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Short Communication

Noncatalytic fast hydrolysis of wood

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ABSTRACT

Willow without any pretreatment, and water were studied in an optical micro-reactor, diamond anvil cell by rapid heating (7–10 °C/s) to high temperatures and high pressures (up to 403 °C and 416 MPa), most of willow (89–99%) dissolved and hydrolyzed in water at 330–403 °C within 22 s. It was found that low-density water (e.g., 571 kg/m^3) solubilized almost all willow with particle size less than 200 μm, and subsequently hydrolyzed to hydrolysates in subcritical water at 354 °C and 19 MPa within 9 s. These results were further used to propose a flow process to fast hydrolyze wood in seconds to valuable sugars.

1. Introduction

Water at a temperature and pressure that is near its critical point (CP; 374 °C, 22.1 MPa) is commonly referred to as hot compressed or hydrothermal water (HTW). Supercritical water (SCW) or subcritical water (SubCW) is defined as water at a temperature and pressure above or below its CP. Near the CP, water becomes weakly-polar solvent that can dissolve many apolar organics (Fang, 2009, 2010). It was found that even polymers such as polyethylene terephthalate, nylon (Fang, 2010) and cellulose (Sasaki et al., 2000) could completely dissolve in SubCW. On the other hand, HTW has a high ion product ($K_w = [H^+] \bullet [OH^-]$, $[H^+] = [OH^-]$) value (Fang, 2009, 2010). Therefore, HTW presents both acidic and basic, and can hydrolyze biomass catalyzed by both $[H^+]$ and $[OH^-]$ ions without adding any acid or base catalysts (Matsumura et al., 2006). Woody biomass is composed of about 50% cellulose, 25% hemi-cellulose and 20% lignin, which is hydrolysable biopolymer built from sugar and phenylpropane units (Nanjing Forestry Institute, 1961). HTW is an ideal solvent to hydrolyze woody biomass because it can provide homogenous and acidic/basic conditions (Sasaki et al., 2000, 2003a,b; Matsumura et al., 2006; Mittal et al., 2009; Zhao et al., 2009a,b). Previous work showed that microcrystalline cellulose was completely solubilized in HTW (Sasaki et al., 2000) but only around 40–60% actual woody or herbaceous biomass was solubilized and hydrolyzed to sugars at 200–300 °C in a semi-flow percolating reactor (Mok and Antal, 1992). It is difficult to operate and controllably hydrolyze solid wood in a continuous flow reactor due to its low solubility. So, the commercial hydrothermal process is commonly carried out in batch or semi-flow reactors that have low production rate capabilities because material flow is low and interrupted (Nanjing Forestry Institute, 1961). It is easy to undergo heterogeneous pyrolysis reaction for non-dissolved woody biomass and secondary decomposition for the hydrolysates due to long residence times particularly at high temperatures. So, solubilization of wood is important for the continuous fast hydrolysis of wood to sugars and phenolics. Here, I report my new findings that using hydrothermal water to rapidly dissolve most of wood and subsequently hydrolyze it to hydrolysates in a diamond anvil cell. A continuous process to fast hydrolyze wood is further proposed.

2. Experimental approach

Willow (~500 μm particles; 22.7% lignin, 26.7% hemi-cellulose and 49.6% cellulose) (Hashaikeh et al., 2007) with 12% moisture, without any pretreatment as a model material for wood was used in all experiments. An optical micro-reactor, diamond anvil cell (DAC) was used for visual study of willow dissolution and hydrolysis in pure water during rapid heating to high temperatures and pressures up to 403 °C and 416 MPa. The reaction chamber consisted of a hole (50 nL; 500-μm internal diameter, 250-μm thickness) drilled in an Inconel stainless steel gasket and sealed by compression of two opposing diamond anvils. Double-distilled water and willow were loaded into the chamber, heated rapidly (7–10 °C/s) by two electric micro-heaters and observed under 110× magnification with a stereomicroscope with the images being recorded by a 3-CCD camera and computer. Negligible

