Complete Dissolution and Hydrolysis of Wood in Hot Water

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When willow and water were heated rapidly (7–16°C/s) to high temperatures and high pressures, most of willow (90 vol %) dissolved in water at 341°C in 2.5 s without complete dissolution. Adding 0.8 wt % Na_2CO_3, complete dissolution of willow (concentration up to 35 vol %) was observed at 329–367°C and water densities of 322–787 kg/m^3 (14–106 MPa) in 1.5 s. By cooling the solublized willow immediately, micron particles were obtained via precipitation. If heated further to 400°C, willow was completely hydrolyzed to sugars/sugar oligomers in 14.6 s at homogeneous conditions. A flow reactor was proposed to completely solubilize willow for the production of micron particles, sugars, bio-fuels and chemicals continuously. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 2751–2758, 2008
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Introduction

Water at a temperature and pressure that is near its critical point (CP; 374°C, 22.1 MPa) is commonly referred to as hydrothermal or hot compressed water, which includes subcritical water (SubCW < CP) and super-critical water (SCW > CP). At ambient conditions, water is polar with a hydrogen-bonding network structure and is a good solvent for many polar and ionic compounds. However, near the CP, the hydrogen bond network of water starts to break up, 70% of the hydrogen bonding is destroyed in SCW, and consists of mainly dimers[1,2] that seem to have a point of symmetry and a zero dipole moment.[3] Consequently, SCW becomes weakly polar solvent with low dielectric constant (ε)[4] value and can dissolve many apolar organics and light inorganic gases such as hydrogen and oxygen. It was found that even polymers such as polyethylene terephthalate[5] and nylon[6] could completely dissolve in subcritical water. This means that water near its CP can provide homogeneous reaction conditions for many organic compounds. On the other hand, it is likely that some fraction of the dimers decompose to monomers and these may breakdown further to evolve protons.[1,2] Hence, SCW has a high value for its ion product (K_w = $[H^+]\bullet[OH^-]$, $[H^+]$ = $[OH^-]$; e.g., at 400°C and 50 MPa, K_w = 132 times that at ambient conditions)[7] and can hydrolyze many compounds catalyzed by $[H^+]$ and $[OH^-]$ ions[8] without adding any acid or base catalysts. Therefore, hydrothermal water with these properties (low ε and high K_w) are used to provide homogenous and acidic/basic conditions for the destruction of hazardous wastes by SCW oxidation (SCWO),[9] organic chemical reactions,[10] nanoparticle synthesis,[11] and biomass conversions.[8,12–14]

Typical lignocellulosic biomass, wood, and grass plants are composed of roughly 50% cellulose, 25% hemi-cellulose, and 20% lignin, which are hydrolysable polymers built from sugar (for cellulose and hemi-cellulose) and phenylpropane (for lignin) units.[8] Therefore, many works have been done to hydrolyze or degrade biomass using hot compressed water.[8,12–17] Sasaki et al.[16] studied cellulose hydrolysis rate at 285–400°C and found that the rate dramatically increased at above 320°C upon fast heating. This phenomenon was attributed to the homogenous reaction condition, which was confirmed with a diamond anvil cell, in which the complete dissolution of cellulose was observed at 320°C.[17] Later, Ogihara et. al.[18] studied the dissolution process over a wide range of water densities (550–1000 kg/m^3) and found that a

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minimum temperature of 320°C for the complete dissolution occurred at 850 kg/m^3. By quick-quenching of the solubilized native *cellulose I* achieved by rapid-heating to 355–400°C in a flow reactor, *cellulose II* was obtained during cooling by restructuring.[19] But, no complete dissolution was observed for actual lignocellulosic biomass. Only around 40–60% woody or herbaceous biomass was solubilized and hydrolyzed to sugars at 200–300°C in a semi-flow percolating reactor.[15,20] As we know even before 1950s, hydrothermal hydrolysis of wood with dilute acid (0.4–0.8% H_2SO_4, 12–13 atm., 180–190°C) to sugars for ethanol production was commercialized in the former Soviet Union.[21] But, the hydrolysis process can only operate in a batch or a percolating reactor due to wood being water-insoluble that will block flow reactors. So, the process has low production rate capabilities because material flow is low and interrupted. Now, most of the hydrolysis plants were closed because of high cost. Therefore, complete solubilization of wood is important for the continuous process of wood to biofuels and chemicals. Early work showed that cellulose and wood can dissolve in ionic liquids but the dissolution process is very slow, the solvents used are expensive and not good for environment.[22,23]

The goal of the work is to use hot compressed water to completely solubilize wood, and the aqueous "*wood solution*" is further to homogeneously hydrolyze to sugars/oligomers for ethanol production while avoid pyrolyzing to solid residues. The "*wood solution*" is easy to be processed to materials, chemicals, food and fuels in a continuous flow reactor at high pressures and high temperatures.

