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Article

Hot Water Pretreatment of Boreal Aspen Woodchips in a Pilot Scale Digester

Jipeng Yan and Shijie Liu *

Department of Paper and Bioprocess Engineering, SUNY College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, NY 13210, USA; E-Mail: jyan02@syr.edu

* Author to whom correspondence should be addressed; E-Mail: sliu@esf.edu; Tel.: +1-315-470-6885.

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Abstract: Hot water extraction of aspen woodchips was treated at about 160 °C for 2 h with a liquor-to-solid ratio of 4.76:1 in a 1.84 m^3 batch reactor with external liquor circulation. Both five-carbon and six-carbon sugars are obtained in the extraction liquor. Xylose and xylooligomers are the main five-carbon sugar in the hot water extract, which reached a maximum concentration of 0.016 mol/L, and 0.018 mol/L, respectively. Minor monosaccharides including galactose, mannose, rhamnose, glucose, and arabinose are also obtained during the hot water extraction. Rhamnose is the main six-carbon sugar in the extraction liquor, which has a maximum concentration of 0.0042 mol/L. The variations of acetyl groups and formic acid are investigated due to their catalytic effect on the extraction reactions. Zeroth-order kinetics models are found to be adequate in describing the dissolved solids, acids, xylose, and xylooligomers.

Keywords: hot-water extraction; kinetics; aspen; xylose; xylooligomers

1. Introduction

Woody biomass mainly contains cellulose, hemicellulose, lignin, and extractives. Cellulose is a homopolysaccharide consisting of glucose units through β (1 → 4) glycosidic bonds. It has a linear structure and provides strength to the plants. Hemicelluloses are heteropolymers composing of five- and six-carbon sugars including xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan.

Hemicelluloses have amorphous structure and weak strength, which can be easily hydrolyzed by acids [1,2], base [3], enzymes [4], and hot water [5,6]. Lignin has a three dimensional structure; possesses a high energy density; and is chemical degradation resistant, between cellulose (most resistant) and hemicellulose (least resistant) [7]. Extractives can be obtained by organic solvents or water extraction under moderate conditions. In order to utilize the woody biomass efficiently, woody biomass are treated by five main steps: pretreatment [8], hydrolysis [2,9], separation and purification [10], fermentation [11], pretreatment residual solid utilization such as pulping [5,12]. Pretreatment is a very important step which could determine the products' and coproducts' composition, and the subsequent treatment conditions [13–15]. It has been proved that the pre-extraction of woody biomass benefit the following pulping processes, which include increasing delignification rate and mill throughput, reducing cooking time and chemical charge [14,15]. Among the common pretreatment methods, hot water extraction is investigated widely due to its environmental-friendly characteristics [8]. With hot water extraction, most extractives and hemicellulose are removed from woody biomass while cellulose and lignin are remained in the residual solid [16]. Kinetic models have been developed in order to optimize the reaction conditions and design reaction systems of hot water extraction to obtain the desired valuable products. Most models interpret the process of hot water extraction in the way: water dissociation release the hydronium cation which acts as catalyst to accelerate the breakage of glycosidic bonds. Hemicelluloses are extracted from the solid biomass and dissolved into the liquor phase. The soluble oligomers are further degraded to monosaccharides. As soon as uronic acids and acetic acid which could contribute large amount of hydrogen ions are extracted from hemicellulose, the extraction reaction rates increase dramatically. With the extended extraction time, monosaccharides are dehydrated to furfural and hydroxymethylfurfural (HMF). There are models describing hot water extraction as a homogeneous system with pseudo-first-order reactions and the extracted xylan having two different reactivities [5,17–19]. Nabarlatz *et al.* proposed a modified pseudo-first-order model that xylan is composed of xylose, arabinose, and acetic acid [20,21]. Other models tend to ignore the possible biphasic nature of xylan and propose more general linear sequence first-order kinetic model [22,23]. Mittal *et al.* also investigated the mass-transfer effects on the kinetic model to predict the concentration of products [24]. Liu proposed a "surface renewal" kinetic model to interpret the extraction and hydrolysis of hemicellulose and extractives, resulting a zeroth order kinetics in the bulk stage of extraction, and near first order by the end of dissolution of xylan [25]. Kim *et al.* investigated the correlation between the recovery of soluble components and the severity factor through multi-stage liquid hot water extraction, which indicate that the recovery of hemicelluloses prefer to a low temperature and long residence time and multi-stage pretreatment benefit the recovery of valuable sugars [26].

