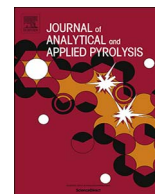




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Modeling the pyrolytic behavior of lignin through two representative monomers: Vanillin and acetovanillone

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ABSTRACT

Vanillin and acetovanillone are typical primary pyrolysis products of β -O-4 lignin dimers, but the thermal reactions have not yet been elucidated. Data on their thermal reactivity and secondary pyrolysis pathway was studied via *in-situ* FTIR within a tube furnace reactor system. The result showed that pyrolysis breakdown products spanned four categories: gas, char, monomers, and polymers and secondary reaction products were polymers and char from re-polymerization and carbonization. In general, vanillin showed higher reactivity than acetovanillone. The removal of the -CHO group in vanillin was first observed at 400 °C, to present a thermal reaction similar with guaiacol at higher temperatures. The reactivity of the -COCH₃ group in acetovanillone was low during the pyrolysis process in which radical-induced rearrangement of the aryl-OCH₃ group into the aryl-CH₃ group initially occurred as the major side-chain-conversion reaction. Finally, side-chain-conversion also included aryl demethylation or demethoxylation, tautomerism of -COCH₃, and cyclization between aryl-OCH₃ and -OH group but at low reaction degrees.

1. Introduction

With dwindling reserves and rising costs of fossil fuels, lignin as an abundant byproduct of the biomass refinery and pulping industry, has recently attracted a great deal of attention to produce the energy and chemical compounds [1]. Lignin, which is normally contained in wood at 20–30% by mass, is a polymer of phenyl propanes linked by ether and carbon-carbon bonds [2]. The most abundant lignin linkage is β -O-4 occupying nearly 50% of softwood linkages and even more than 60% in hardwoods [3]. By breaking down such linkages, value-added aromatics will be obtained, precursors to high-grade biofuels or functionalized fine chemicals [4]. Pyrolysis is a promising thermochemical technology to break down ether and carbon-carbon linkages in lignin [5]. However, the quality and yield of phenolic chemicals are unsatisfactory due to complex structures and random chemical bonds. Hence, the elucidation of the molecular mechanisms of pyrolysis is necessary to better understand modes of utilization.

Over the past three decades, lignin pyrolysis has been widely studied, but the studies have been mainly focused on formation mechanisms of primary products [6–10]. Typically, β -O-4 dimers have been the model compounds for studying the pyrolysis mechanism. Lignin pyrolysis produces primary and secondary reactions of these primary products [11]. Chu et al. [12] found that the β -O-4 linkages thermally

decomposed between 250 °C and 350 °C with the formation of solid products at 350 °C. Britt et al. [13] studied the rapid vacuum pyrolysis of phenethyl phenylether (PPE) and proposed a complex reaction pathway dominated by free-radical reactions, molecular rearrangements, and concerted elimination reactions. Huang et al. [14] studied the mechanism of pyrolysis of β -O-4 model compounds using density functional theory and proposed three pyrolysis pathways: (1) the homolytic cleavage of C _{β} -O bond, (2) the homolytic cleavage of C _{α} -C _{β} bond, and (3) the concerted reactions. To identify the chemical pathways for the formation of main products during pyrolysis, the primary reactions of *o*-methoxy phenethyl phenyl (*o*-CH₃O-PPE) pyrolysis were investigated by Wang and Liu [15]. It was found that the *o*-methoxy group reduced bond dissociation energies (BDEs) of the β -O-4 linkage. Despite these latter advances, the underlying molecular mechanisms of lignin pyrolysis are still lacking. The secondary reactions of monomeric model compounds, which are regarded as primary products derived from lignin pyrolysis, are therefore of great significance for any in-depth understanding of these underlying molecular mechanisms.

Asmadi et al. [16] utilized guaiacol and syringol to study the thermal reactivity of different lignin aromatic nuclei. Their results suggested that homolysis of the O-CH₃ bond to form methyl and pyrocatechol radicals and radical-induced rearrangement of aromatic OCH₃ into aromatic CH₃ structure were two important reactions for

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guaiacol. In addition, it was also found that the odds doubled for coke formation with syringol. Such reactivity difference was explainable by invoking differences in reactivity among the *o*-quinone methide intermediates [16,17]. However, pyrolysis coupled with gas chromatography/mass spectrometry (GCMS) gave useful information on the chemical structures of the volatile products, but failed to provide evidence of *o*-quinone methide intermediates. In past studies from this lab [18], guaiacol, vanillin and acetovanillone were three main products found from the cleavage of the C_β–O bond and C_α–C_β band of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-ethanone (referred to as M1). Considering the advantages of online analysis, the technology of *in-situ* FTIR was adopted for investigating the pyrolysis pathway of guaiacol [19]. It was noteworthy that the *o*-quinone methide intermediates were detected at about 350 °C, a powerful lever which provides direct evidence of secondary reactions pathways of guaiacol [19]. Nevertheless, the secondary pyrolysis mechanism of vanillin and acetovanillone are not completely understood. It has been observed that both vanillin and acetovanillone are unstable during pyrolysis, and both might play an important role on polymerization and side-chain-conversion during pyrolysis.

Hence, both vanillin and acetovanillone were chosen as model compounds. Firstly, the reaction was investigated under N₂ at 400–600 °C in a closed ampoule reactor to understand product distribution. Secondly, various functional groups from the thermal decomposition of vanillin and acetovanillone were compared by *in-situ* FTIR spectroscopy as part of real-time monitoring the reaction mechanism and the active intermediates. The focus was especially on the role of the –CHO, –OH, –OCH₃ and –COCH₃. Based on those experimental results, the reaction pathways of β–O–4 lignin dimeric model compound (M1) were elucidated by analysis of the transformation and/or degradation routes of vanillin and acetovanillone.