Experimental Approach

An optical microreactor, diamond anvil cell (DAC),[24] was used for visual observations of wood dissolution and reaction in water during rapid heating to high temperatures up to 403°C. The DAC can be readily applied to hydrothermal systems at pressures up to 30 GPa and temperatures up to 1200°C and allows for in situ analyses or observations of samples in the fully visible chamber via optical microscopy. Willow (22.7% lignin, 26.7% hemi-cellulose and 49.6% cellulose)[20] with 12% moisture as a model compound for wood was used for the study. Aqueous solution (pH of 11.4) with 0.8 wt % Na_2CO_3 was made for the experiments in the DAC. The reaction chamber (ca. 50 nL) consisted of a hole (500 μm i.d.; 250-μm thickness) drilled in an Inconel stainless steel gasket and sealed by compression of two opposing diamond anvils. Mixtures of {willow + H_2O + Na_2CO_3} were loaded into the chamber, heated rapidly at rates of 7–16°C/s by two electric microheaters and observed under 110× magnification with a stereomicroscope with the images being recorded by a 3-CCD camera and computer. Negligible changes of chamber volume could be considered during heating. The isochore chamber was confirmed through the observation of the interference fringes (chamber thickness) between anvil faces radiated by a green light (λ = 532 nm) and the recoded images (chamber i.d.).[24] After reaching the maximum temperatures, the chamber was rapidly cooled (−10°C/s) to room temperature. The residues deposited on the diamond faces were analyzed by Fourier Transform Infrared (FT-IR) microscopy and Scanning Electron Microscope (SEM). Temperature of the system was measured and recorded by a data acquisition unit. Water density (ρ = mass of water/volume of the chamber, kg/m^3) was adjusted by changing the size of N_2 gas bubbles introduced in the chamber, and determined from the homogenization temperature (T_h) of the gas bubbles disappearance caused by water expansion during isochoric heating.[12,24] The density of the water was assumed to be that of the liquid water along the liquid-vapor (L-V) saturation curve at T_h. The initial density can also be known by estimating gas bubbles size with digital image analysis. Wood concentration (vol %) was defined as the wood area concentration (wood area/chamber area, %) that was estimated by digital image analysis of the recorded two dimensional (2D) images using a commercial software package (Scion Image, Frederick, MD) and normalized by water density.[5,25] Because the image analysis is 2D, the calculated concentrations are semiquantitative. However, the depth of the reaction chamber corresponded to the sample thickness, thus allowing for minimizing inaccuracies associated with the 3D structure of the materials studied. Pressure was calculated from the density and temperature by an equation of state of water,[26] assuming the pressure was contributed only by water because the pressure from N_2 in the gas bubbles and CO_2 from 0.8 wt % Na_2CO_3 aqueous solution (according to the reactions: $Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3$; $H_2CO_3 \rightarrow H_2O + CO_2$) are negligible due to the low density of the gases. Bassett et al.[24] have compared the pressures by the calculation using air gas bubbles with the P-T boundary of the α-β transition in quartz. The difference was less than 4% for the water and quartz system with air bubbles.

Results and Discussion

Two groups of experiments for willow dissolution in pure water and in 0.8 wt % Na_2CO_3 aqueous solution were conducted in the DAC.

Willow dissolution in pure water (test 1)

It was found that when slowly heated to 400°C, willow dissolved little.[20] But, the dissolution increased significantly upon fast heating. Figure 1 (test 1) shows a sequence of images of the {31 vol % willow + water} system that was heated rapidly to 403°C at a heating rate of 10°C/s and a water density of 526 kg/m^3. The willow particle started to dissolve at 283°C as judged by the appearance of light yellow color in the solution. The dissolved compounds were mainly from the low-molecular-weight extractives and hemicellulose because 100% hemi-cellulose was solubilized and hydrolyzed to sugars (with 90% monomers) at 200–300°C[15]. The main dissolution was just in 2.5 s in the L-V phase (with gas bubbles) from 324°C (Figure 1b) to 341°C (corresponding pressure of 12 to 15 MPa). At 341°C, about 90 vol % willow dissolved that was calculated by the difference between the initial and the instant sample concentration divided by the initial sample concentration. From the visual observation, we could see two different components in wood, a tiny fiber-like and an elastic glue-like material that had different phenomena. The fiber-like material completely dissolved in water while the glue-like material that bound the

