

Decomposition of lignin alkaline and chemicals recovery in sub- and supercritical water

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Abstract

Lignin is the second most abundant polymeric aromatic organic substance in the wood biomass after cellulose and it contains many oxygen functional groups. Lignin has been proposed to be an alternative source of chemical compounds. Phenolic chemicals can be obtained from lignin by some chemical processes. Water at sub- and supercritical conditions can provide a high destruction and removal efficiency for variety of hazardous chemical waste. The decomposition of lignin was studied in sub- and supercritical water at temperatures 623-673K. With a reaction time, amount of the higher molecular weight compounds first decreased and then the lower molecular weight compounds increased. The chemical species in the aqueous products were analyzed using high performance liquid chromatography with a Jasco MD-2010 Plus. The main products were catechol, phenol, *m,p*-cresol and *o*-cresol. In this study, experiments of non-catalytic lignin decomposition in sub- and supercritical water by using a batch-type reactor at various operating conditions have been conducted. The rate of lignin decomposition has been determined and a reaction mechanism at the identical conditions will be proposed. Furthermore, this method can be expected for efficient lignin decomposition and high yield of valuable chemicals or not on the basis of the experimental results.

Key words: Lignin, sub- and supercritical water, phenol, decomposition

INTRODUCTION

Biomass is a term used to describe all organic material derived from living matter. Biomass represents a renewable and alternative source for the production of chemicals. And also, biomass is potentially one of the most promising alternatives for electrical power production owing to its ecological advantages [1]. The development of process has been proposed to recover chemical resources from biomass waste. The effective removal of organic pollutants from agriculture and industries is a problem of great importance. Waste treatment is one of the most important and urgent problems in environmental management. Effective treatment technologies and a zero emission process for the efficient treatment which accomplish the destruction these wastes into harmless and products need to be established and should be developed [2].

The plant biomass consists of 40~45 wt% cellulose, 25~35 wt% of hemicellulose, 15~30 wt% of lignin and up to 10% other compounds, approximately. Generally definition of lignin is a biopolymer in which hydroxyphenylpropane units such as trans-*p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol are connected with ether and carbon-carbon bonds [3]. Lignin as another primary component of plant biomass, it contains many oxygen functional groups (phenolic compounds, hydroxyl, carboxyl, carbonyl groups, ether and ester bonds). Therefore, phenolic chemicals can be obtained from lignin by chemical decomposition processes.

Water at sub- and supercritical conditions are a unique solvent for decomposition of solid

waste polymers and swelled biomass resources. Water becomes supercritical fluid, if its temperature and pressure exceed its critical point (647K and 22.1 MPa). Supercritical water has unique features in terms of density, dielectric constant, ion product, viscosity, diffusivity, electric conductance and solvating ability. In the supercritical state, water acts like dense gas and organic compounds and gases become soluble in water, while inorganic compounds such as salt become insoluble [4,5]. The relative dielectric constant and ion product can be manipulated by changing the temperature and pressure with a great change of water density. The density of water is an important property to determine reaction kinetics and mechanism at supercritical water conditions.

Lignin decomposition processes can be considered to proceed in two steps: first, lignin dissolution in solvent and, second, transformation of the initially formed primary liquefaction products to light liquids. The extent of either process depends on the nature of lignin and reaction conditions, such as the presence or absence of donor solvents. When the lignin is heated, numerous radicals were obtained as a result of thermal cleavage. These radicals can be stabilized by the addition of hydrogen, provided from a donor solvent. Saisu et al. [6] reported the decomposition of lignin to chemical compounds in supercritical water-phenol mixtures. They suggested that phenol could prevent the char formation in supercritical water. Yokoyama et al. [7] conducted decomposition of lignin in sub- and supercritical water. They reported that the water density have strong influence on the yield of oil and char. In this condition, it indicated that the hydrolysis is important reaction to decompose lignin. Supercritical water acts not only as solvent but also as reactant where hydrolysis readily occurs. This is the reason why sub-critical and supercritical water is used to reduce biomass [8]. On the other hand, water is an interesting medium for extraction and oxidation because it is cheap, inflammable, non-toxic and easy available.

