

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/m³. 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/m³, corresponding to maximum pressures of 93 MPa. These results were further used to propose reaction paths.

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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 (C₆–C₃) 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 \rightarrow water soluble (monomeric units) + acetone soluble (oligomers; higher molecular lignin fragments) \rightarrow 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 performed 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/m³. 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 CO₂, CO, C₁–C₄ hydrocarbons (HCs), H₂S and H₂. The major gaseous products were CO₂, CO and CH₄. 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, xyleneol, 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).

Bobleter and Concin (1979) studied the hydrothermal degradation of poplar lignin at 270–372 °C. More than 50% water-soluble, 90% acetone–water (10:1) soluble products were obtained. Seven hydrolyzates in the water-soluble phase from hydrothermal degradation of Poplar wood at 215 °C were identified that were single-ring compounds (4-hydroxybenzoic acid, vanillic acid, syringic acid, vanillin, coniferyl alcohol, syringaldehyde, sinapyl alcohol) (Pecina et al., 1986).

3. Experimental

3.1. Materials

Organosolve lignin (THF soluble), phenol (99.5% purity, density of 1071 kg/m³) and H₂O₂ (50 wt%) used in the experiments was obtained from Sigma-Aldrich (St. Louis). The chemical structure consisted of guaiacyl-syringyl lignin composed of coniferyl alcohol and sinapyl alcohol units in varying ratios. The mean molecular weight ($M_w = 1500$) and composition (C_{3.25}H_{3.54}O) of the sample were reported in the previous work (Saisu et al., 2003; Okuda et al., 2004).

3.2. Diamond anvil cell (DAC)

The microreactor, diamond anvil cell (DAC) allows for in-situ observations of samples in the fully-visible chamber via optical microscopy in SCW (Bassett et al., 1993). The DAC micro-chamber (ca. 50 nL) consisted of a hole (500 μm i.d.; 250 μm thickness) and sealed by compression of two opposing anvils made of diamond. The chamber was rapidly heated by two electric microheaters (up to 30 °C/s) or cooled (up to 30 °C/s) by cutting power, which is convenient for the study of phase behavior and chemical reactions.

The initial density of water inside the chamber was evaluated by the saturation curve data of water (Saul and Wagner, 1989) or by knowing its pressure measured by ruby fluorescence (Forman et al., 1972) as described below. When the sample and water were loaded into the DAC chamber, argon gas bubbles would appear. Heating the chamber caused the liquid to expand and the gas bubbles to shrink until they disappeared at homogenization temperature (T_h). The bulk density of the water was assumed to be that of the liquid water along the liquid–vapor ($L-V$) curve at T_h . Water density was adjusted by compressing the two anvils for the desired size of entrained gas or to totally eliminate the gas. In the case of no gas bubbles, a ruby fragment was loaded into the chamber at room temperature. Pressure was calculated by the wave number shift of ruby fluorescence R_1 (or R_2) line from ambient pressure to pressure of interest measured by Raman microscopy (JASCO NRS-2000C, Tokyo) with argon ion (488 nm) laser. The pressure (kbar) is proportional to the shift (cm⁻¹) with slope of 1/0.77 (or 1/0.84) for R_1 (or R_2) line (Forman et al., 1972).

Pressure could be calculated from the instantaneous values of the temperature and the initial water density based on the negligible changes of the chamber volume of the DAC (Bassett et al., 1993). For pyrolysis, the chamber was filled with argon gas and sample, and pressure was calculated with the equation of state for an ideal gas.

In the experiments, temperature was controlled by a high speed PID controller (RKC Instrument Inc., REX-G9 Series/A, Tokyo) and recorded by a scanner (Hewlett-Packard Model 34970A, Palo Alto, CA). The phase transitions and phase behavior of the samples in the DAC were recorded by a CCD camera (Olympus KY-F55MD, Tokyo) after 100× magnification by a microscope (Olympus SZH10, Tokyo). Digital imaging analysis of the sample area % was calculated by using digital image analysis software (Scion Image, Frederick, MD). The area% were treated as apparent concentration or volume concentration assuming that the sample and the chamber had the same depth.

After the reaction, the solid residues and oils located on the diamonds were analyzed by the laser-Raman microscopy (JASCO NRS-2000C, Tokyo) and FT-IR microscopy (UMA 500, Bio-Rad, Cambridge, MA). Details of the experimental set-up and procedures can be seen in our previous works (Fang et al., 1999, 2004a, b).