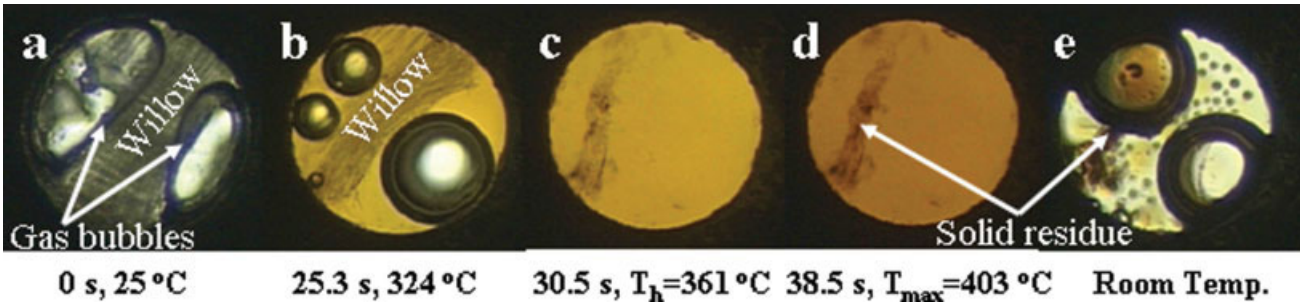

Figure 1. Visual observation of willow being dissolved by 90 vol % in pure water for test 1: rapid heating willow with a concentration of 31 vol % to 403°C at a heating rate of 10°C /s and initial water density (ρ) of 526 kg/m^3.

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fiber-like material was subsequently shrunk to form a transparent non-dissolved residue. As temperature increased further to the maximum of 403°C (Figure 1c, d), the residue carbonized and changed to black color along with red solution, which indicated the heterogeneous pyrolysis for the nondissolved residue and homogeneous hydrolysis for the dissolved material, respectively. At 361°C (Figure 1c), gas bubbles disappeared and the water density was calculated as 526 kg/m^3. After reaching the maximum temperature, the reactor was cooled rapidly (−10°C/s) to room temperature and residues were obtained (Figure 1e). The dissolved residue was sugar-like (Figure 3; image a) and was analyzed by FT-IR. IR spectra (Figure 3; curve a vs. 1–4) 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 (curves 1–4). The dissolved 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.[8,12–17,27–31] Many other experiments were done at different water densities (320–1000 kg/m^3) and wood concentrations (1–35 vol %) but no complete dissolution was observed. On the other hand, it was found that willow dissolved little at higher water densities (>800 kg/m^3) due to high polarity of water (or strong hydrogen bonding)[4] while cellulose can completely dissolve at water density up to 1000 (kg/m^3)[18] because cellulose is easy to hydrolyze to water-soluble glucose and its oligomer.[16,17] The polysaccharide components in wood are highly hydrophilic due to containing many OH groups and thus permeable to water. It was proved that cellulose and hemicellulose can completely dissolve in hot water[12,15,17,18] that was probably due to the combination of the cleavage of intra- and intermolecular hydrogen linkages in the polysaccharide components and decrease of hydrogen bonding among water molecules as well as partly attributed to the hydrolysis reaction in subcritical water.[12] The low-molecular-weight extractives in wood should dissolve in a weak-polar hot water too. Lignin, as it occurs in all woody plants, is a three-dimensional polymer consisting of rather hydrophobic phenylpropane units, and only slightly soluble in water.[8,32] Even heated up to supercritical region, lignin dissolves little in hot water.[31] In the visual observation, the glue-like component that bound fiber-like material (cellulose) did not dissolve in hot water. Therefore, the glue-like component is probably lignin. Because, lignin, like a glue in wood, is covalently linking to hemicellulose and thereby crosslinking polysaccharides, conferring mechanical strength to the cell wall and by extension the plant as a whole.[8,33] Since willow can not completely dissolve in pure hot water. In the following experiments, Na_2CO_3 was used to see if a homogeneous phase can be reached because Na_2CO_3 is widely used in Kraft process for delignification of wood into wood pulp[33] and in hydrothermal liquefaction of biomass[12,34,35] as well as it is cheap suitable for practical applications.