The aim of this work is to conduct decomposition of lignin in sub- and supercritical water to recover chemical compounds. The effects of temperature and reaction time on the decomposition of lignin were investigated through the experiments using a batch reactor, and the data obtained were analyzed to determine the reaction rates and propose a main reaction pathway for lignin decomposition at identical condition.

EXPERIMENT SECTIONS

I - MATERIALS

Lignin (alkaline) powder obtained from Tokyo Kasei Kogyo Co. Ltd. was used as a feed and distilled deionized water as a solvent. At room temperature, the lignin was completely soluble in methanol. Catechol, phenol, *m,p*-cresol and *o*-cresol were purchased from Wako Pure Chemicals Industries Ltd. and had purities of 99.0%, 99.0%, 98.0% and 99.0%, respectively. The analytical reagents used were methanol (99,7%, HPLC grade) and acetonitrile (CH₃CN; 99,8%, HPLC grade) from Wako Pure Chemicals Industries Ltd. and all chemicals were used without further purification.

II - EXPERIMENT PROCEDURES

The experiments were carried out in batch reactors at a controlled temperature. Reaction of lignin took place in supercritical water, using hastelloy tube reactor (AKICO Co., Ltd., Japan; with internal volume 5.0 cm³, 16.0 mm o.d.; 6.0 mm i.d.; 180.0 mm in length). The reactor was loaded with 0.1 g of lignin and the amounts of water corresponding to 0.17-0.67 g·cm⁻³ water density. Then argon gas was sprayed in the reactor as inert and purging gas and sealed. The reactor was placed into an electric furnace (ISUZU Co. Ltd., model NMF-13AD) heated up to temperature 623-673K. During reaction, the reactor was shaken using a

mechanical device. After 30-240 min (include the heating time about 3 min), the reactor was turned out from an electric furnace and quickly quenched in a water bath at room temperature. After cooling the reactor, the reactor was opened and the liquid and solid products were collected and the remaining material in the reactor was washed out with methanol (5 ml).

The gas products could not be recovered. The compounds in methanol were directly analyzed by high performance liquid chromatography (HPLC) and identified by gas chromatography mass spectrometry (GC-MS).

III - ANALYTICAL METHODS

The product was identified by GC-MS Hewlett Packard model 6890 series GC system and 5973 mass selective detector with a DB-5 capillary column (J&W Scientific, length 15 m, i.d. 0.25 mm, film 0.25 μm). The temperature program was 1.0 min at 40°C, 5.0°C/min to 300°C, and 1 min at 300°C. Helium carrier gas was used at a flow rate of 1.5 ml/min. The quantitative products were performed by HPLC with a Jasco MD-2010 Plus under the following conditions: column Inertsil ODS-3; flow rate 1.0 ml/min; eluent CH₃CN/H₂O, 20/80; detector UV 280 nm; temperature 40°C.

Methanol insoluble product (char) was dried in desiccator for 1 day at room temperature, and then it was weighed. The insoluble product was defined as residual solid (RS). The residual solid yield (RSY) was defined as the weight of residual solid divided by initial weight of lignin loaded into the reactor and methanol soluble product yield (MS) was defined according to equations 1 and 2, respectively.

The yield of the product was defined as the weight of the product recovered to initial weight of lignin loaded into the reactor, according to equation 3.

$$RSY [\text{wt}\%] = \frac{RS [\text{g}]}{\text{Lignin loaded} [\text{g}]} \times 100 \quad (1)$$

$$MS [\text{wt}\%] = 100 - RSY [\text{wt}\%] \quad (2)$$

$$\text{Yield} [\text{wt}\%] = \frac{\text{Product} [\text{g}]}{\text{Lignin loaded} [\text{g}]} \times 100 \quad (3)$$