4. Results

Many experiments have been done at different water densities, heating rates, maximum temperatures and lignin concentrations. But, only six typical tests are presented here due to large amount of data. Tests were repeated to verify reproducibility. Table 1 summarizes the experiments.

4.1. Decomposition in supercritical water

In run 1, {21% lignin + water} system was heated at a water density of 954 kg/m³ to 400 °C (Table 1). The lignin started to melt at 174 °C and then expanded and changed color to red up to 377 °C. At this temperature, the solution became red and particles began to precipitate from the aqueous phase, which means that some amount of lignin fragments had dissolved and dispersed into the aqueous phase. As temperature increased to 400 °C (ca. 567 MPa) and was held at these conditions for 5 min, the expanded lignin became black while more particles precipitated and the solution gradually changed to red color. After reaction, three products were obtained: a non-dissolved black residue I, a black precipitated residue II and a reddish oil III formed from solution. IR spectrum showed that the non-dissolved residue I was decomposed, but still had a lignin character compared with lignin standard. Residue I still retained the characteristic peaks at 2800–3200 cm⁻¹ but several peaks at low wave-number range (400–1600 cm⁻¹) were absent. However, no differences could be seen in the Raman spectra among residue I, oil III, or the original lig-

Table 1
Summary of experimental conditions

Run	Solvent	Reactants	Max <i>T</i> (°C)	Max <i>P</i> (MPa)	Density (kg/m ³)	Appar. conc. area (%)	Heating rate (°C/s)	Holding time at <i>T</i> _{max} (min)
1	Water	Lignin	400	567	954	21	7.7	5
2	Water	Lignin	400	785	1165	46	4.1	5
3	Water	Lignin	600	994	964	17	10	5
4	Gas	Lignin	600	0.3	–	–	12.5	5
5	Gas	Lignin + phenol	400	–	428	1:1 ^a	2.8	5
6	Water	Lignin + phenol	400	93	683	1.8:1.1:1 ^b	1.8	60

^a Area ratio of lignin:phenol.

^b Area ratio of lignin:phenol:water.

nin because only the C=C aromatic stretching band was detected at 100–4000 cm⁻¹.

In run 2, much higher water density of 1165 kg/m³ was applied to the {46% lignin + water} system. Initial pressure (density) was measured by a spherical ruby particle since the sample homogenization temperature could not be used to assess the density. As the temperature increased to 400 °C and was held at these conditions for 5 min, the lignin changed slightly in position without any apparent color change, no melting or expansion. At 361 °C, reaction chamber was expanded, compressed by high-density water, to 115% and caused water density drop from 1165 to 1011 kg/m³, and tiny particles precipitated and then the lignin began to shrink slightly as more particles precipitated from solution until 400 °C. Little change was found during the time that the sample was kept for 5 min at 400 °C. The non-dissolved residue I had a similar Raman spectrum as that for the low pressure run 1 but with a lighter black color. The light color probably means that the residue I is low in molecular weight due to the retarding radical formation by high density water. Minor oil III and some precipitated residues were found for this high water density run (Max *P* = 0.8 GPa; Table 1).

In run 3, {17% lignin + water} was heated to 600 °C at a water density of 964 kg/m³. After melting, expansion and particle precipitation, the non-dissolved lignin and precipitates became black at 600 °C. After reaction at 600 °C, the chamber became completely opaque and formed two films that covered the chamber. The non-dissolved residue I, precipitated residue II and reddish oil III were analyzed with IR spectrum, which showed that the non-dissolved residue I decomposed severely as it exhibited only one weak peak at 1605 cm⁻¹. However, the residue I had an additional Raman band at 1378 cm⁻¹, which was a C–C bond vibration. The reddish oil III had a similar Raman spectrum but with a stronger and broad peak at 1378 cm⁻¹. The non-dissolved residues at lower temperatures and shorter reaction times were also analyzed. The results show that the residue from 430 °C and 0 s reaction time was similar to that at 400 °C and 5 min, and at 600 °C, where lignin was severely decomposed. An experiment with 15% H₂O₂ was conducted at 600 °C. Complete dissolution did not occur, however, the non-dissolved residue was found to have an

additional peak at 3040 cm⁻¹ that was likely from oxidation.