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changes of chamber volume could be considered during heating to high temperatures (Fang, 2009). After reaching the maximum temperatures, the chamber was rapidly cooled (about −10 °C/s) to room temperature. The residues deposited on the diamond faces were analyzed by Fourier Transform Infrared (FT-IR) microscopy. Temperature of the system was measured and recorded by a data acquisition unit. Water density (ρ = mass of water/chamber-volume, kg/m^3) was adjusted by changing the size of N_2 gas bubbles introduced in the chamber, and kept as a constant that was determined from the homogenization temperature (T_h) of the gas bubbles disappearance caused by water expansion during isochoric heating (Fang, 2009). Pressure was calculated from the density determined and temperature measured by an equation of state of water (Fang, 2009). Wood concentration was defined as the wood area concentration (wood-area/chamber-area, %) that was estimated by digital image analysis of the recorded two dimensional (2D-XY) images using a commercial software package (Scion Image, Frederick, MD). The relative wood concentration (V/V_0, %) was defined as the instant volume (V) dividing by the initial volume (V_0), thus dissolution rate = (100% − V/V_0%). The wood depth-Z changes were estimated by assuming the cross section areas had the same disappearance rate as those areas of the recoded 2D-XY images.

3. Results and discussion

Many experiments were done in the DAC with different wood concentration, particle size, heating rate, maximum temperature and water density. Only selected five experimental results are presented here. Relative wood concentration changed with temperature is given in Fig. 1. A fast hydrolysis process of wood is proposed in Fig. 2. In our previous work, it was found that when willow was slowly heated to 400 °C, it dissolved little (Hashaikeh et al., 2007). Therefore, all the experiments were conducted at high heating rate (7–10 °C/s). The detailed results are introduced and discussed below.

3.1. High-concentrated wood (test 1)

In test 1, willow and water with a high-wood concentration (51.5%) were heated rapidly to 403 °C at an average heating rate of 10 °C/s. The willow particle (about 500 μm length) started to dissolve at 294 °C, and dissolved further up to 315 °C as judged by the color change in the solution. The dissolved compounds were mainly from low-molecular-weight extractives fraction and hemi-cellulose because 100% hemi-cellulose was solubilized at 200–300 °C (Mok and Antal, 1992; Makishima et al., 2009), and cellulose and lignin dissolved little at such low temperatures (Sasaki et al., 2000; Fang et al., 2008). The main dissolution occurred at temperatures from 326 to 343 °C within 2.67 s. At
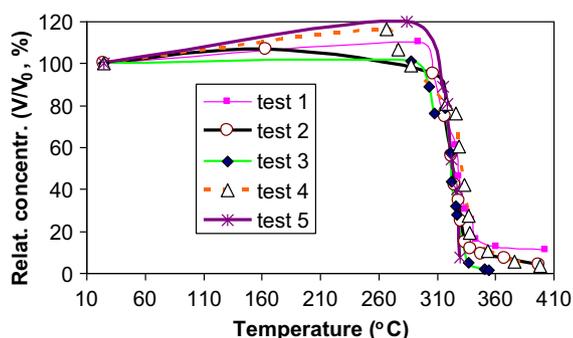
343 °C, willow dissolved about 84% and changed little until 361 °C. As temperature increased further to the maximum of 403 °C and 42 MPa, non-dissolved sample changed to light-black color along with reddish solution, which indicated the heterogeneous pyrolysis for the non-dissolved residue and homogeneous hydrolysis for the dissolved material, respectively. At 361 °C, gas bubbles disappeared and the water density was calculated as 526 kg/m^3. After reaching the maximum temperature, 89% willow dissolved. The reactor was cooled rapidly (at about −10 °C/s) to room temperature, and sugar-like residue was obtained from the dissolved willow. IR spectra showed that it was hydrolyzed because the broad willow characteristic peak at 2913 cm^{-1} was split to two peaks at 2848 and 2945 cm^{-1}, which had lignin and glucose characters as compared with the standard willow, lignin and glucose samples. The sugar-like residue was composed of a majority of hydrolysates (monomers and oligomers) and minor portion of secondary decomposed products according to the previous works in larger reactors (Sasaki et al., 2000; Fang et al., 2008; Matsumura et al., 2006).

