure). Oxidation is also an effective depolymerization strategy for lignin, which has been successfully applied to pulping and bleaching in paper industry [14–17]. The oxidation could effectively and selectively depolymerize and remove lignin from wood pulp under relatively mild reaction conditions [14,15].

Many oxidizing agents, such as oxygen, ozone, hydrogen peroxide, chlorine dioxide, and peroxy acids, have been used for oxidative lignin depolymerization [18–22]. Chlorine-containing oxidants (such as hypochlorite and chlorine dioxide) are efficient in lignin depolymerization, but they are environmentally hazardous due to the formation of chlorinated aromatics [15,23]. Peroxide is an environmentally benign oxidizing agent, but poor stability, weak oxidative power, and high cost are its drawbacks [24,25]. Ozone and peroxy acids are highly efficient oxidants, but high cost limits their application at large scale [26].

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Molecular oxygen is the most attractive oxidant because of its abundance, low cost, nontoxicity, and environment-friendly nature [20,27]. Since oxygen is a relatively weak oxidizing agent, strong base (such as NaOH) is usually required. Under alkaline condition, lignin is ionized and then oxidized and depolymerized by oxygen to aromatic aldehydes or acids [28]. In addition to pulping and bleaching, oxygen has been used to oxidize the lignin in pulping black liquor for producing vanillin, although the yield is relatively low [29]. In a study, oxidation of hardwood kraft lignin by oxygen resulted in phenolic derivatives and organic acids [30]. Araújo et al. demonstrated a fast batch oxidation protocol for vanillin production from lignin with a yield of 3.5–7.6% depending on the lignin source [31]. Pácek et al. reported that catalytic oxidation of sodium lignosulfonate under strong alkaline condition produced vanillin, acetovanillone, vanillic acid, and other compounds [32]. In another study, Azarpira et al. investigated the oxidation of lignin model compounds to aromatic acids and aldehydes by molecular oxygen [33]. In summary, molecular oxygen has been used in delignification for pulping and bleaching and vanillin production from lignin in paper industry, but little has been conducted for oxidative cracking of biorefining lignin with molecular oxygen to aromatics and organic acids.

The present study explored high-yield production of mono-aromatic compounds (MACs) and organic acids (OAs) from a biorefining lignin, the ammonia-extracted lignin (AEL) from the soaking in aqueous ammonia (SAA) pretreatment of corn stover, through alkaline oxidative cracking with molecular oxygen. The SAA process had been successfully demonstrated to be an efficient pretreatment method for herbaceous biomass like corn stover under mild conditions, which meanwhile could extensively extract lignin from the biomass for potential co-products [34,35]. However, how to utilize the extracted lignin (AEL) during the pretreatment has not been sufficiently explored yet. Therefore, inexpensive and environmentally friendly oxygen with low-cost NaOH as catalyst was used to oxidize AEL into the mono-aromatics as potential platform chemicals or the precursors of hydrocarbon fuels in this study. Different from the previous studies on oxygen oxidation of lignin [29–32], which aimed mainly at vanillin production, this study pursued high-yield conversion of the lignin to value-added products such as MACs and OAs. The specific objectives were to investigate the effects of reaction parameters including alkaline chemical, oxidant, temperature, and time on the production of MACs and OAs from the AEL and to understand the mechanisms of the oxidative depolymerization of lignin.

2. Material and methods

2.1. Materials

Corn stover (cultivar Pioneer 36H56; stalks and leaves excluding corn cob) was harvested and chopped into 3–5 cm in length using a combine harvesting system in the field of Arlington Agricultural Research Station of the University of Wisconsin-Madison (43°20'19"N 89°22'36"W, Arlington, WI) in summer 2013. From a pile of the chopped corn stover, approximately 5 kg of the corn stover was collected and air-dried at ambient temperature (20 °C) in lab for 1 week. The air-dried corn stover was ground with a Wiley mill, and the fraction between 0.3 and 2.0 mm was collected using sieves and used as feedstock for the present study. The ground feedstock was stored in a sealed plastic container at room temperature in a cabinet until further experiments. The initial composition of the corn stover included 365 g kg⁻¹ glucan, 226 g kg⁻¹ xylan, 7 g kg⁻¹ galactan, 21 g kg⁻¹ arabinan, 199 g kg⁻¹ lignin, 50 g kg⁻¹ ash, and 129 g kg⁻¹ extractives. Moisture content of the corn stover was 50 g kg⁻¹. The chemical composition of the corn stover was analyzed as described in the NREL standard procedures [36].