RESULTS AND DISCUSSIONS

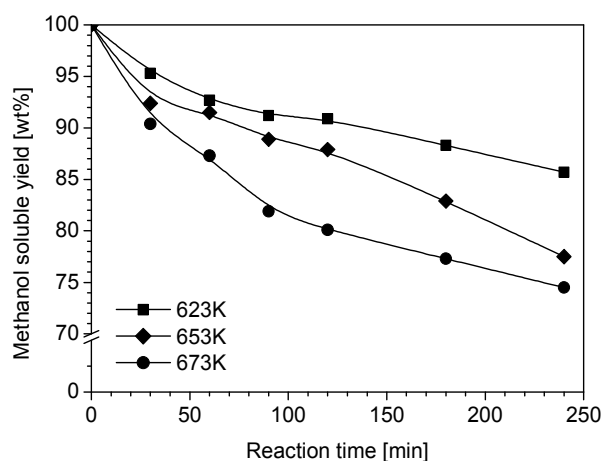


Figure 1: Methanol soluble yield with reaction time at pressure 25 MPa and temperature 623, 653 and 673K. Water at sub- and supercritical conditions are one of the candidates for decomposition of biomass, because it can be

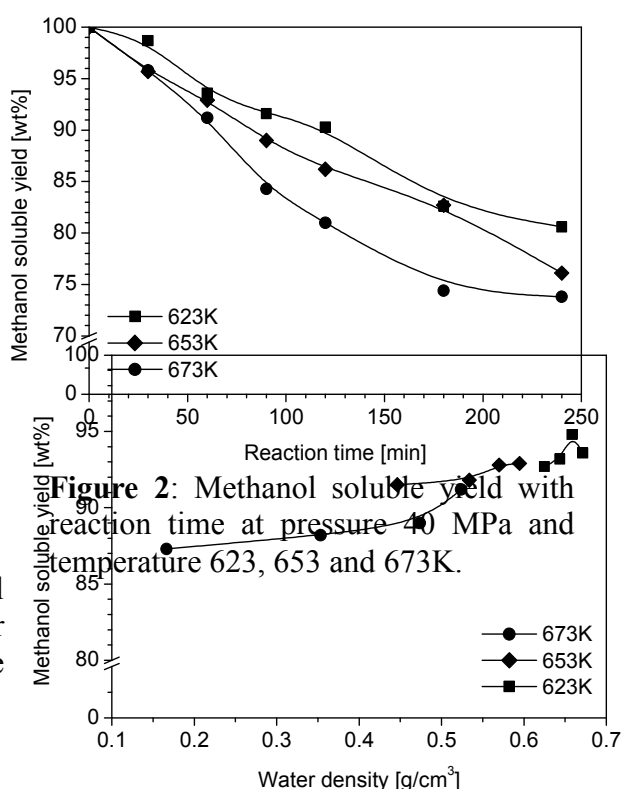


Figure 2: Methanol soluble yield with reaction time at pressure 40 MPa and temperature 623, 653 and 673K.

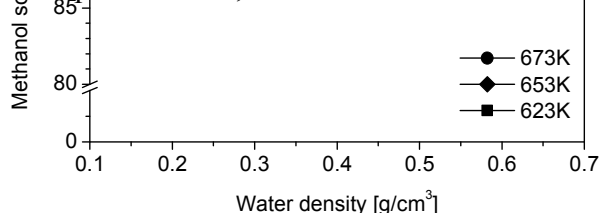


Figure 3: Effect of water density on the methanol soluble yield after reaction time 60 min at temperature 623, 653 and 673K.

applied at lower temperatures. Under sub- and supercritical conditions, organic substances are completely soluble in water. It is one of the reasons that the water can provide as a reaction medium for organic materials [5].

Figures 1 and 2 showed the effect of the reaction time on the yield of the methanol soluble products by the reactions at temperatures 623, 653 and 673K and pressures 25 and 40 MPa. In these experiments, although the pressure has not been measured, but the pressure for water solvent is estimated to precisely. At each temperature, the methanol soluble yield changed distinctly with a reaction time and it decreases with increasing reaction time. The formation of char from decomposition of lignin under these conditions is a result of the breaking of the relatively weak bonds in lignin. Figure 3 shows the methanol soluble yield, relative to water density at a reaction time of 60 min and at temperatures of 623, 653 and 673K. From this figure it can be known that the methanol soluble yield increased with increasing the water density. At these conditions, the lignin was decomposed and liquefied effectively. The decomposition of lignin also gave higher-molecular-weight fragments, as well as lower-molecular-weight fragments. The residual solid (char) decreased with increasing water density, which is probably due to the formation of the lower-molecular-weight fragments becoming dominant with increasing water density. In this case, the water density also inhibited the formation of the residual solid.