Hot water extraction of aspen has been investigated in small scale digesters. Lu *et al.* employed hot-water extraction of industrial aspen woodchips before soda pulping in an M/K digester. The mass removal reached 21.38% at 160 °C for 210 min. Extended extraction time (longer than 150 min) lead to the sharp increase of furfural [15]. Mittal *et al.* carried out quantitative analysis of sugars with ^{1}H NMR during hot water extraction. They found that 75%–80% hemicelluloses were extracted from woody biomass. Most of the extracted xylan in the liquor phase exists in the form of xylan [24]. However, there is not much literature that mentions the process of hot water extraction of aspen in a pilot scale digester. The operation conditions are different between small scale and pilot scale digesters. For example, it takes a much longer time to heat up the pilot scale digester, which could lead

to significant mass removal and have an important effect on the kinetics modeling of hemicellulose solubilization [27]. In this study, the component variations of the aspen hot water extract along with extraction time at 160 °C in a pilot-scale digester were investigated. The experimental data were used to fit the pseudo-zeroth order degradation kinetics models developed by Liu to obtain calculation parameters [25].

2. Materials and Methods

2.1. Materials

Aspen woodchips investigated in this paper were obtained from Alberta Pacific Forest Industries Inc. (Boyle, AB, Canada) and screened to a size of 2.5 cm × 2.0 cm × 0.5 cm which is normally used in the industry. All the woodchips were stored in the sealed barrels to balance the moisture content which is determined by oven-drying the woodchips samples at 105 °C overnight. The moisture content of woodchips ranged from 36% to 42%.

2.2. Hot Water Extraction

Hot water extraction was carried out in a pilot-scale reactor of 1.84 m^3 with an external steam heating system and internal liquor circulation system. The extraction liquor was recirculated through the heat-exchanger during the extraction process. In total, 263.2 kg (oven-dry weight) of woodchips and 1262.2 kg water were placed in the reactor which was heated up by high-pressure steam. Figure 1 shows the temperature profile during hot water extraction. One can observe that it takes about 210 min to heat the reaction system up to the desired temperature (160 °C). The extraction was to maintain the desired temperature for 2.5 h. Liquor samples were withdrawn through an external condenser every 15 min starting from the beginning of heating process, in which a significant number of components transfer from woody biomass to the bulk liquor [27]. When the liquor samples were further cooled to the room temperature, dissolved solids and pH of the samples were determined. Dissolved solid was determined by oven-drying an aliquot (10 mL) of hot water extract at 100 °C for 16 h.

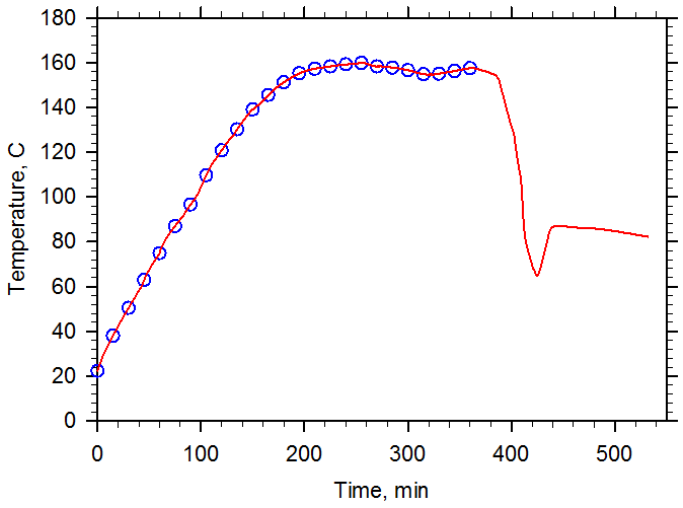

Figure 1. Temperature profile during the hot-water extraction of Northern Boreal Aspen woodchips, with symbols indicating the time at which extraction liquor samples are taken.

