



Effect of torrefaction temperature on lignin macromolecule and product distribution from HZSM-5 catalytic pyrolysis

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ABSTRACT

Torrefaction is a low-temperature process considered as an effective pretreatment technique to improve the grindability of biomass as well as enhance the production of aromatic hydrocarbons from Catalytic Fast Pyrolysis (CFP). This study was performed to understand the effect of torrefaction temperature on structural changes in the lignin macromolecule and its subsequent influence on *in-situ* CFP process. Lignin extracted from southern pine and switchgrass (*via* organosolv treatment) was torrefied at four different temperatures (150, 175, 200 and 225 °C) in a tubular reactor. Between the two biomass types studied, lignin from pine appeared to have greater thermal stability during torrefaction when compared with switchgrass lignin. The structural changes in lignin as a result of torrefaction were followed by using FTIR spectroscopy, solid state CP/MAS ¹³C NMR, ³¹P NMR spectroscopy and it was found that higher torrefaction temperature (200 and 225 °C) caused polycondensation and de-methoxylation of the aromatic units of lignin. Gel permeation chromatography analysis revealed that polycondensation during torrefaction resulted in an increase in the molecular weight and polydispersity of lignin. The torrefied lignin was subsequently used in CFP experiments using H⁺ZSM-5 catalyst in a micro-reactor (Py-GC/MS) to understand the effect of torrefaction on the product distribution from pyrolysis. It was observed that although the selectivity of benzene-toluene-xylene compounds from CFP of pine improved from 58.3% (torrefaction temp at 150 °C) to 69.0% (torrefaction temp at 225 °C), the severity of torrefaction resulted in a loss of overall aromatic hydrocarbon yield from 11.6% to 4.9% under same conditions. Torrefaction at higher temperatures also increased the yield of carbonaceous residues from 63.9% to 72.8%. Overall, torrefying lignin caused structural transformations in both type of lignins (switchgrass and pine), which is ultimately detrimental to achieving a higher aromatic hydrocarbon yield from CFP.

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1. Introduction

Biomass has been considered to be a sustainable carbon source for producing chemicals and liquid intermediates through fast pyrolysis, which could be upgraded to renewable fuels and other valuable products [1–7]. It consists of three major components cellulose, hemicellulose and lignin, whose composition varies from one species to another. Cellulose is a linear polymer composed of 1,4 beta-D linked anhydroglucose subunits, whereas hemicellulose is a branched, amorphous polysaccharide made of five carbon sugar

compounds. Lignin is the third constituent, which can be defined as an amorphous aromatic polymer of phenyl propane units. It is a complex and high molecular weight polymer formed by the dehydrogenation of hydroxyl cinnamyl alcohols such as coniferyl and sinapyl alcohols. The degree of methoxylation differs between the various lignin precursors and various types of intermolecular linkages (β -O-4, α -O-4, 5-5, β -5, and β - β) can occur, which varies in composition between different types of biomass. The decomposition of lignin results in the formation of compounds such as guaiacol, vanillin, syringol, anisole and other phenolic compounds. Due to such complexity in the structure of biomass, the thermal breakdown of these constituents (cellulose, hemicellulose and lignin) during pyrolysis results in the formation of a complex mix-

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ture of condensable compounds along with non-condensable gases and char.

This liquid intermediate from pyrolysis (bio-oil) suffers from certain undesirable properties such as [1] high oxygen content (~30–40%) making the product immiscible with conventional fuels; [2] presence of organic acids, causing corrosion and instability during storage; [3] low heating value (~19 MJ/kg) when compared to fossil-based fuels; [4] alkali and alkaline earth metals (Na, K, Ca and Mg) in biomass, which alters pyrolysis chemistry. A number of studies in the past decade have focused on improving these properties by deoxygenating the bio-oil from pyrolysis through catalytic upgrading and hydrodeoxygenation [7–13]. Promising catalysts including zeolites are being actively studied for *in-situ* catalytic fast pyrolysis (CFP) to upgrade the pyrolysis vapors and produce a highly deoxygenated liquid product. However recently, mild thermal pretreatment (torrefaction) has been suggested as an effective process to improve the properties of biomass before it is used as a feedstock for pyrolysis. Some of the advantages of torrefaction, such as [1] improved grindability of biomass; [2] lower O/C ratio; [3] improved biomass hydrophobicity; make it a promising technique to improve the economics of biomass-to-energy conversion.