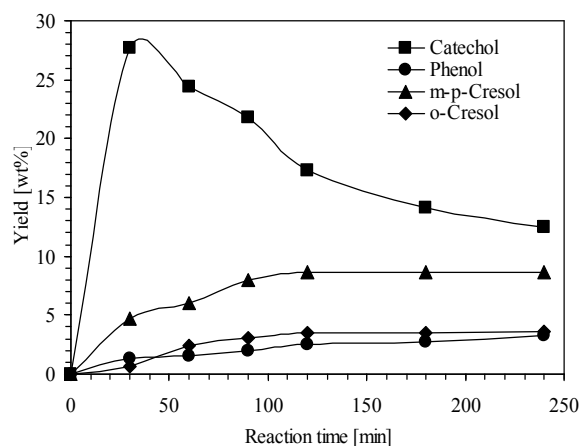


Figure 4: Products distribution, relative to reaction time at temperature 623K and pressure 40 MPa.

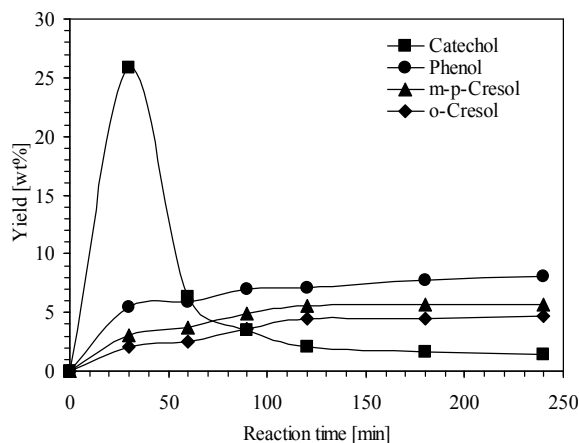


Figure 5: Products distribution, relative to reaction time at temperature 653K and pressure 40 MPa.

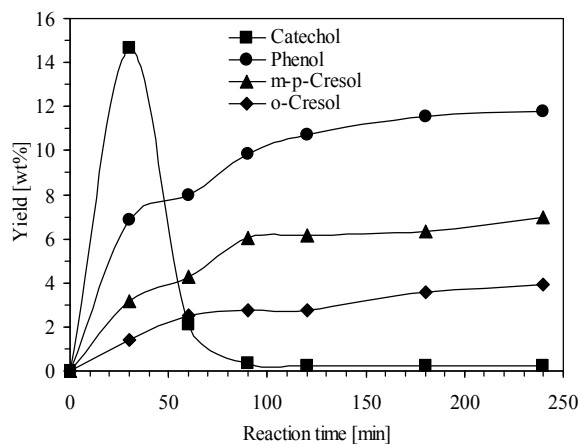


Figure 6: Products distribution, relative to reaction time at temperature 673K and pressure 40 MPa.

Water at sub- and supercritical conditions as a medium for chemical reactions, it is depending on its density. The gas-like low viscosity promoted mass transfer and the liquid-like density promotes solvation. The high temperature increased thermal reaction rate and the low dielectric constant promotes dissolution of non-polar organic materials [5]. There are two types of products from decomposition of lignin in sub- and supercritical water. They were gas phase

and aqueous phase products, but gas phase could not be recovered and aqueous phase include various organic compounds solute in water were detected. The amount of organic compounds in aqueous solution could be determined quantitatively. The organic compounds in aqueous phase were identified as catechol, phenol, *m,p*-cresol and *o*-cresol. In principle, every compound is able to react via different reaction pathways. Figures 4, 5 and 6 show the products distribution relative to reaction time at same pressure and at temperatures 623, 653 and 673K, respectively. Initially, catechol increased dramatically at each condition with increasing reaction time (27.72%, 25.81%, and 14.65%). Then, catechol quickly decreased after 30 min reaction time at temperatures 653 and 673K. The products of phenol, *m,p*-cresol and *o*-cresol increased with increasing reaction time at each condition. The products of phenol, *m,p*-cresol and *o*-cresol could approach 3.31-11.75%, 5.65-8.67% and 3.65-4.66%, respectively. These results indicated that the increasing temperature reaction can enhance the bonds cleavage reaction in lignin.

