

Comparative study of the fast pyrolysis behavior of ginkgo, poplar, and wheat straw lignin at different temperatures



Lei Wang^{a,b,1}, Ran Zhang^{a,1}, Jian Li^c, Li Guo^d, Haiping Yang^c, Fuying Ma^{a,e,*}, Hongbo Yu^{a,*}

^a Key Laboratory of Molecular Biophysics of MOE, College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

^b Hubei Provincial Key Laboratory of Green Materials for Light Industry, School of Materials and Chemical Engineering, Hubei University of Technology, Wuhan 430068, China

^c State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

^d Key Laboratory of Hubei Province for Coal Conversion and New Carbon Materials, School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, China

^e Jiangsu Key Laboratory for Biomass Energy and Material, Jiangsu Province, Nanjing 210042, China

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ABSTRACT

Fast pyrolysis of milled wood lignin (MWL) isolated from ginkgo (soft wood), wheat straw (herbaceous biomass), and poplar (hardwood) were conducted at various temperatures (400/600/800 °C) and the liquid products were analyzed by GC–MS. Then all MWLs were fully characterized using GPC, TGA, FT-IR, 2D NMR, and elemental analyses. Ginkgo MWL showed higher selectivity toward guaiacols (92.38%) at low temperature (400 °C), especially a higher selectivity for five useful compounds (67.7%), namely creosol (10.24%), 2-methoxy-4-vinylphenol (17.83%), vanillin (15.65%), isoeugenol (14.84%), and apocynin (9.14%), as compared to MWLs from wheat straw or poplar. Overall, ginkgo lignin exhibits vast potential for volatilization at low temperature-selective pyrolysis, because it retains highly concentrated guaiacol-type structures which are easy to deconstruct and a few β-5' phenylcoumarans that are hard to crack.

1. Introduction

Lignin, as a class of natural aromatic polymers, is an underutilized resource available in massive quantities; it can be sourced from agricultural products, municipal wastes, paper and pulp processing, biomass-to-ethanol processing, and processing in other bio-refineries (Hasunuma et al., 2013; Tan et al., 2010). However, today, lignin is widely used only in industries such as those producing low-grade fuels and those generating electricity via direct combustion, particularly in pulp and papermaking processes, leading to wastage of this resource and aggravation of environmental pollution (Davis et al., 2016; Ragauskas et al., 2014). The structure of lignin is quite complex with varied proportions of different types of monolignols (p-coumaryl alcohol, coniferyl alcohol, and synapyl alcohol), depending on the source (Zakzeski et al., 2010). As one of the few renewable sources of aromatic chemicals, the depolymerization of lignin to low-molecular-mass phenolic monomers is increasingly recognized as an important pathway for lignin valorization (Pandey and Kim, 2011; Amen-Chen et al., 2001).

Over the past few years, fast pyrolysis techniques of lignocellulosic biomass to biofuels or bio-based chemicals/materials has attracted

considerable interest (Kang et al., 2018; Kan et al., 2016; Saidi 2013; Mohan et al., 2006; Xiao et al., 2001). Lignin constitutes 15–30% of the biomass weight and 40% of the biomass energy (Ma et al., 2015; Trinh et al., 2013), and shows huge potential in the synthesis of high-valued chemicals and liquid fuels. However, the thermal conversion of lignin with irregular and recalcitrant structure is significantly different in pyrolysis kinetics and product distribution from that of hemicellulose and cellulose (Ragauskas et al., 2014; Wang et al., 2018). Lignin valorization by pyrolysis is still a challenging process due to its complex behavior and relatively high solid yields under pyrolysis conditions (Pandey and Kim, 2011; Kleinert and Barth, 2008). Therefore, understanding the pyrolysis characteristics of different types of lignin could contribute to be essential for the further optimization of reaction conditions, reactor design, and developing effective scale-up technology of lignin pyrolysis.

