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Reaction chemistry and phase behavior of lignin in high-temperature and supercritical water

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Abstract

Decomposition of organosolve lignin in water/phenol solutions was studied in a 50 nL micro-reactor coupled with optical, Raman and infrared microscopies at temperatures up to 600 °C and water densities up to 1165 kg/m^3. It was found that when phenol was used with {lignin + water} mixtures that a homogenous phase was formed that seemed to promote the decomposition of lignin into phenolic fragments by hydrolysis and pyrolysis. Phenol, along with the homogenous reaction conditions also inhibited re-polymerization of the phenolics and promoted oil formation. On the other hand, in the absence of phenol, lignin remained as a heterogeneous phase with water over the range of conditions studied. The homogeneous conditions and conditions for inhibiting char formation by phenol were elucidated and it was found that mixtures of phenol and lignin become homogeneous at 400–600 °C and high water densities of 428–683 kg/m^3, corresponding to maximum pressures of 93 MPa. These results were further used to propose reaction paths.

Keywords: Lignin; Supercritical water; Hydrothermal; DAC; Biomass; Liquefaction; Raman; FT-IR

1. Introduction

Lignin (20% in wood), cellulose (50%) and hemicellulose (25%) are the three major constituents of plant biomass (Bobleter, 1994). Lignin is produced in large amounts by wood pulping process (e.g., black liquor). Lignin is a highly stable biopolymer built from three highly cross-linked phenylpropane (C_6–C_3) units of *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Amen-Chen et al., 2001), which are bonded together with over two-thirds being ether bonds (C–O–C) and the rest being C–C bonds (Haluc and Irmouli, 1998). Lignin can be hydrolyzed via cleavage of the ether bonds that are catalyzed by [H^+] and [OH^-] or water molecules (Bobleter, 1994). Almost all of the lignin produced is used as a low-grade fuel by direct combustion and it is not upgraded to oil, gas or recovered as chemicals. Supercritical water (SCW; 374.2 °C and 22.1 MPa), as a weak-polar solvent with a high value of ion product, is a possible solvent that can dissolve and hydrolyze lignin for potentially production of phenolic chemicals or for upgrading lignin for fuels.

Much work has been done on the reaction of lignin in SCW or hydrothermal water, including liquefaction (Ochi et al., 1984; Johnson et al., 1988; Funazukuri et al., 1990), gasification (Watanabe et al., 2003; Osada et al., 2004, 2006; Sato et al., 2006), pretreatment (Kim and Holtzapple, 2006), extraction lignin from actual biomass (Sasaki et al.,

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2003) and decomposition leading to various chemicals (Bobleter and Concin, 1979; Libanati et al., 1988; Saisu et al., 2003; Okuda et al., 2004, 2007; Sagehashi et al., 2006) with and without catalysts. Bobleter and Concin (1979) proposed a simplified reaction model: lignin → water soluble (monomeric units) + acetone soluble (oligomers; higher molecular lignin fragments) → polymer (lignin-like substances). Saisu et al. (2003) and Okuda et al. (2004) gave a detailed scheme for lignin reactions in SCW. According to their proposal, lignin first decomposes by hydrolysis and dealkylation yielding formaldehyde and low-molecular-weight fragments that have reactive functional groups and compounds such as syringols, guaiacols, catechols and phenols. Then, cross-linking between formaldehyde and these fragments occur, and the residual lignin gives higher-molecular-weight fragments. Okuda et al. (2004) found that when phenol was used in SCW, no char formation was found, because char formation was depressed due to entrapment of active fragments (e.g., formaldehyde) and capping of active sites occurs by excess phenol. However, the phase behavior or conditions for these phenomena and their relationship to char formation could not be clearly understood due to the nature of experiments preformed with bomb type batch reactors. In the reaction of lignin, the phase behavior is probably one of the most important factors to understand its conversion to liquid products.

In this paper, we apply a diamond anvil cell (DAC) technique to observe in-situ the phase behavior of lignin and water/phenol systems under high temperature and high pressure conditions. The reaction products were analyzed with FT-IR and Raman microscopies. The experiments were conducted at 400 and 600 °C for 5–60 min reaction times, and with initial water densities from 683 to 1165 kg/m^3. The high density conditions have the possibility to retard radical formation.