It well known that the lignin contains phenolic structure. The most major ether bonds in lignin is that between one propyl side chain of a hydroxylphenylpropane unit and the hydroxyl group attached to a benzene ring of another hydroxylphenylpropane unit [3]. So, disassembly of ether bonds and carbon bonds are important factor in the decomposition of lignin.

The decomposition of lignin in sub- and supercritical water can be considered to a certain extent as the same process. The main difference is the existence of two phases in the sub-critical condition and only one phase at supercritical condition. At these conditions, the properties of water change drastically and will make control of the reaction equilibrium and the rates of the major reactions possible by adjusting the temperature and pressure.

Figure 7 showed the simple reaction pathway for decomposition of lignin in sub- and supercritical water. Lignin was decomposed into its derivative compounds by dealkylation and

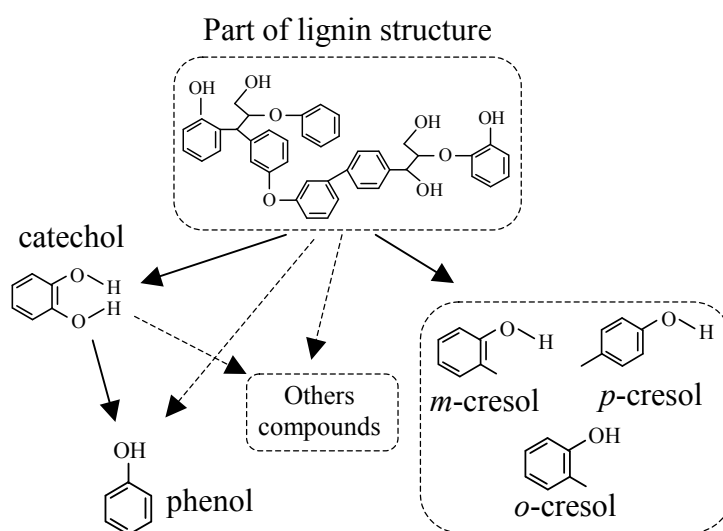


Figure 7: The proposed of simple reaction pathway for decomposition reaction of lignin in sub- and supercritical water.

$$X = e^{-kt} \times 100 \text{ (wt\% on the original lignin basis)} \quad (4)$$

hydrolysis reaction. From this figure can be known that the dealkylation of lignin gives catechol, and then catechol was hydrolyzed into phenol. The decomposition of lignin has also been studied kinetically in sub- and supercritical water by assuming that the reaction according to pseudo-first-order kinetics, and it was evaluated by the following equation:

where X is the residue of lignin and t is the reaction time (min). The reaction rate constants (k) were determined from the experimental data at the reaction time until 240 min. As a result, the decomposition rate constants of lignin in sub- and supercritical water are $1.5 \times 10^{-3} - 8.3 \times 10^{-4} \text{ min}^{-1}$.

CONCLUSION

The decomposition of lignin was carried out in sub- and supercritical water at 623, 653 and 673K. The methanol soluble yield decreased with increasing reaction time but the methanol soluble yield increased with increasing water density. The aqueous phase products were identified as catechol, phenol, *m,p*-cresol and *o*-cresol. The kinetic rate constants (k) obtained from simple kinetic equations and simplified reaction pathway. With plot Arrhenius was found that the values of k are 1.5×10^{-3} , 1.1×10^{-3} and $8.3 \times 10^{-4} \text{ min}^{-1}$ when the reaction occurred at temperature 623, 653 and 673K, respectively. Based on the results were obtained that the sub- and supercritical water could become a useful method to decompose lignin and to recover useful chemical compounds.

ACKNOWLEDGMENT

This work was supported by 21st century COE Program "Pulsed Power Science".

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