4.2. Pyrolysis

Pyrolysis (run 4) of lignin was conducted in the same chamber as the aqueous experiments but without water. High heating rates of 12.5 °C/s to 600 °C were used. After melting and color change, the lignin completely volatilized to gas at 434 °C. As temperature and time increased, a black residue was formed. The black residue I was charcoal-like, and had similar IR and Raman spectra as those in run 3. There was no change in the Raman spectrum between the oil III and that formed in SCW in run 3.

4.3. Decomposition with phenol

In run 5, {phenol + lignin; 1:1, vol.} was heated to 400 °C at an initial phenol density of 428 kg/m³. At 364 °C, the gas bubble disappeared and formed a reddish solution within the chamber. The reddish solution still remained at temperatures up to 400 °C but it became opaque gradually as time increased due to the precipitation of numerous particles. After reaction, the black residue II from precipitation as the main product and a very thin transparent oil film III was formed, clearly the 2 products were from the homogeneous phase. IR spectrum showed that the residue II had a lignin-like character and was similar to that formed in water (run 1) but with more peaks at 400–1600 cm⁻¹. For both phenol and water being used, the residue still retained a lignin-like character after 30 min reaction time at 400 °C.

In run 6, {lignin + phenol + water; 1.8:1.1:1, vol.} were heated to 400 °C and held at that temperature for 1 h with an initial water density of 683 kg/m³. After the gas bubble disappeared, the lignin sample dispersed and flowed to the wall of the chamber at 297 °C and formed a homogeneous phase. At 400 °C, a reddish product precipitated from the solution and as heating continued, the sample gradually became black due to the precipitation of black particles. At 20 min, the sample chamber could still be seen but became completely opaque after 30 min. Both residue II and oil III precipitated from solution and still had a lignin-like character. However, oil III had strong peaks at

2800–3200 cm^{-1} . The mixture of {phenol + water} seemed to inhibit char formation and yield more oil and black precipitated residues.

5. Discussion

In our DAC experiments, after opening the DAC, gases were released and could not be collected. Therefore, three types of products were typically obtained on the surface of low diamond: a non-dissolved black residue I, a precipitated residue II and a reddish oil III. The oil and precipitated residue were formed via precipitation from the aqueous solution. The lignin sample was also studied in larger batch reactors (6 mL) to allow for more detailed products to be obtained (Watanabe et al., 2003; Osada et al., 2004; Saisu et al., 2003; Okuda et al., 2004). Four products: a gas mixture (6–13 mol%; H_2 , CO , CO_2 and C_1 – C_4 HCs), an aqueous solution {water-soluble: 20–25 mol%, e.g., catechol, methanol [4.4 wt% yield from lignin sulphonate (Funazukuri et al., 1990)]}, an oil (THF soluble: phenolics and aromatics, e.g., toluene, propyl benzene and a residue (THF insoluble: 1–8 wt%) phases were obtained (Watanabe et al., 2003). Saisu et al. (2003) found that the oil contained eight single-ring phenolic hydrolyzates (syringol,

methylsyringol, ethylsyringol, guaiacol, ethylguaiacol, acetoguaiacol, catechol, methoxycatechol). Guaiacols and catechols were also from neat pyrolysis. No ethylsyringol, guaiacol and ethylguaiacol were detected for long reaction times. The oils consisted of lighter compounds with an average molecular weight of 200 after 1 h reaction time as compared with the value of 1500 for the original lignin. Less residue was obtained in SCW (18.4 C% without catalyst and 0% with Ru/TiO_2) as compared with pyrolysis experiments (46.4 C%) at 400 °C for 15 min (Osada et al., 2004; Okuda et al., 2004). These results show that SCW inhibits char formation, which was also reported for lignin sulphonate (Funazukuri et al., 1990), and that Ru/TiO_2 catalyst promoted gas production and prevented the aqueous products from being polymerized to char.

Saisu et al. (2003) and Okuda et al. (2004) proposed a simplified scheme for lignin reactions in SCW. At first, lignin 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, a cross-linking reaction between formaldehyde and these fragments as well as residual lignin gives higher-molecular-weight fragments.