3.2. High-density water (test 2)

In test 2, a high-density water (905 kg/m^3) was used to dissolve willow (34.3%) by rapid heating (9 °C/s) the reactor to 397 °C and 416 MPa. At 163 °C, gas bubbles disappeared and the water density was calculated as 905 kg/m^3. As the chamber was further isochoricly heated, the willow particle (about 500 μm length) started to dissolve at 307 °C with light-yellow solution. The main dissolution occurred at lower temperatures from 317 to 334 °C within 2.34 s, and about 85% willow dissolved. The particle dissolved further to 96% at 397 °C but it seemed the dissolution was mainly due to its pyrolysis to soluble light-molecular compounds as judged by the blacking and shrinking of the particle. Numerous fine particles were precipitated from the solution that started at 339 °C and increased more until the maximum temperature. After reaction, the dissolved willow hydrolyzed to hydrolysates that had the similar structure to those obtained in test 1. As compared with the above low-density water test 1 (526 vs. 905 kg/m^3), high-density water promoted pyrolysis reactions for both non-dissolved and dissolved materials that can be seen from the blacking of the undissolved willow started from low temperature of 325 °C and the precipitation of numerous fine particles from the solution started at 339 °C. Even though higher dissolution rate of 96% was achieved at 397 °C, apparently, part of the dissolved products were from pyrolysis.

3.3. Fine-particle wood (test 3)

In test 3, several fine willow particles (~200 μm; 47.5%) and water (ρ = 571 kg/m^3) were rapidly heated (8 °C/s) to 354 °C and 19 MPa. The willow particles started to dissolve at 303 °C. The main dissolution occurred at temperatures from 317 to 337 °C within 3.8 s, and about 95% willow dissolved. After 4.94 s, at the maximum temperature of 354 °C and 19 MPa, 99% willow dissolved and that was further hydrolyzed to sugar-like products. Therefore, using low-water density (571 kg/m^3) can solubilize almost all willow particles with size less than 200 μm, and subsequently hydrolyze them to hydrolysates in low temperature and pressure SubCW at 354 °C and 19 MPa within 8.74 s.

3.4. Medium-density water (test 4)

In test 4, a medium-density water (736 kg/m^3) was used to dissolve willow (35%) by rapid heating (7 °C/s) the reactor to 398 °C and 132 MPa. At 288 °C, gas bubbles disappeared and the water density was calculated as 736 kg/m^3. The willow particle (about

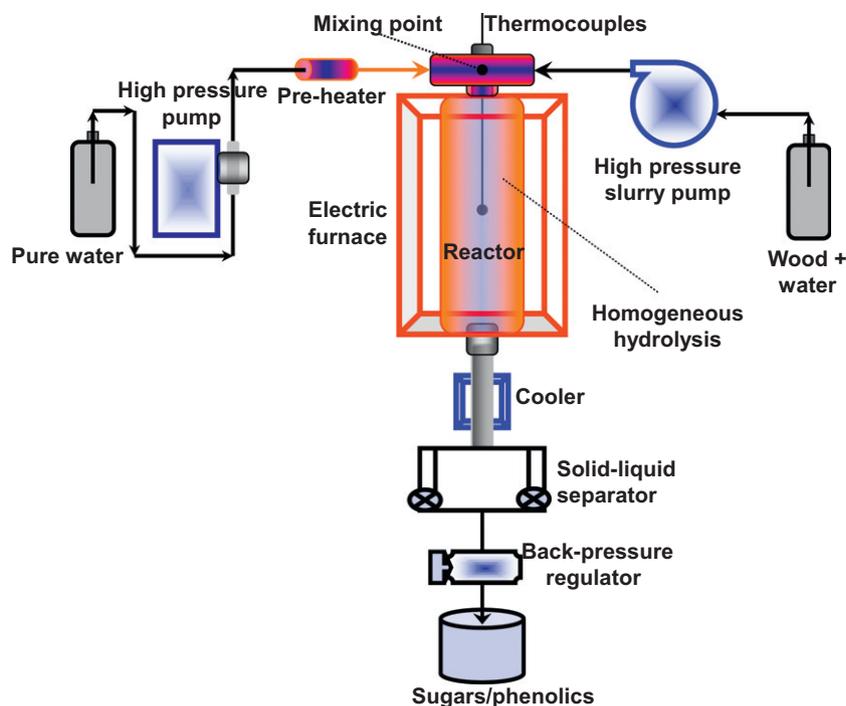**Fig. 1.** Relative concentration of wood (V/V_0, %) vs. temperature.