Ammonium hydroxide (Cat. No. A669C) and sodium hydroxide (Cat. No. AC259860250) were purchased from Fisher scientific, and oxygen was supplied by Airgas. All other chemicals used in this study

were purchased from Fisher Scientific or Sigma-Aldrich and used as received.

2.2. Lignin extraction using aqueous ammonia

The AEL was extracted from the corn stover using the process of the SAA pretreatment at mild temperature, which is one of effective pretreatment methods for grasses and agricultural residue [34,35]. Briefly, corn stover was treated with aqueous ammonia solution with a concentration of 150 kg m⁻³ in a glass media bottle (Fischer Cat# 06-414-1C) with screw-cap at 70 °C for 24 h. Solid-to-liquid ratio was 1:9. After the treatment, the solid and liquid were separated by vacuum filtration with fluted filter paper (Fisher Cat# 09-790-14F). The solid fraction was thoroughly washed with deionized (DI) water until the pH reached neutral. The filtrate (liquid) and the washing were collected and concentrated under reduced pressure. The concentrated was acidified with 36.5 kg m⁻³ HCl solution to pH below 2.0 to precipitate the lignin (AEL). The lignin was collected by centrifugation at relative centrifugal force (RCF) of 3.6 kg for 20 min. The crude lignin was then treated to remove residual hemicelluloses with an enzyme mixture including cellulase (Novozymes NS-50013) and xylanase (Novozymes NS-50030), washed twice with acidified water (pH 2.0) and thoroughly with water, separated by centrifugation at RCF of 3.6 kg for 20 min, and dried by freeze-drying.

2.3. Alkaline oxidative cracking of lignin

Oxidative cracking was conducted using a Parr 5500 pressure reactor (100 cm³ internal volume) with a Parr 4848 temperature controller (Parr Instrument Company, Moline, IL). Specifically, 200 mg AEL prepared above and 30 cm³ NaOH solution (40 kg m⁻³) were loaded into the reactor. The reactor was purged three times and then pressurized with O₂ to the target initial pressure. Reaction time was counted when the temperature in the reactor reached the target temperature (heating time ~20 min). After the reaction was completed, the reactor was cooled down in an ice bath. The overall process from the separation of AEL to the alkaline oxidative cracking to MACs and OAs is summarized in Fig. 1. In this study, varying reaction temperatures (70–190 °C), reaction times (0–2 h), and initial O₂ pressures (0–2 MPa) were investigated. The overall depolymerization yield of lignin during

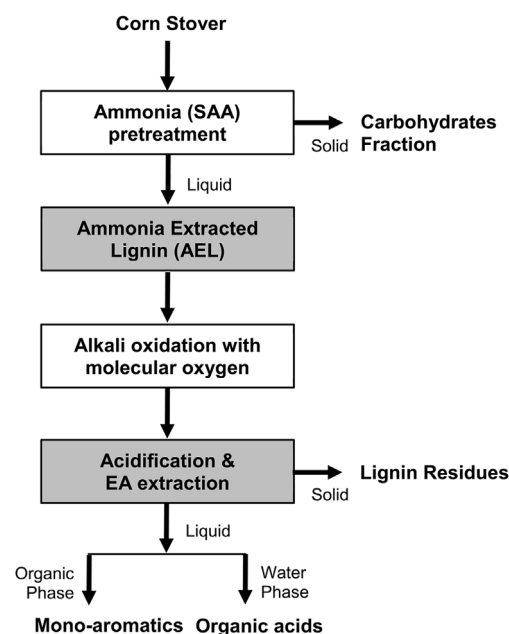


Fig. 1. Overall flow diagram of ammonia extraction and alkali oxidative cracking of corn stover lignin. Note: SAA – Soak in Aqueous Ammonia; EA – ethyl acetate.

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