As early as 1920s, Fierz-David[36] found that using an alkali salt, liquid product can be produced from cellulose with H_2 at high pressure. Since then, many researchers in United States and Canada have done hydrothermal liquefaction of biomass that using alkali salts (including Na_2CO_3) and H_2/CO or H_2/CO donor solvents as reviewed by Ogi and Yokoyama.[34] Appell et al.[37] proposed the biomass liquefaction mechanism with Na_2CO_3 and CO:

$$Na_2CO_3 + 2CO + H_2O \rightarrow 2HCOONa + CO_2 \quad (1)$$

$$\begin{aligned} &\text{——}\mathbf{CH(OH)}\text{——}\mathbf{CH(OH)}\text{——} \rightarrow \text{——}CH{=}C(OH)\text{——} \\ &\rightarrow \text{——}CH_2\text{——}CO\text{——}HCOO^- + \text{——}CH_2\text{——}CO\text{——} \\ &\rightarrow \text{——}CH_2\text{——}CH(O^-)\text{——} + CO_2 \end{aligned} \quad (2)$$

$$\begin{aligned} &\text{——}CH_2\text{——}CH(O^-)\text{——} + H_2O \\ &\rightarrow \text{——}\mathbf{CH_2}\text{——}\mathbf{CH(OH)}\text{——} + OH^- \end{aligned} \quad (3)$$

$$OH^- + 2CO + H_2O \rightarrow HCOO^- \quad (4)$$

Deoxygenation (Eqs. 2–4), from —CH(OH)—CH(OH)— to —CH_2—CH(OH)—, occurs through de-carboxylation (Eq. 3) from ester formed by hydroxyl group (Eq. 2) and formate ion derived from carbonate (Eq. 1). Formate ion is regenerated according to Eq. 5. Japanese researchers successfully liquefied woody biomass without adding any gases (CO or H_2) in water[34,35,38,39] because CO can be obtained by decomposition of biomass as confirmed by Ogi et al.[39] Ogi and Yokoyama[34] tested nine alkali catalysts ($CaCO_3$, $Ca(OH)_2$, Na_2CO_3, NaOH, HCOONa, KOH, K_2CO_3, NaCl, HCOOK) at 300°C for the liquefaction of wood, and found that 0.8 wt % Na_2CO_3 is the most effective catalyst with 50.8 wt % oil yield and little solid residue formation. Even though the oil