2. Materials and methods

2.1. Materials

4-Hydroxy-3-methoxy-acetophenone (Acetovanillone) and 4-hydroxy-3-methoxy-benzaldehyde (vanillin) were purchased from Aldrich Ltd, and the purity was higher than 98%. All chemicals were used without further purification.

2.2. Tubular reactor pyrolysis system

2.2.1. Typical pyrolysis experiments

Approximately 100 mg acetovanillone or vanillin was placed at the bottom of a tubular reactor using quartz U-tube. The details of the apparatus was shown in Fig. 1 and described in past reports [20]. The air inside the tube was exchanged with N₂, and sealed at atmospheric pressure. Pyrolysis was conducted by inserting the whole ampoule into a muffle furnace preheated to a desired temperature of 400, 450, 500, 550 or 600 °C. After 2 min, the U-tube was removed from the furnace

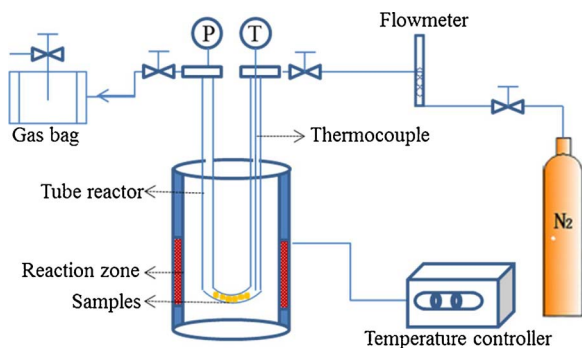


Fig. 1. A schematic for the U-tube reactor.

and cooled using ice water for 2 min. The ampoule was opened and the gas yield was obtained by measuring the mass. Mixtures were collected by pouring and washing the reactor with ethyl acetate three times. The reaction mixture was filtered to separate char. After drying in an oven at 105 °C overnight, the remaining char was weighed for yield and subsequent analysis. Water was absorbed by adding anhydrous Na₂SO₄ to the liquid mixture overnight. After using a filtration funnel to separate, the solvent phase was diluted with ethyl acetate to 100 mL (EA-soluble fractions) for further analyses.

2.2.2. Product analysis

The qualitative and quantitative analyses of EA-soluble fractions (including monomer products and the unreacted samples) were conducted on a GC equipped with a mass selective detector (Agilent HP6890-5973 GCMS; with a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas at a flow rate of 1 mL/min. The temperature program was as follows: 40 °C, hold 1 min; 250 °C (rate 10 °C/min), hold for 4 min; 280 °C (rate 5 °C/min), hold for 5 min. The injector temperature was 250 °C with a split ratio of 10:1. The components were scanned in the mass range (*m/z*) of 28–400 Da at an electron ionization voltage of 70 eV. Identification of the products was conducted by means of National Institute of Standards and Technology (NIST) library of mass spectra.

Fourier Transform infrared spectroscopy (FT-IR) measurements of char were carried out on a Nicolet iS50 Fourier transform infrared spectrometer (Thermo Fisher Nicolet, American) by using potassium bromide measured over 4000–400 cm⁻¹ wavenumbers at a resolution of 2 cm⁻¹ wavelength.

2.2.3. Calculations

The monomer yields were calculated by an external standard method. The yields of various products and conversion were calculated using the following equations:

$$\text{Gas yield (wt\%)} = (m_1 - m_2)/m_{\text{sample}} \times 100\%;$$

$$\text{Char yield (wt\%)} = m_{\text{char}}/m_{\text{sample}} \times 100\%;$$

$$\text{Oil yield (wt\%)} = (m_{\text{sample}} - m_{\text{gas}} - m_{\text{char}})/m_{\text{sample}} \times 100\%;$$

$$\text{Monomer yield (wt\%)} = m_{\text{monomer}}/m_{\text{sample}} \times 100\%;$$

$$\text{Polymers yield (wt\%)} = \text{Oil yield} - \text{Total monomer yield};$$

$$\text{Conversion (wt\%)} = (m_{\text{sample}} - m_3)/m_{\text{sample}} \times 100\%;$$

$$\text{Monomer molar yield (\%)} = n_{\text{monomer}}/n_{\text{sample}} \times 100\%;$$

Where m_{sample} = the initially added mass of samples (100 mg), m_1 = initially added mass of samples (100 mg) + the mass of quartz U-tube, m_2 = the residual mass of samples + the mass of quartz U-tube, m_{char} = mass of char, m_{monomer} = the mass of monomers in oil, m_3 = the residual mass of samples, n_{monomer} = the molar mass of monomers in oil, n_{sample} = the initially added molar mass of samples. All characterizations were repeated 2 or 3 times, and the presented data display average values.

2.3. *In-situ* diffuse reflectance infrared pyrolysis

The *in-situ* diffuse reflectance infrared pyrolysis system used Fourier transform infrared spectroscopy (*in-situ* FTIR) (Nicolet IS50, Thermo Fisher Scientific Company, USA) and an *in-situ* pool with a deuterated sulfuric acid GSH detector. To ensure full beam transmittance and good heat resistance, CaF₂ with protective water-cooling was used as the window. The real time temperature of the *in-situ* pool was adjusted using a temperature controller with a PID (proportion, integration and differentiation) thermo-coupling controller, with a temperature control accuracy of ± 1 °C. Specific operation parameters were as follows: nitrogen having a purity of 99.999% was used to purge the system at a

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