2. Thermal reaction chemistry of lignin

Thermal reactions of lignin via pyrolysis and decomposition in water can be segregated into four products: gas, aqueous (water-solubles), oil [tetrahydrofuran (THF) or acetone solubles] and residue (THF insolubles).

2.1. Pyrolysis

Jegers and Klein (1985) studied pyrolysis of kraft lignin at 300–500 °C. A total of 34 products (12 gases, 2 light liquids and 20 single-ring phenolics) were quantified. The 12 gases were CO_2, CO, C_1–C_4 hydrocarbons (HCs), H_2S and H_2. The major gaseous products were CO_2, CO and CH_4. Two liquids formed were water and methanol. Methanol was produced from side-chain methoxy groups in lignin. The 20 phenolics produced were phenols (phenol, *o*-cresol, *m*-cresol, *p*-cresol, 2-ethylphenol, 3-ethylphenol, 4-ethylphenol, xylenol, 4-propylphenol), guaiacols (guaiacol, 4-methylguaiacol, 6-ethylguaiacol, 4-ethylguaiacol, 4-propylguaiacol) and catechols (catechol, 6-methylcatechol, 4-methylcatechol, 6-ethylcatechol, 4-ethylcatechol, 3-methoxycatechol). Other pyrolysis products of benzene, aromatics, formaldehyde, acetaldehyde, acetic acid were also found at 500–900 °C (Caballero et al., 1997). Reaction pathways were proposed at 400–600 °C (Petrocelli and Klein, 1984): At 400–500 °C, roughly half of the Kraft lignin's inter-unit links would cleave, yielding single-ring phenolic products, a residual lignin and multi-ring phenolic fragments that contain mainly diphenylmethane (DPM) and diphenyl ether linkages. At higher temperatures of 500–600 °C, these should generate additional single-ring phenolics through cleavage of more thermally stable DPM bonds and also yield derivatives of fluorine, phenanthrene, and other fused-ring products through condensation reactions.

2.2. Decomposition under hydrothermal and supercritical conditions

The decomposition of lignin in water at elevated temperatures and pressures should be significantly different from pyrolysis because of the existence of additional hydrolysis reactions catalyzed by H^+ and OH^-, and the associated phase behavior. Phenols were the main products from both pyrolysis (Jegers and Klein, 1985) and SCW decomposition (Martino and Savage, 1997; Sato et al., 2004a,b). Substituted phenols can be dealkylated to phenol (phenol is stable in SCW; Thornton, 1991) as main product (Martino and Savage, 1997; Sato et al., 2004a,b).

Townsend et al. (1988) found that ether compounds in lignin, such as dibenzyl ether (DBE), phenethyl phenyl ether (PPE), benzyl phenyl ether (BPE) and guaiacol, all underwent parallel pyrolysis and hydrolysis. DBE pyrolyzed only to toluene and benzaldehyde, but decomposed in SCW to benzyl alcohol, toluene, benzaldehyde, and oligomers. The yield of benzyl alcohol reached a maximum and then decreased at longer times as it reacted to form oligomers in SCW. PPE decomposed in SCW according to two pathways. In the first pathway, PPE pyrolyzed to phenol and styrene, and then styrene underwent secondary reactions to yield ethyl benzene, toluene, benzene, and other minor products: benzaldehyde, DPE, DPM, 1,3-diphenylpropane (DPP), and compounds having a molecular weight higher than that of PPE. In the second pathway, PPE hydrolyzed to phenol and phenethyl alcohol. Reaction of BPE in SCW occurred as a combination of a thermal pathway leading to phenol and toluene and a hydrolysis pathway yielding phenol and benzyl alcohol. In SCW, guaiacol decomposed to catechol and methanol, and then secondary decomposition of catechol formed char and the minor products of *o*-cresol and phenol. The pyrolysis pathway led primarily to catechol and char, whereas the hydrolysis pathway produced catechol and methanol (Townsend et al., 1988; Lawson and Klein, 1985). However, in SCW, C–C bonded hydrocarbon dimers (e.g., DPE, DPP) underwent only pyrolysis (Townsend et al., 1988; Lawson and Klein, 1985; Ehara et al., 2000).