During torrefaction, biomass is generally heated at moderate temperatures (200–300 °C) in an inert environment, which results in reduced oxygen content in the torrefied biomass mainly due to extensive decomposition of hemicellulose in this temperature range. Hemicellulose decomposition products such as acetic acid, furfural, water, CO and CO₂ are released from biomass during this process [14]. Meanwhile, the structure of cellulose remains relatively intact during this process since higher temperatures (>300 °C) are required for complete decomposition. Recent studies on torrefaction of biomass have shown that torrefaction is an effective pre-treatment which improves the yield and selectivity of aromatic hydrocarbons from CFP of torrefied biomass [15–20]. Recent publications by Neupane et al. [15] and Srinivasan et al. [19] discussed the effect of torrefaction parameters such as residence time and temperature on the structural changes in biomass and its subsequent influence on the product distribution from catalytic pyrolysis of biomass. Neupane et al. observed higher carbon yield of aromatic hydrocarbons from CFP of torrefied biomass and proposed that this could be a result of de-etherification and demethoxylation of lignin during torrefaction. However, since very limited studies have focused on the torrefaction and CFP of individual components of biomass, this hypothesis could not be confirmed. Further, the structural changes in lignin as a function of torrefaction at various temperatures is also not clear. Thus, the objective of this study was to understand the effect of torrefaction temperature on the structural changes in lignin and its influence on the product distribution from pyrolysis. Torrefaction of lignin extracted from southern pine and switchgrass through organosolv treatment was performed in a tubular reactor. Subsequently, the non-catalytic and *in-situ* CFP of torrefied lignin were performed in a micro-pyrolyzer.

2. Materials and methods

2.1. Biomass preparation

The southern pine used in this study was obtained from a local wood chipping plant in Opelika, Alabama and switchgrass was obtained from E.V. Smith Research Center, Macon County, Alabama. Biomass was first air dried for 72 h and a hammer mill (New Holland Grinder Model 358) fitted with a 1.58 mm (1/16 in.) sized screen was used to grind the samples. Subsequently, it was fractionated using a sieve shaker and particles in the desired size range (400 μm–840 μm) were used for organosolv lignin extraction.

2.2. Organosolv extraction

A known amount (350 g) of the biomass (dry weight) was soaked for 24 h in 65% ethanol and 1.0% (w/w) sulfuric acid (based on biomass) in a solid to liquid ratio of 1:7. The mixture containing biomass and liquor was loaded in a 4.0 L Parr reactor and pretreated at 170 °C for 1 h with a stirring rate of 60 rpm. After pretreatment, the reactor was cooled in a water bath and the resulting slurry was separated into a solid fraction and a liquid fraction by filtration. The solid fraction was washed with warm ethanol three times to remove the extractable lignin and stored at –20 °C. To prepare ethanol organosolv lignin (EOL) from biomass, 3-fold volume of water was added to organosolv spent liquor (the liquid fraction) after pretreatment. Organosolv lignin was precipitated and collected by vacuum filtration on Whatman No. 1 filter paper, washed with warm water to remove the water-soluble compounds and then dried. Since the pyrolysis was to be performed in a micro-pyrolyzer, the lignin had to be sieved further using a 200 mesh (74 μm) and the fraction that passed was used for characterization, torrefaction and pyrolysis experiments in this study.

2.3. Lignin torrefaction and characterization

Lignin from pine and switchgrass was torrefied at four temperatures (150, 175, 200, 225 °C) for 15 min in a tubular reactor (18 in. long, 1 in. outer diameter) placed in a programmed furnace (Thermo Scientific model TF55035A-1). 5 g of organosolv lignin was used for torrefaction at each condition, and the volatiles released from lignin during torrefaction were swept away by nitrogen gas flow at 1 L/min. Treatment time began when the furnace reached the desired set point. At the end of the treatment time, the torrefied samples were pulled from the furnace and immediately placed in desiccators to prevent further treatment and combustion. The samples (shown in Supplementary information Fig. S1) were weighed before and after torrefaction to calculate the mass loss as a result of torrefaction using a microbalance (Mettler Toledo, model XP6). Moisture and ash contents were determined for the lignin samples according to ASTM E872 and E1755 standards, respectively. Ultimate analysis to measure the carbon, hydrogen, nitrogen, oxygen and sulfur contents was performed for raw and torrefied lignin using a CHNS elemental analyzer (Thermo Scientific, model Flash 2000). Component analysis to measure extractives, cellulose, hemicellulose and lignin contents was performed according to Laboratory Analytical Procedure (LAP) developed by National Renewable Energy Laboratory [21]. Thermogravimetric (TG) analysis to calculate the weight loss as a function of temperature of raw and torrefied lignin was performed (TA Instruments, 2050 TGA) with a heating rate of 10 °C/min and helium flow rate of 20 mL/min. FTIR analysis to study the structure of raw and torrefied lignin was done using a Perkin Elmer Spectrum model 400 (Perkin Elmer Co., Waltham, MA). Each spectrum was recorded after 32 scans from 4000 to 650 cm⁻¹, by applying a vertical load on the sample at room temperature. Solid-state CP/MAS ¹³C NMR analysis was performed on a Bruker Avance III 400 MHz spectrometer, according to the methods previously described by Neupane et al. [15].

The lignin samples for Gel Permeation Chromatography (GPC) analysis were manually milled in a jar for 5–10 min. The molecular weight of lignin was analyzed by GPC after lignin acetylation. The derivatization of lignin was conducted on a basis of 10 mg lignin in 1 mL of 1:1 pyridine/acetic anhydride in the dark at room temperature for 24 h, 200 RPM. The solvent/reagents were removed by co-evaporation at 45 °C with ethanol, several times, using a rotary evaporator until dry. The resulting acetylated lignin was dissolved in tetrahydrofuran (THF) and the solution was filtered through 0.45 μm membrane filter before GPC analysis. The hydroxyl groups in lignins were quantitated by ³¹P

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