2.3. NMR Analysis

Minor compounds, including furfural, acetate group, hydroxymethylfurfural (HMF), and formic acid were determined by proton NMR spectroscopy (Bruker AVANCE III 600 MHz, Bruker Biospin Corporation, Billerica, MA, USA) [28], while the heteronuclear single quantum coherence spectroscopy (2D-HSQC, Bruker AVANCE III 600 MHz) [29] was employed to determine the monosaccharides and oligosaccharides obtained during the extraction. The internal standard solution consisted of D_2O (95.532%), trimethylamine hydrochloride (TMA) (0.2281%), 3-(trimethylsilys) propionic-2,2,3,3-d4 acid (TSP) (0.05304%), and glucosamine (4.187%). Glucosamine and TMA served as a calibration standard, while TSP was used as a chemical shift reference (0.0 ppm). All HSQC were recorded with standard pulse sequences (hsqcetgpsp) using Echo/Antiecho-TPPI (time-proportional phase incrementation) gradient selection, and shaped pulse for the uniform inversion of the f2 channel (13C). The recycle delay was 2.0 s and the acquisition time was 0.125 s. Since the concentration of the xylooligomer and xylose were low especially at the early stages of hot water extraction process and moderately "higher" concentration was desired for 2D-HSQC analysis, the samples were concentrated in a vacuum rotary evaporator at 70 °C in order to increase the sugar concentrations before 2D-HSQC determination. The standard curves were created using pure monosaccharide standard solutions. A linear function was found in the relationship between concentration of sugars and their normalized peak intensity, which passed through the origin and is shown in Figure 2. Glucosamine served as the internal standard and the integral of α-C1H1 was normalized uniformly to 100. All the other peak integrals are normalized to α-C1H1 for glucosamine. Either α-anomeric C1H1 peak or together with β-anomeric C1H1 peak can be used to calculate the concentration of monosaccharides [29]. Both data from proton NMR and 2D-HSQC were analyzed using Mestranova NMR software.

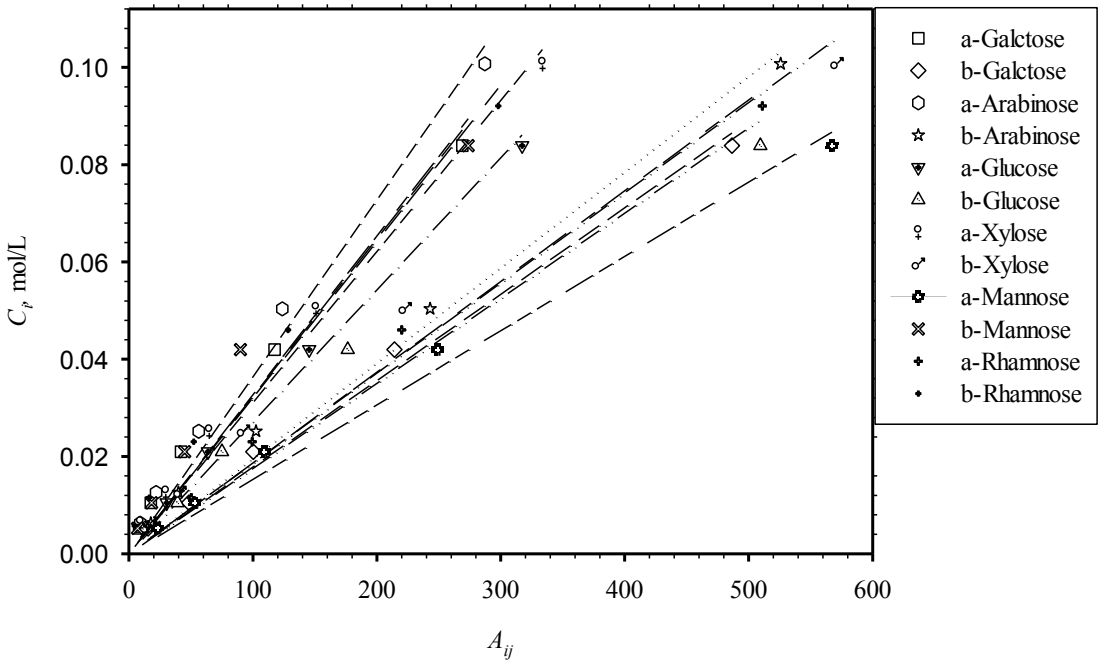

Figure 2. Standard curves for 2D-HSQC [30]. C_i is the mole concentration of species *i* and *j* designations the functional group (C1H1) identified by NMR belonging to species *i*. A_{ij} is the 2D-HSQC resonance integral for the *j* functional group of species *i*.