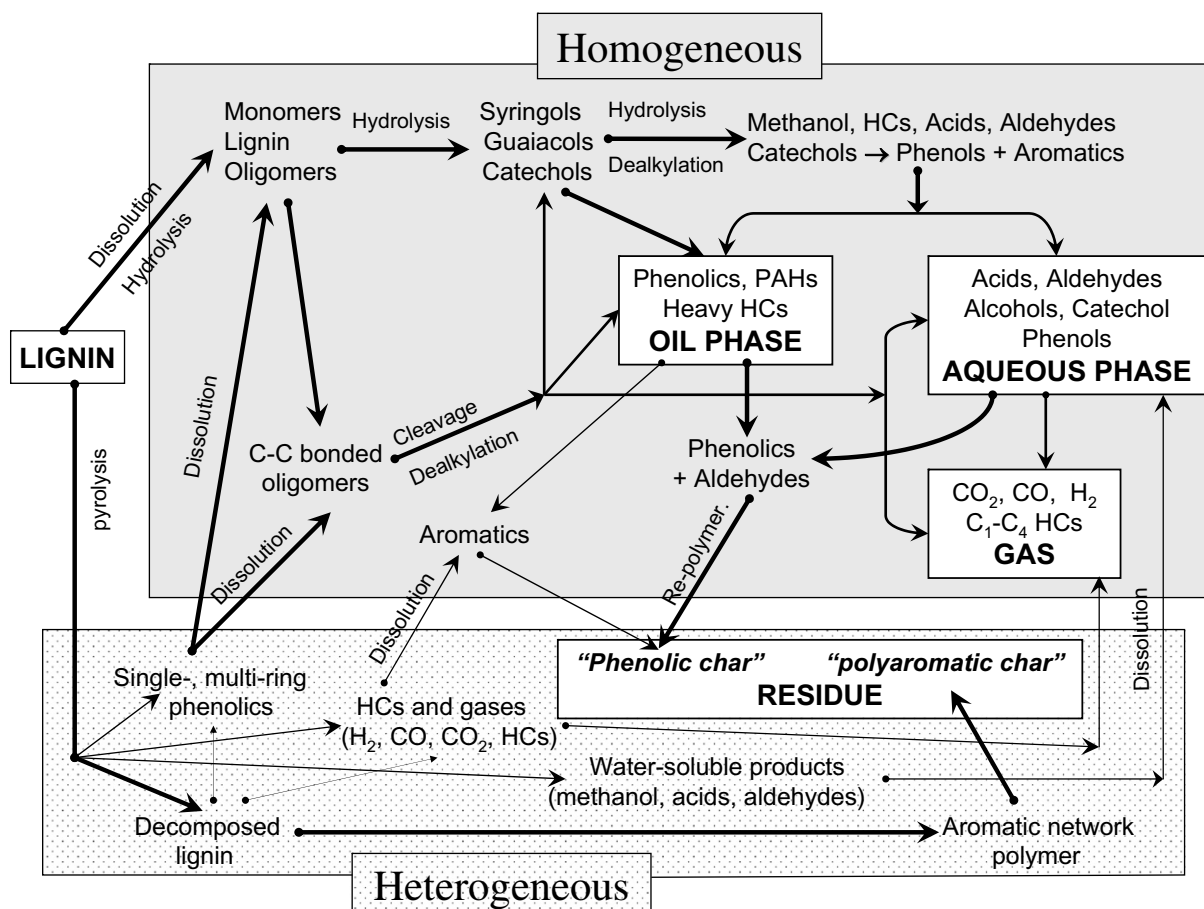


Fig. 1. Reaction paths of lignin decomposition promoted in homogeneous and heterogeneous environments in supercritical water.

Syringols and guaiacols were converted to catechols at long reaction times (e.g., 20–45 min) (Johnson et al., 1988). Phenolic oil (catechol, phenol, *m* or *p*-cresol, *o*-cresol, 2,4- or 3,5-xylenol) was changed to PAHs (e.g., naphthalene, phenanthrene, anthracene and benz[a]anthracene) at long reaction times (ca. 1–2 h) with NiO–MoO₃–Al₂O₃ at 450 °C (Ochi et al., 1984).