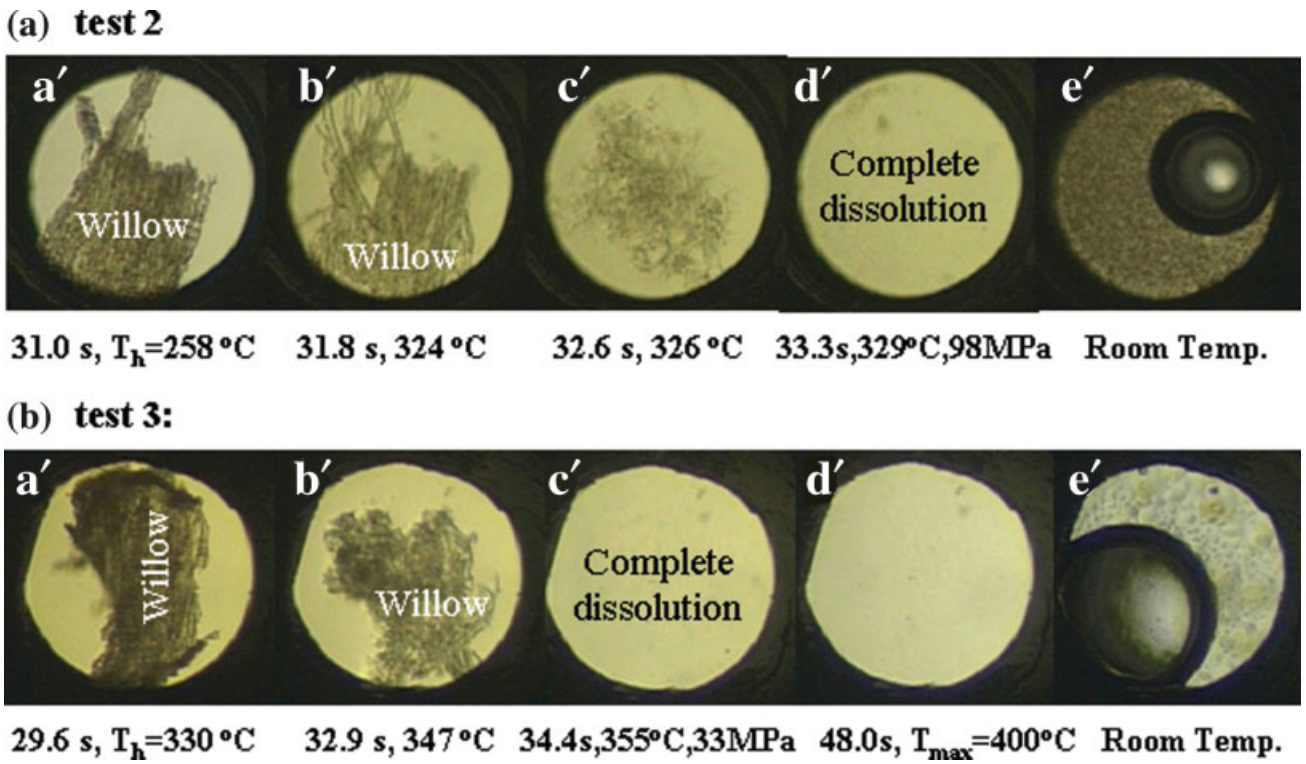

Figure 2. Visual observation of complete dissolution of willow in 0.8 wt % Na_2CO_3 aqueous solution for (a) production of micron particles (test 2): rapid heating willow with a concentration of 32 vol % to 330°C at a heating rate of 9°C /s and initial water density (ρ) of 787 kg/m^3; (b) hydrolysis to sugar-like products (test 3): rapid heating willow with a concentration of 35 vol % to 400°C at a heating rate of 8°C /s and initial water density (ρ) of 641 kg/m^3.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

yield is high and liquefaction mechanism is known but we still don't know if Na_2CO_3 can promote wood dissolution and whether a homogenous phase is formed that can enhance wood liquefaction. In the following experiments, 0.8 wt % Na_2CO_3 was used.

Complete dissolution of willow in 0.8 wt % Na_2CO_3 aqueous solutions (tests 2–3)

In test 2 (Figure 2a), 0.8 wt % Na_2CO_3 was added to {32 vol % willow + water} to see its effect to the willow dissolution process by rapid heating (9°C/s) to 330°C.

At 258°C (Figure 2a-a′), gas bubbles disappeared and the water density was calculated as 787 kg/m^3. As the chamber was further isochoricly heated, willow particle shrank, and subsequently numerous tiny fibers unbound, dispersed and started to dissolved at 324°C (Figure 2a-b′). In just 1.5 s, all willow dissolved in water at 329°C and 98 MPa (Figure 2a; b′–d′). After cooling, numerous particles were precipitated (Figure 2a-e′). The particles (Figure 3; image b) were decomposed but with a strong willow character, because the broad willow characteristic peak at 2913 cm^{-1} still remained and a peak at 1740 cm^{-1} disappeared (Figure 3; curve b vs. 1). SEM image (Figure 4) showed that the particles were micron sized (about 0.5 μm). We tested a lignin (Tetrahydrofuran soluble, M_w = 1500, Sigma-Aldrich) and found that it can completely dissolve in the 0.8 wt % Na_2CO_3 aqueous solution at ambient condition. But no dissolution was found for willow particles because lignin cross-links or covalently links to cellulose and hemicellulose that are not soluble at room temperature. At high temperature (130 to 180°C), however, in the Kraft process for several hours, the linkages are broken, and lignin and some hemicellulose in wood are degraded to give fragments that are soluble in the strongly basic liquid.[33] The solubility of a lignin sample in alkaline solution besides the depolymerization is mainly due to the charges created in the lignin structure as a result of alkaline ionization of phenolic groups.[32] In the previous works, it is found that hemicellulose and cellulose (but lignin) completely dissolved in pure water at 200–300°C[15] and 320–350°C[18], respectively. Lignin is soluble in the Na_2CO_3 solution. Therefore, when heated rapidly to 320–350°C, the three major constituents (cellulose, hemicellulose and lignin) cross-linked by lignin as wood could dissolve completely in the Na_2CO_3 solution. In test 2, willow or the three major constituents completely dissolved simultaneously at 329°C because little reaction occurred as confirmed by IR.