Fig. 2. Fast hydrolysis of wood to hydrolysates without catalyst.

500 μm length) started to dissolve at 318 °C. The main dissolution occurred at temperatures from 318 to 353 °C within 7.56 s, and about 89% willow dissolved. At the maximum temperature of 398 °C, 96% willow dissolved that was further hydrolyzed to sugar-like products.

3.5. Medium-density water and fine-particles of wood (test 5)

In test 5, a medium-density water (743 kg/m^3) was still used but to dissolve fine willow particles ($\sim$250 μm; 27%) by rapid heating (8 °C/s) the reactor to 330 °C and 59 MPa. The main dissolution occurred at temperatures from 315 to 330 °C within 3.38 s, and about 92% willow dissolved and hydrolyzed subsequently. Medium-density water has lower solubility for willow than that of low-density water.

The relative concentration of willow *vs.* temperature is summarized in Fig. 1 where a steep slope shows the main dissolution is at subcritical region of 315–353 °C in less than 8 s. When heated to high temperatures in DAC according to an isochoric curve (ρ = constant), water becomes weakly-polar due to the decrease of its dielectric constant (ε) (Fang, 2009, 2010) or hydrogen-bonding. On the other hand, its ion product (K_w) also increases (Fang, 2009, 2010) that will catalyze biomass hydrolyze to water-soluble hydrolysates. Therefore, when heated to 315–353 °C, water has the ability to dissolve willow that is composed of the four major components of extractives, hemicellulose, cellulose and lignin. Light-molecular-weight extractives fraction is easy to dissolve in weakly-polar HTW. In the previous works, it is found that hemicellulose and cellulose completely dissolved in pure water at 200–300 °C (Mok and Antal, 1992) and 320–350 °C (Ogihara et al., 2005), respectively. But, no complete dissolution was found for lignin in HTW (Fang et al., 2008). So, no complete solubilization was found for willow, the remained non-dissolved material (e.g., in test 1) was probable lignin component. In an isothermal curve, the dielectric constant (ε) of water rises as water density or pressure increases (Fang, 2009, 2010). So, high-density water has a strong hydrogen-bonding structure at a given temperature, thus presents

more polar that has less ability to dissolve the non-polar willow biopolymer. However, high-density water will create high pressures when heated to high temperatures. The pressure at about 400 °C in test 2 (905 kg/m^3) is about 10 times that in test 1 (523 kg/m^3) (416 MPa *vs.* 42 MPa) that will promote pyrolysis reactions to produce more water-soluble products and yield more char from both soluble and insoluble samples (Antal and Grønli, 2003). For all the experiments studied with 27–51.5% willow concentration, 523–905 kg/m^3 water density, less than 200$\sim$500 μm particle size and 7–10 °C/s heating rate, 89–99% willow was solubilized and hydrolyzed at 330–403 °C, 19–416 MPa within 3.38–21.79 s. After willow was solubilized, it was rapidly hydrolyzed to its oligomers and monomers (sugars and phenolics) that were decomposed further to secondary products for long reaction times at high temperatures. A simplified reaction model is proposed: Wood → dissolved wood → hydrolysates (monomers, oligomers) → monomers (sugars, syringols, guaiacols, catechols) → lighter water-soluble products → polymer (aromatics structures). Detailed reaction products, pathways and mechanisms for sugars, phenolics, hemicellulose, cellulose and lignin promoted in homogeneous and heterogeneous environments can be seen in the previous works (Sasaki et al., 2000, 2003b; Fang et al., 2008; Matsumura et al., 2006).