Pyrolysis linked with GC–MS techniques are frequently employed to address lignin recalcitrance and limited solubility in common solvents (Moghaddam et al., 2017; Gutierrez et al., 2006). It is helpful to understand the linkage behaviors and their underlying reaction details in lignin pyrolysis and thus meet the challenges of how lignin can be

* Corresponding authors at: College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China.

E-mail addresses: mafuying@hust.edu.cn (F. Ma), yuhongbo@hust.edu.cn (H. Yu).

¹ These authors contributed equally to this work.

broken into smaller molecular units and further converted to more value added products. Zhou et al. used a fixed bed to pyrolyze milled wood lignin (MWL) and organosolv lignins at 500 °C (Zhou et al., 2016). Lou et al. invested considerable efforts into the mechanistic investigation of rice straw lignin subunit bond cleavages and the subsequent formation of monophenols (Lou et al., 2018). In addition, the pyrolytic behavior of Alcell lignin (organosolv pulp processed from a mixture of hardwoods) and Asian lignin (soda pulp processed from a mixture of wheat straw and Sarkanda grass) was explored (Jiang et al., 2010). Zhao et al. studied and compared the pyrolysis of alkali lignin provided by Sigma-Aldrich with that of cellulose and hemicellulose (Zhao et al., 2017).

Lignins derived from different sources, as well as the evolution of ether linkages during pyrolysis, have widely been studied, with pine and poplar as well as corn stover mostly reported. Preferably, the lignin pyrolysis temperature should be as high as 600 °C. However, the structures of lignin from different origins are quite different, and the structures of the raw material and the pyrolysis temperature both have a great influence on the pyrolysis products. Moreover, products with narrow distributions at lower pyrolysis temperatures are much more required for the sake of downstream processing, which is still rarely reported.

Ginkgo biloba is rare species in the mesozoic era, which is endemic and widely cultivated in China. This uniqueness makes it quite important in forestry resources of China. The ginkgo tracheid walls are quite morphologically similar to those of representative conifers and lignin isolated from ginkgo has enormous potential as a renewable resource. However, the detailed characterization of its structure and pyrolysis behavior has rarely been performed. In this study, fast pyrolysis of milled wood lignin (MWL) isolated from ginkgo, wheat straw, and poplar were conducted at various temperatures (400 °C, 600 °C, and 800 °C), then all MWLs were fully characterized mainly using gel-state 2D HSQC NMR to understand the fast pyrolysis behavior based on the correlation between structures, pyrolysis parameters, and the changes of individual components in the products. To further evaluate the effect of temperature on the fast pyrolysis behavior of different lignin species, MWLs extracted from wheat straw (herbaceous biomass widely available in China) and poplar (hardwood generally used in the pulp and paper industry) were also fully characterized and investigated.

2. Materials and methods

2.1. Materials

Three representative plants, ginkgo, poplar and wheat straw were collected from Hubei Academy of Agricultural Sciences. The MWL of ginkgo, wheat straw, and poplar were obtained according to the classical method (Björkman, 1956). Pre-treatment procedures are done as follows. The biomass were air-dried, milled, extracted with benzene/ethanol (2/1, v/v) for 12 h to remove resin, fats, waxes, soluble tannin and pigment, and successively degreased with boiling water for 8 h. The obtained powder was dried in vacuum for 96 h, ground with ultrafine pulverizer for 30 min to destruct the cell walls, and then reserved for MWL isolation. The following lignin isolation procedures were illustrated in Fig. 1. The lignin yield extracted from ginkgo, wheat straw and poplar is 4.87%, 4.35%, and 4.72%, respectively.

2.2. Characterization of lignin

The chemical composition analysis was according to methods established by the National Renewable Energy Laboratory (NREL) (Sluiter et al., 2008; Hames et al., 2008). The elemental analysis (CHNS-O) was conducted in an elemental analyzer (Vario Micro Cube, Elementar, Germany) using approximately 5 mg of lignin each time.