In test 3 (Figure 2b), {35 vol % willow + water + Na_2CO_3} system was heated to a higher temperature of 400°C (heating rate = 8°C; ρ = 641 kg/m^3). After gas bubbles disappeared, willow particle started to dissolve at 347°C, and 1.5 s later, completely dissolved at 355°C and 33 MPa (Figure 2b, a′–c′). Willow was undergoing homogenously hydrolysis for 14.6 s as the temperature increased further to 400°C (Figure 2b, c′–d′). After cooled, willow was completely hydrolyzed to sugar-like product (Figure 2b-e′; or

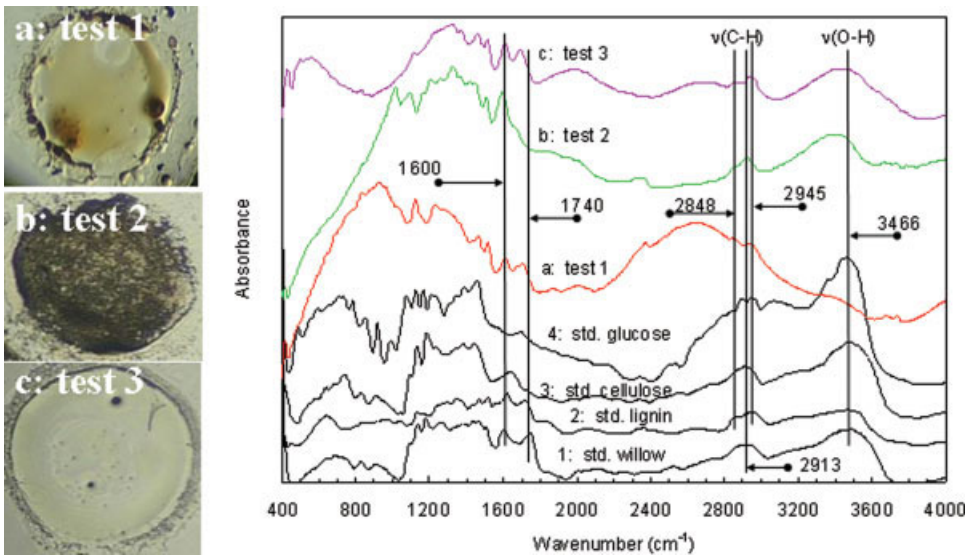

Figure 3. IR spectra for residues obtained from willow decomposition in (a) pure water (test 1: sugar-like product-image a or image in Figure 1e); (b) 0.8 wt %-Na_2CO_3 aqueous solution (test 2: solid particles-image b or image in Figure 2a-e′); (c) 0.8 wt %-Na_2CO_3 aqueous solution (test 3: sugar-like product-image c or image in Figure 2b-e′), and spectra for the standard samples: willow, lignin, cellulose and glucose (curves 1–4).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3-image c) without any solid residue, which had a similar chemical structure as that obtained in test 1 in pure water (Figure 3; curve c vs. a). Detailed reaction products, pathways and mechanisms for sugars, hemicellulose, cellulose, and lignin promoted in homogeneous and heterogeneous environments can be seen in the previous works.[27,28,30,31,40] Besides the hydrolysis and hydrothermal reactions, there should be some liquefaction reactions catalyzed by Na_2CO_3 for wood in a homogeneous condition according to the above Eqs. 1–5, that would inhibit repolymerization of the degraded products. In fact, in our previous works, no solid residue was found even reacted for 30 min when cellulose was heated slowly to 350°C.[12,35] After adding Na_2CO_3, [OH^-] concentration becomes higher that will promote wood hydrolysis and protect the reactor made of stainless steel from corrosion by neutralizing the acidic hydrothermal solution that is a common problem in the applications of hydrothermal process.[9]

Many experiments were done to find the complete dissolution temperatures at different water densities (322–787 kg/m^3), willow concentrations (11–35 vol %) and heating rates (7–16°C/s), and the results are given in Figure 5. At low water densities (< 550 kg/m^3; dotted line), dissolution temperatures were at 336–365°C (or pressure of 14–20 MPa) for 11–28 vol %