Based on the above research and results in this work, a scheme for the reaction paths of lignin in SCW was proposed in Fig. 1. The four phases were: (i) oil phase (phenolics, PAHs and heavy HCs); (ii) aqueous phase (acids, aldehydes, alcohols, catechol and phenols); (iii) gas phase (CO₂, CO, H₂ and C₁–C₄ HCs); and a (iv) solid residue phase. Dissolved products (e.g., lignin, oligomers, monomers) and non-dissolved lignin have different reaction mechanisms towards the four phases. The dissolved samples (see Fig. 1, dark area) with ether linkages were probably homogeneously hydrolyzed to single-ring phenolic oil (syringols, guaiacols, catechols and phenols). Syringols and guaiacols in the oil phase were further hydrolyzed and dealkylated into aqueous products of methanol and catechols in the aqueous phase (Johnson et al., 1988; Saisu et al., 2003). Minor catechols were probably decomposed to phenols and aromatics, and aromatics subsequently changed to PAHs and aromatic char (Townsend et al., 1988). At high temperatures, stable C–C bonds in lignin and oligomers were most likely cleaved to single- and multi-ring phenolics. Dealkylation reactions probably led to the formation of gas, HCs and aqueous products (alcohols, aldehydes and acids). At higher temperatures and long reaction times, phenolics (monomers and oligomers) re-polymerized with aldehydes to form heavier cross-linked *phenolic char* (Saisu et al., 2003; Okuda et al., 2004) and precipitated as residue II. The non-dissolved samples (see Fig. 1, shaded area) probably underwent pyrolysis to yield gas, HCs, a mixture of phenolics, water-soluble products (methanol, acids and aldehydes) and decomposed lignin via free-radical and concerted mechanisms (Klein and Virk, 1983) or acid-catalyzed decomposition (Britt et al., 1995).

Hydrocarbons should decompose to gas (C₁–C₄ HCs) and heavy HCs & aromatics. The phenolics probably dissolved into water, and were homogeneously hydrolyzed, cleaved and dealkylated to lighter phenolic oil, gas and aqueous products. Then, these phenolics were re-polymerized with aldehydes in the aqueous phase to precipitate as *phenolic char*. The decomposed lignin probably degraded further heterogeneously to form highly condensed char with cross-linked aromatics (Sekiguchi et al., 1983). Here such char is referred to as *polyaromatic char*, which is water insoluble residue. Therefore, *phenolic char* and *polyaromatic char* have different structures. The *phenolic char* was formed and precipitated from the aqueous solution, and it was lighter, initially, than the *polyaromatic char*. However, at high temperatures and long reaction times, both chars should decompose to some form of highly aromatic char. When {phenol + water} were used, all lignin dissolved in the aqueous phase and homogenous hydrolysis occurred and led to

decomposition of lignin to phenolics. Re-polymerization reactions of phenolics were hindered by phenol thus resulted in less char formation (Okuda et al., 2004). Only oil and lighter *phenolic char* were produced for the case of reaction of lignin in mixtures of {phenol + water}. However, more *phenolic char* with minor oil was produced in the {phenol + lignin} system because of the lack of hydrolysis reactions and char inhibition under a SCW environment (Fang et al., 2004a). Therefore, from our results and analyses, oil yield of lignin can be maximized using SCW and phenol mixtures: SCW to de-polymerize the lignin, and phenol to inhibit re-polymerization of the fragments. These phenolic compounds can possibly applied stepwise according to the phase behavior of the system to reduce the amounts of solid residue. It is clear that visualization of the reaction in DAC helps to analyze the system and improve our understanding of lignin decomposition in SCW.

6. Conclusions

According to direct visual observations at conditions of high temperature (up to 600 °C) and high pressure (up to 1 GPa), a homogenous phase was formed for the {phenol + lignin} system, then a *phenolic char* precipitated as the main product. Adding water to {phenol + lignin} mixtures promoted de-polymerization of lignin by hydrolysis in a homogeneous phase and its re-polymerization by phenol was most likely inhibited. No homogeneous phase was found for the {lignin + water} system. After initial dissolution at above 377 °C, lignin underwent hydrolysis and pyrolysis to phenolics, which were further changed to oil in the aqueous phase. At higher temperatures, solid particles precipitated from the aqueous via homogeneous re-polymerization of the phenolics and water-soluble compounds to form a *phenolic char*. At these same conditions, non-dissolved lignin underwent heterogeneous pyrolysis and formed *polyaromatic char*. At high water densities (e.g., 1011 kg/m³ at 400 °C), very little of the lignin dissolved. Therefore, *polyaromatic char*, with a lighter molecular weight, was the main product along with a smaller fraction of *phenolic char*. The non-dissolved sample still had lignin-like spectral features at 400 °C but decomposed to a char-like compound when reacted at 600 °C. From direct experiment observation, we can conclude that for water and phenol mixtures, lignin can be completely solubilized and undergoes homogeneous hydrolysis and pyrolysis that prevents further re-polymerization. These findings are useful in developing designs for continuously processing lignin with flow reactors for the production of biofuels and chemicals.

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