The molecular weight distributions of lignin was determined using a gel permeation chromatography (GPC) instrument (SHIMADZU, HPLC-

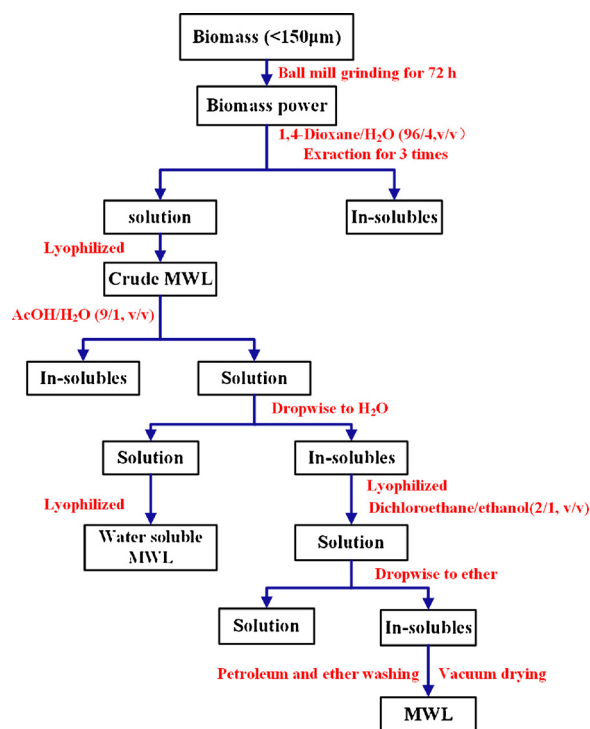


Fig. 1. The main extraction procedures of MWLs.

20AT) equipped with differential refraction detector (SHIMADZU, RID-10A) and ultraviolet detector (SHIMADZU, SPD-20A) at 254 nm, calibrated with polystyrene (EasiVial PS-M, 4 ml) standards with molecular weight range of 162–400000 g/mol. Chromatographic column (Styragel HR4E, 7.8*300 mm, WATERS) and guard column (Styragel, 4.6*30 mm, WATERS) were connected in series and maintained at 50 °C. Dimethylformamide (DMF) with 0.1 mol/L LiCl with a flow rate of 1.0 mL/min was used as the eluent.

Fourier Transform Infrared Spectrometry (FT-IR) analysis of lignin samples were obtained on Nicolet 6700 infrared spectrometer (US Thermo Nicolet Company) scanned from 4000 to 400 cm^{-1} .

Two-Dimensional Heteronuclear Single-Quantum Correlation Nuclear Magnetic Resonance (2D HSQC NMR Analysis) were carried out referring to methods described by John Ralph (Del Río et al., 2012). In the case of the MWL, around 100 mg was dissolved in 0.75 mL of $\text{DMSO-}d_6$ by ultrasonic treatment for 30 min. NMR spectra were recorded at 25 °C on a Agilent 600 MHz DD2 instrument equipped with a cryogenically cooled 3 mm HCN auto triple resonance probe with inverse geometry with spectral widths of 5000 Hz (from 10 to 0 ppm) and 25,000 Hz (from 165 to 0 ppm) for the ^1H - and ^{13}C - dimensions. The number of collected complex points was 2048 for the ^1H dimension with a recycle delay of 1.75 s. The number of transients was 64, and 256 time increments were always recorded in the ^{13}C dimension. The $^1\text{J}_{\text{CH}}$ used was 140 Hz. The central solvent peak was used as an internal reference (δ_{C} 39.5; δ_{H} 2.50).

Thermal gravimetric analysis (TGA) experiments were performed with sensitive thermobalance (Perkin-Elmer, Diamond) by Analytical and Testing Center, Huazhong University of Science and Technology. The lignin sample was heated in a nitrogen environment up to 110 °C at 10 °C/min, and held for 10 min to remove the moisture. Later, the sample continued to be heated up to 900 °C at 10 °C/min and held at the same temperature for 10 min.

2.3. Fast pyrolysis of lignin

Fast pyrolysis tests were performed using a Pyroprobe 5200 analytical pyrolyzer (CDS Analytical Inc.) and the samples were heated up at

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