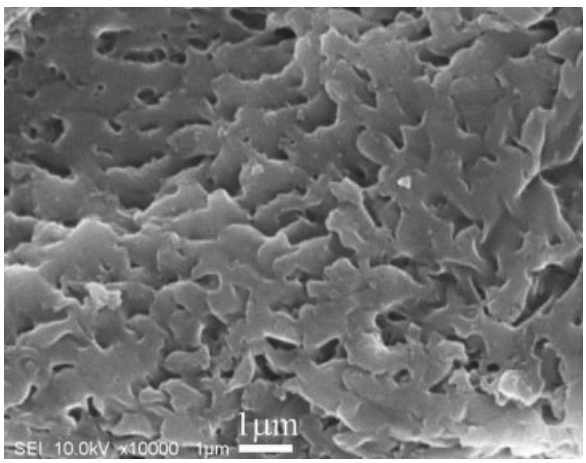

Figure 4. SEM image of the micron particles obtained from rapid cooling of the solubilized willow in test 2 (it is the SEM image of particles in Figure 2a-e′ or in Figure 3b).

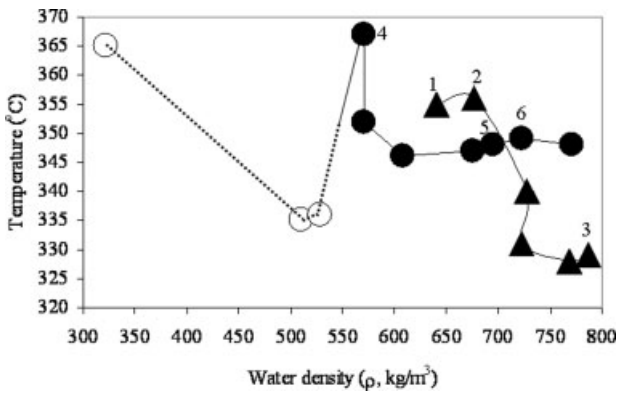

Figure 5. Temperature vs. water density (ρ) for the complete dissolution of willow (11–35 vol %) in 0.8% Na_2CO_3 aqueous solution (liquid phase-solid lines; liquid-vapor phase-dotted line): heating rate (°C/s): ▲: 7–10; ○: 12–14 ●: 13–16. willow concentration (vol %): ▲: 13–35; ○: 11–28; ●: 12–30. selected concentrations: #1: 35; #2: 28; #3: 31; #4: 30%; #5: 14; #6: 27.

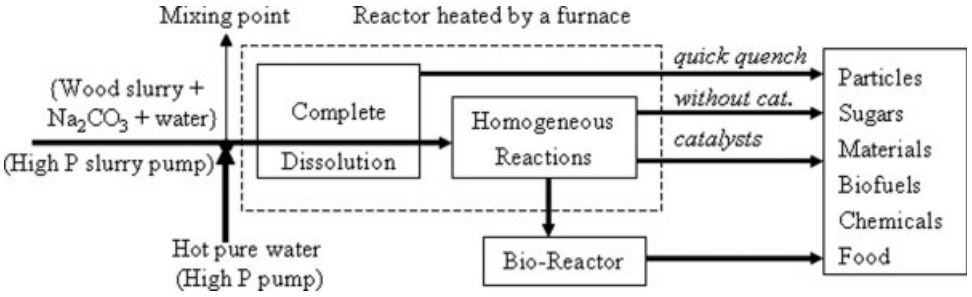

Figure 6. Proposed various applications by refining of the solubilized wood.

willow concentrations at heating rates of 12–14°C/s°C in the L-V phase with gas bubbles. At higher water densities (570–790 kg/m^3; solid lines), dissolution was undergoing in the liquid phase after gas bubbles disappeared, and dissolution temperature had a decreased trend as water density rose. At heating rates of 7–10°C/s, dissolution temperatures decreased from 355 to 330°C (Figure 5; triangle maker ▲, 13–35 vol % willow) when water density increased from 640 to 790 kg/m^3 (33–98 MPa). At higher heating rates of 13–16°C/s, dissolution temperatures became higher but with the same trend that dropped from 367 to 350°C (Figure 5; black circular maker ●, 12–30 vol % willow) as water density rose from 640 to 790 kg/m^3 (17–106 MPa). It seemed that the willow concentration had little effect on the dissolution temperature, for example in Figure 5, experiments 5 and 6 have very different concentrations (14 vs. 27 vol %) but close dissolution temperatures at a similar density because willow dissolved very fast just in 1.5 s. As water density was down from 771 kg/m^3, dissolution temperature increased and reached the maximum of 367°C at 571 kg/m^3 (Figure 5, #4), which was possibly caused by less of the water to penetrate amorphous regions of wood at low water density. This phenomenon was also found for cellulose dissolution in pure water that dissolution temperature rose from 320°C and reached the maximum of 350°C as water density went down from 850 to 560 (kg/m^3).[18] When water density went down further (less than 530 kg/m^3), dissolution temperature surprisingly dropped. The possibly reason is that the dissolution was in the L-V phase where gas bubbles moved turbulently and pushed willow mix with water violently when heated, that promoted the dissolution process as can be seen in the recorded video. Similar to the above experiments with pure water, at very high water densities (> 830 kg/m^3), the solubility in the aqueous Na_2CO_3 solution became low thus no complete dissolution of willow was observed.

