



The influence of alkali and alkaline earth metals on char and volatile aromatics from fast pyrolysis of lignin



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ABSTRACT

The effect of alkali and alkaline earth metals (AAEM) on fast pyrolysis of polysaccharides has been well documented. This paper examines the effect of AAEM on fast pyrolysis of lignin, which has not been as thoroughly investigated. Acetates of several metals were infused into organosolv cornstover lignin at a concentration of 1.0 mmol AAEM cation per gram lignin followed by pyrolysis at 300–800 °C.

One of the most notable effects was an increase in the yield of char with alkali metals producing more char than alkaline earth metals. Char yield was correlated to the electropositivity of the infused metal cations. Alkali metals increased the overall yield of volatile aromatic compounds while alkaline earth metals had the opposite effect.

The infusion of AAEMs into lignin led to an increase in methanol and a decrease in alkenyl side chains on the aromatic products. Methanol is hypothesized to result from cleavage of β -carbons from the 3-hydroxyprop-1-enyl side chains of lignin linkages while the alkenyl side chains are hypothesized to result from cleavage of γ -carbons. Therefore, alkali metals appear to catalyze cleavage of linkages in the lignin structure.

1. Introduction

Lignocellulosic biomass consists of three major components: cellulose, hemicellulose, and lignin. Lignin represents up to 30% of lignocellulosic biomass [1] and has a much higher carbon-to-oxygen ratio than carbohydrates, giving it an energy content similar to many bituminous coals [2]. Accordingly, the economic feasibility of cellulosic biofuels is strongly dependent upon utilization of lignin co-product.

Plant cell walls consist of a matrix of lignin and hemicellulose surrounding cellulose fibrils. Lignin protects the more digestible holocellulose from microbial attack [3]; however, the recalcitrance of lignin complicates the conversion of the lignocellulosic biomass to fuels and chemicals. High yields of fermentable monosaccharides require extensive pretreatments such as mechanical comminution, steam explosion, or ammonia fiber explosion to increase the porosity of the biomass particle and make the holocellulose accessible to the enzymes or acids used for hydrolysis [4]. Pretreatment is expensive, contributing to the cost of cellulosic ethanol being almost twice as expensive to produce as grain ethanol [5]. Biochemical conversion of cellulosic feedstocks leaves lignin as a co-product, which is mainly used as boiler fuel and other low value applications [6].

Many thermochemical processes fully utilize lignocellulosic biomass in the production of fuels, giving them an advantage over purely biochemical pathways. One such thermochemical pathway is fast pyrolysis, which involves the rapid heating (0.5–2 s) of biomass to moderate temperatures (400–600 °C) in the absence of oxygen to produce solids, liquids and gases. The liquids, known as bio-oil, can account for up to 78% of the total feedstock mass [7].

Fast pyrolysis of pure holocellulose produces predominately anhydrosugars, furans, and light oxygenates while lignin depolymerizes to a wide range of phenolic monomers and oligomers. Fractionating the products of biomass pyrolysis has been investigated by several researchers as a potential approach to optimizing the intermediates to fuels and chemicals [8].

Although the major components of lignocellulosic biomass are cellulose, hemicellulose, and lignin, biomass also contains lesser amounts of proteins, lipids, non-structural carbohydrates, nitrogenous compounds, chlorophyll, waxes, and mineral matter [9]. Mineral matter includes alkali and alkaline earth metals (AAEM), which are known to catalyze pyranose and furanose ring fragmentation in holocellulose rather than the preferred pathway of cleaving glycosidic bonds [10–13]. Work by Kuzhiyil et al. [14] showed that passivating AAEM in

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biomass can be accomplished by titrating with sulfuric or phosphoric acids to produce thermally stable sulfate or phosphate salts. Passivating the AAEM in biomass prior to pyrolysis can lead to a substantial increase in sugar yield [15]. An increase in char and decrease in lignin-derived compounds was observed for AAEM passivated biomass, suggesting that AAEM also influence lignin depolymerization [15]. The goal of this work is to gain a better understanding of the effect of AAEM on the depolymerization of lignin.

2. Material and methods

2.1. Lignin washing method

Lignin obtained from the Archer Daniels Midland (ADM) company was isolated from cornstover using the organosolv process. Organosolv lignin is expected to have a slightly different structure than native lignin; however, El Hage et al. [16] found organosolv lignin to have a similar core structure to that of native lignin. Therefore, organosolv lignin was deemed an adequate surrogate for native lignin. Impurities commonly introduced by the organosolv process include residual hemicellulose, acetic acid, and minerals. The lignin was therefore washed using the following procedure to minimize contaminants.

Approximately 30 g of the lignin powder were ball milled in a Retsch PM 100[®] planetary ball mill using a 250 mL stainless steel milling jar and 50–10 mm stainless steel balls. The mill was programmed to rotate at 400 rpm for 30 min with the rotation direction alternated at 5 min intervals. The milled lignin was washed with 300 mL of 0.1 N hydrochloric acid in a beaker stirred magnetically at 600 rpm for 30 min. Next, the mixture of dilute acid and lignin was separated using 70 mm Whatman[®] GF/F glass microfiber filter paper with 0.7 μ m particle size retention. The filter paper was placed in a Buchner funnel and a mild vacuum was applied to assist in pulling the wash solution through the filter paper. The nearly dry lignin was recovered from the filter paper and the washing process repeated using deionized water for three repetitions. The lignin was next spread over a watch glass and dried overnight in an oven at 40 °C. The washing procedure reduced the lignin ash content to 0.14 wt.%.