3. Results and Discussions

3.1. Dissolved Solids and pH

In the process of hot water extraction, most of the hemicellulose and part of cellulose and lignin were extracted from the woody biomass, which were non-volatile at 105 °C and treated as dissolved solids. The main sugar components in the dissolved solid were xylose oligomer and monomers as well as minor 5-carbon and 6-carbon monomer sugars. Besides these sugars, dissolved solids also contains small amount of lignin, glucuronic acid, galacturonic acid, 4-O-methyl-glucuronic acid, ash, and other unidentified solids [24,31]. Therefore, dissolved solids are an important indicator for this pretreatment process and can be used to estimate the extraction performance and calculate the mass balance and yield. Another important extraction indicator is the pH. Since hot water extraction is a self-catalyzed process, the extraction rate depends on the proton concentration of the liquor, which was mainly determined by the deacetylation of woody biomass and degradation of monosaccharides. Liu mentioned that the bulk of the extraction can be described by a zeroth-order kinetics [25]. Mass balance of the dissolved solids in the reactor leads to:

$$\frac{\mathrm{d}M_C}{\mathrm{d}t} = -k_{ED} \tag{1}$$

where M_C is the mass of extractable biomass remaining in the wood chips and k_{ED} is the rate constant of dissolution [25]. Assuming isothermal operation, constant pH, and no degradation reactions, integrating both sides of Equation (1) leads to:

$$M_{\mathrm{C}} = M_t - k_{ED}t \tag{2}$$

Applying mass balance to the extractable biomass between the solid woodchips and the extraction liquor, we obtain:

$$M_t = M_C + D_S V \tag{3}$$

where D_S is the dissolved solids concentration in the extract and V is the volume of extract which is 1262 L. Substituting Equation (3) into Equation (2), we obtain:

$$D_S = \frac{k_{ED}t}{V} \tag{4}$$

Figure 3 shows the variation of dissolved solids and pH in the process of hot water extraction. The k_{ED} is 288.4 g·min^{-1}.

One can observe from Figure 3 that dissolved solids increased with the increase of extraction time. In the initial stage ranging from 0 to 200 min (heating up process), about 25% of dissolved solids were extracted in the liquor due to the increase of proton concentration, which can also be proven by the variation trend of pH. When extraction time extended to 200 min, the concentration of dissolved solids increased sharply, from 3.8 to 30 g/L. The second stage is the main extraction process in which a large number of deacetylation and degradation reactions occurred. The pH also decreased obviously in the second stage due to the increasing concentration of acids in the liquor. One can observe that the extraction rate is slow initially, and increases with the decrease of pH due to the extraction of acidic

components [32]. By the end of the hot water extraction, ranging from 310 to 360 min, both the dissolved solid and pH were nearly constant which indicates that most of the extractable woody biomass has been degraded and transferred to the extraction liquor. The maximum concentration of dissolved solid was 31 g/L obtained at 330 min. One can also observe that the kinetic model built for the dissolved solids fit well with the experiment data, which indicate that the extraction rate of dissolved solids is indeed zero-order in the bulk of extraction stage.