It can be concluded that low-density water can effectively dissolve fine wood particles and subsequently fast hydrolyze them in aqueous phase at low temperatures and pressures. In test 3 (ρ = 571 kg/m^3), 99% fine-sized willow ($\sim$200 μm) was dissolved and hydrolyzed within 8.74 s at low temperature and pressure of 354 °C and 19 MPa. If heated to a higher temperature (i.e., >354 °C) instantaneously, wood may dissolve immediately because heating time can be neglected to reach the condition that hydrogen-bonding of water breaks down further to become weak-polar enough to dissolve biomass. Sasaki et al. (2003a) rapidly heated and completely dissolve microcrystalline cellulose *I* at 355–400 °C in just 0.02–0.4 s by using preheated hot water to mix the cellulose slurry sample in a flow reactor. By quick-quenching of the solubilized cellulose, little reaction occurred in such short time

that was confirmed as cellulose II was obtained after cooling. Willow (99%) was solubilized upon rapid heating in the micro DAC batch reactor, where a high heating rate is easy to achieve. However, a larger batch reactor used for practical applications cannot reach such high heating rate. On the other hand, the batch process has low productive rate particularly at high temperatures and pressures. Therefore, a flow process is proposed in the following section to rapidly heat and dissolve wood, and subsequently hydrolyze the wood solution to hydrolysates.

4. Noncatalytic fast hydrolysis of wood

Because 99% willow can dissolve in hot water, it is convenient and practical to design and build a flow reactor to rapidly solubilize and hydrolyze willow continuously. A Tubular flow reactor is proposed here, and it is made of a stainless tube and heated by an electric furnace (Fig. 2). Pressure is controlled with a back-pressure regulator. Two streams (sample and pure water) are fed into the reactor. A slurry pump is used to feed {willow + water} mixture into the reactor as the sample stream without preheating. In another stream, pure water is pressurized and then preheated to a high temperature and mixed with the sample stream at the mixing point just before entering the reactor. At the mixing point (Fig. 2), the sample stream is rapidly heated (e.g. heating to 355–400 °C in just 0.02–0.4 s; Sasaki et al., 2003a) and subsequently enters into the reactor undergoing dissolution and hydrolysis. After leaving the reactor, the mixture is rapidly quenched by a cooling water-jacket to terminate the reaction. Non-dissolved and other solid residues are separated on-line from the mixture by using one of the two solid–liquid separators alternatively that design can keep the continuous flow during cleaning and replacement. In our previous work in a continuous flow reactor, 100% cellulose (20 wt.%) was dissolved and converted to water-soluble products containing 80% hydrolysates (glucose and oligomers) at 400 °C in just 0.05 s (Sasaki et al., 2000) as compared with only 63% hydrolysates achieved in SCW at 380 °C and residence time of 16 s in a micro batch reactor (5 mL) heated by salt bath. (Zhao et al., 2009b). The mixing of the two streams and flowing can also promoted biomass dissolution and hydrolysis. Therefore, using the flow reactor, almost all willow can be solubilized immediately, and subsequent homogeneous hydrolysis reaction is controlled and optimized by changing reaction time, temperature, pressure (water density), wood size, flowing (e.g., laminar, turbulent), flow rate and reactor's designing (e.g., diameter, length, structure of the mixer for the two streams).

5. Conclusions

Almost all willow (89–99%) dissolved in water by rapid-heating (7–10 °C/s), and subsequently the dissolved willow underwent fast hydrolysis to its monomers & oligomers in aqueous phase that promoted hydrolysis and inhibited pyrolysis to solid residue. The main dissolution temperature is at subcritical region of 315–353 °C. Low-density water (e.g., 571 kg/m^3) had a high dissolution ability to dissolve 99% willow with fine particle size (~200 μm) at low temperatures and pressures (e.g., 354 °C and 19 MPa) that makes it possible to design and build up a flow system for the fast, continuous and controllable production of hydrolysates.

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