2.2. Infusion of alkali and alkaline earth metals into the lignin

Alkali and alkaline earth metals (AAEM) were infused in biomass samples as acetate salts. These were used instead of more common salts because they decompose upon heating to pyrolysis temperatures [17], thus releasing the AAEM in a catalytically active form. Washed lignin was infused with approximately 1.0 mmol AAEM cation per gram of lignin. Although this ratio of AAEM to lignin was higher than is typically found in native biomass, it was chosen to amplify any catalytic effects for purposes of statistical analysis. The metals lithium, cesium, barium, and copper are not found in any appreciable quantity in biomass, but they were tested along with potassium, sodium, magnesium, and calcium to discern any trends within the periodic table. For example, copper (II) cation shares the same valence charge (+2) and a similar effective ionic radius as magnesium (72pm for Mg vs. 73pm for Cu (II)) but has a much different electronegativity (1.31 for Mg vs. 1.90 for Cu (II)). Any differences in pyrolysis products between the Mg and Cu (II) infused samples likely can be attributed to the electropositivity differences of the metals.

To ensure homogeneous infusion of the salts into the lignin, the salts were first dissolved in water and the resulting solution was mixed with the lignin. Approximately 300 mg of washed lignin was weighed in a small plastic weigh boat and enough AAEM salt solution added to achieve the desired ratio of salt-to-lignin. Slightly more DI water was then added to bring the total mass up to 700 mg of combined water and AAEM salt solution, which was enough water to homogeneously saturate the lignin sample. The mixture was thoroughly mixed until a uniform slurry was obtained. The slurry was evenly distributed in the

Table 1

Alkali and alkaline earth metal content of lignin samples after infusion of AAEM acetates.

Treatment	mmol AAEM cation per gram lignin	Weight% AAEM Cation
Control (Pure Lignin)	0.00	0.000
Lithium	0.95	0.66%
Sodium	0.92	2.1%
Potassium	0.98	3.8%
Cesium	0.93	12.4%
Magnesium	0.93	2.3%
Calcium	0.95	3.8%
Barium	1.00	13.7%
Copper (II)	0.94	6.0%

plastic weigh boat and placed in an oven at 40 °C to dry for approximately 24 h. Table 1 shows the final mmol concentration of AAEM per gram of lignin and its equivalent weight percentage.

2.3. Proximate analysis

A Mettler-Toledo TGA/DSC 1[®] integrated with STAR[®] software was used to perform proximate analysis of the AAEM infused lignin samples. Approximately 10 mg of lignin was loaded into a 150 μ L alumina pan that was loaded into the TGA and subjected to a temperature program developed from ASTM method D7582. The temperature program started at 25 °C and ramped at 10 °C/min to 105 °C where it was held for 40 min in a nitrogen flow of 100 mL/min. Any mass loss from this stage was considered to be moisture. Next, the oven was ramped at 10 °C/min to 900 °C where it was held for 20 min in a nitrogen flow of 100 mL/min. Any mass loss during this stage was considered volatiles. While holding the oven at 900 °C, the gas flow was switched to air at 100 mL/min for 30 min. Any mass loss during this combustion stage represents fixed carbon. The final residue was considered ash.

Each of the pure salts was subjected to proximate analysis to determine the amount of residue remaining after the salts are heated to pyrolysis temperatures. The known mass of residue contributed by the AAEM salts was subtracted from the mass of residue remaining after pyrolysis of the lignin samples. Therefore, the reported char yield represents only carbonaceous residue resulting from the lignin that may include incompletely pyrolyzed lignin and char.

2.4. Micropyrolysis-gas chromatography of lignin

A Frontier single-shot 2020iS[®] micropyrolyzer with an AS-1020E[®] autosampler was used for fast pyrolysis. For the 300 °C tests, both the interface and furnace were held constant at 300 °C. For samples pyrolyzed at temperatures higher than 300 °C the interface temperature was held constant at 320 °C and the furnace temperature varied from 400 to 800 °C in 100 °C increments. A Bruker 430-Gas Chromatograph[®] (GC) with a flame ionization detector (FID) was used for analysis. A 60 m by 0.25 mm Agilent VF-1701ms[®] capillary column with 14% cyanopropylphenyl, 86% polydimethylsiloxane stationary phase was used for separation of volatile compounds. The GC method operated with an injector temperature of 300 °C at a split ratio of 100. The oven program started at 35 °C, held for 3 min, ramped at 5 °C/min to 300 °C and held for 4 min (60 min per experiment). The column pneumatics were set at constant flow at 1 mL/min helium carrier gas. The FID operated at 300 °C with 25 mL/min helium makeup flow, 30 mL/min hydrogen flow, and 300 mL/min air flow.

The instrument was calibrated using liquid standards. Pure standards purchased from Sigma Aldrich[®] were dissolved in methanol within the range expected for pyrolysis of approximately 500 μ g of pure lignin. Each compound was calibrated at 3–5 levels with 2–8 injections per level depending on reproducibility of the results. Each compound produced a linear calibration with an R² of at least 0.99 with the

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