Applications

Because willow can completely dissolve in aqueous Na_2CO_3 solution, it is convenient and practical to build a flow reactor to solubilize willow continuously. A Tubular flow reactor is proposed here, and it is made of a stainless tube and heated by an electric furnace. 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 + Na_2CO_3} 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 (Figure 6) just before entering the reactor. At the mixing point, the sample stream is rapidly heated (e.g., heating to 355–400°C in just 0.02–0.4 s[19]) and subsequently enters into the reactor undergoing complete dissolution and reactions. After leaving the reactor, the mixture is rapidly quenched by a cooling water jacket to terminate the reaction. Using the flow reactor, willow is solubilized immediately, and subsequent reactions were controlled easily by changing reaction times, pressures and temperatures with and without catalysts for the following applications (see Figure 6):

(i) Production micron particles by quick-quenching the homogeneous mixture immediately just after willow completely dissolves.

(ii) Pretreatment of willow to oligosaccharides and polysaccharides by heating the homogeneous mixture to high temperatures or with long reaction times.

The degraded willow can be hydrolyzed to glucose by cellulose enzyme. Furthermore, the glucose obtained is fermented to ethanol.[41] The lignin can be used directly as low graded fuel or converted further to chemicals, biofuels, and materials.

(iii) Hydrolysis of willow to sugars and phenolics by heating the homogeneous mixture to higher temperatures or with longer reaction times.

The sugars produced can be directly used for ethanol production via fermentation[42] without further neutralizing if reactions are controlled well because many organic acids are formed from the sugars decomposition after hydrolysis.[12,27,28,34,35] In fact, in the previous works,[34,35] the effluent's pH, after reaction at 300–350°C, was about 5.5 with Na_2CO_3 and 3.5 with pure water. The sugars from polysaccharides and phenolics from lignin can be further refined to chemicals, biofuels, and materials.[43]

(iv) Refining of the solubilized willow to bio-fuels or chemicals by packing catalysts in the rear part of the reactor.

The solubilized willow enters into the rear part of the reactor where it is easily accessible to the active sites of catalysts for gasification (e.g., with Ni, Ni-Sn, Pt/Al_2O_3),[12,30,44,45] liquefaction (e.g., with H_2 and Pt/SiO_2-Al_2O_3)[46] and synthesis of chemicals (e.g, with Pt/γ-Al_2O_3).[47,48]

Since willow can completely dissolve in water, this finding can also help to explain the formation mechanisms of natural gas, coal and petroleum from lignocellulosic biomass under hydrothermal conditions where alkaline minerals existed.[49,50]

Conclusions

Willow completely dissolved in water by fast-heating and adding 0.8 wt % Na_2CO_3, and subsequently underwent com-

plete hydrolysis to its monomers & oligomers in a single homogenous phase that inhibited pyrolysis to solid residue. Adding Na_2CO_3 promoted dissolution, hydrolysis and liquefaction, inhibited solid residue formation as well as protect reactor from corrosion. Aqueous "*wood solution*" like oil is easy to be processed to many products than solid wood, this result may explore a new research area for biomass refining process like liquid oil. Other type of actual lignocellulosic biomass is expected to completely dissolve in hot water with alkaline salts (pH $>$ 11.4) such as Na_2CO_3, HCOOK, KOH, NaOH, HCOONa. It is concluded that wood ethanol, particles, biofuels, chemicals, and plastics can be produced by continuously solubilization, pretreatment/hydrolysis in a well-designed flow reactor, and subsequent refining through chemical, biological, and mechanical conversions.

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