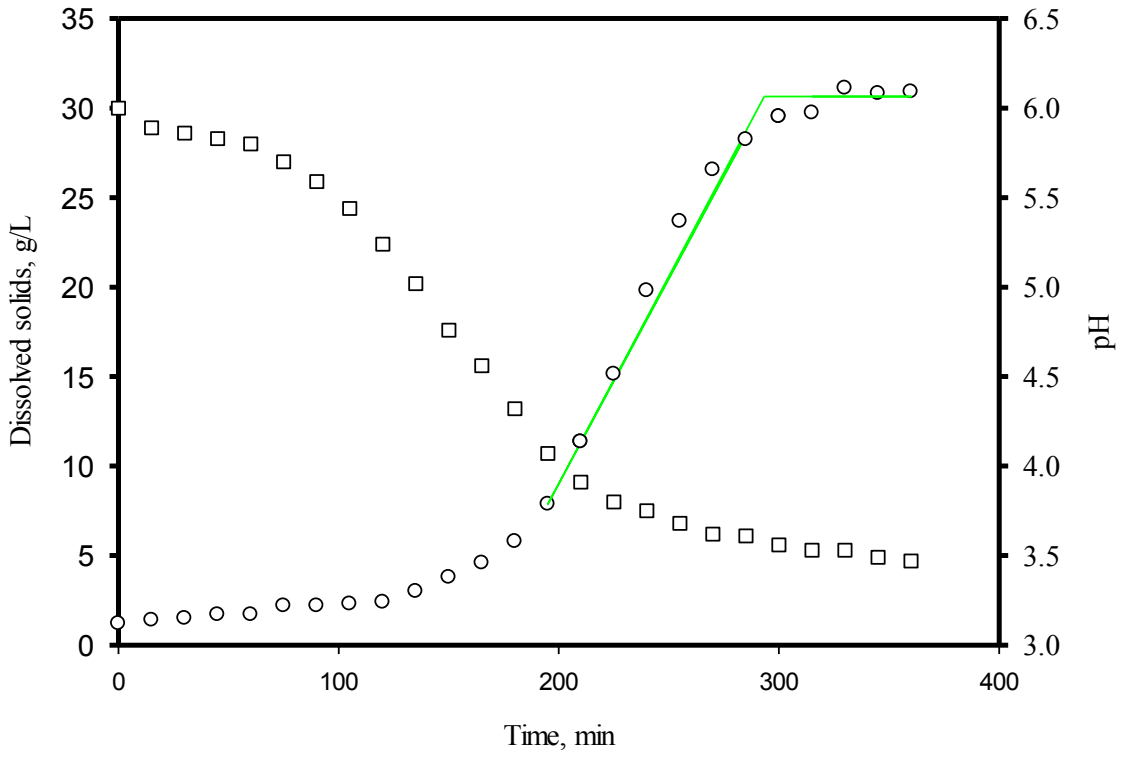

Figure 3. Variations of dissolved solids and pH during hot water extraction of aspen. Square (□) represent pH. Circle (○) represents dissolved solid. The lines are based on Equation (4). The K_{ED} is 288.4 g·min^{-1}.

3.2. Acids

During hot water extraction, the reactions were catalyzed by the proton in the liquor which was also one of the extraction products and originating from acetyl groups at the C-2 or C-3 position of the backbone of xylan. Along with the extraction of xylan from woody biomass, bound acetyl groups were transferred from solid phase to liquor phase. With the extension of extraction time, the bound acetyl groups are cleaved and contribute to the concentration of the free acetyl group. Except for the acetyl groups, formic acid from side chain degradation is another important resource of proton. The concentration of acids were low initially and increased quickly with the increase of extraction time. The deacetylation process can be described by [25]:

$$\text{R–POAc (s)} + \text{H}_2\text{O*} \text{ (aq)} \rightleftharpoons \text{R–POAc·H}_2\text{O (s)} \quad (5)$$

$$\text{R–POAc·H2O (s)} \rightleftharpoons \text{R–POH (s)} + \text{AcOH (aq)} \quad (6)$$

$$\text{R–POAc·H2O (s)} \rightleftharpoons \text{R–OH (s)} + \text{HPOAc (aq)} \quad (7)$$

where H_2O^* is the activated water molecule, R is the cellulose and lignin bonding linked to the fibers, and P is a segment/subunit of hemicellulose (xylan). Based on Liu's surface reaction theory [25], the reaction rates for acetyl and formic acid in the early stage of extraction can be obtained:

$$r_{\mathrm{AcOP}} = k_{\mathrm{EAcOP}}\left(1 + b_{\mathrm{HAcOP}}C_{\mathrm{H^+}}\right)\left(N_{\mathrm{OAC}} + 1\right) - k_{\mathrm{HAcOH}}(1 + b_{\mathrm{HAcOH}}C_{\mathrm{H^+}})C_{\mathrm{AcOP}} \quad (8)$$

$$r_{\mathrm{AcOH}} = k_{\mathrm{EAcOP}}\left(1 + b_{\mathrm{HAcOP}}C_{\mathrm{H^+}}\right) + k_{\mathrm{HAcOH}}(1 + b_{\mathrm{HAcOH}}C_{\mathrm{H^+}})C_{\mathrm{AcOP}} \quad (9)$$

$$r_{\mathrm{FOH}} = k_{\mathrm{EFOH}}(1 + b_{\mathrm{HF}}C_{\mathrm{H^+}}) \quad (10)$$

where r_{AcOP}, r_{AcOH}, and r_{FOH} are the rate of formation of the bound acetyl groups, "free" acetyl groups (or acetates), and formic acid in the extraction, respectively; k_{EAcOP} and k_{EFOH} are the formation rate constant of bound acetyl and formic acid, respectively. b_{HAcOP}, b_{HAcOH}, and b_{HF} are factors used to investigate the effect of proton on bound acetyl, acetic acid, and formic acid, respectively. k_{HAcOH} is the formation rate constant of acetates. C_{AcOP} is the concentration of bound acetyl in the extraction liquor. N_{OAC} is the maximum number of acetyl groups in a solubilized oligosaccharide. $C_{\mathrm{H^+}}$ is the proton concentration, which can be calculated by:

$$C_{\mathrm{H^+}} = \frac{-C_{+0} + \sqrt{{C_{+0}}^2 + 4(K_{\mathrm{W}} + K_{\mathrm{AcOH}}C_{\mathrm{AcOH}} + K_{\mathrm{FOH}}C_{\mathrm{FOH}})}}{2} \quad (11)$$

where C_{+0} is the net normality of all the electrolytes that excludes H^+, OH^-, $HCOO^-$, OF^- and OAc^-.

K_{W}, K_{AcOH}, and K_{FOH} are calculated by [32]:

$$\log_{10} K_{\mathrm{W}} = 109.14 - \frac{57249.93}{RT} - 29.455\log_{10}(RT) \quad (12)$$

$$\log_{10} K_{\mathrm{AcOH}} = -4.73 - 0.0000202(T - 273.15)^2 \quad (13)$$

$$\log_{10} K_{\mathrm{FOH}} = 57.528 - \frac{2773.9}{T} - 9.1232\ln T \quad (14)$$

where T is the temperature in Kelvin. R is the ideal gas constant, 8.314 J/(mol·K). Figure 4 shows the variations of acids as a function of extraction time. The lines in Figure 4 were developed by Equations (8)–(10).

Figure 4 shows that all the acids concentration increased with extraction time. By the end of extraction, free acetate, bound acetyl, and formic acid reach a maximum value of 0.058 mol/L (3.48 g/L), 0.044 mol/L (1.89 g/L), and 0.013 mol/L (0.6 g/L), respectively. The acetyl groups' concentrations are much larger than that of formic acid, which indicate that acetyl groups are the main proton resource. Formic acid could be obtained from the extraction of carboxylic group and degradation of six carbon sugars. Since the concentrations of six carbon sugars are low during the hot water extraction, the formic acid from the degradation is negligible [25]. One can also observe that there are few acids that appear in the heating process. When the reactor reached its desired temperature, acids concentrations increased gradually. One may notice that concentrations of free acetate are higher than that of the bound acetyl before 220 min, which indicates that free acetates are easier to extract than the bound acetyl. With the extended extraction time, the concentration of bound acetyl increased sharply, which also contributes to the fast increase of free acetate. By the end of extraction (300–360 min),

the concentration of free acetate surpasses the bound acetyl due to the decrease of extractable bound acetyl in the woody biomass. A similar variation trend of acetyl groups was observed by Lu *et al.* [15]. However, the concentrations of acetyl groups obtained from pilot scale digester are lower than M/K digester under the same conditions [15]. One possible reason is that the mass transfer rate is slow in the big digester, which limited the extraction rate. Figure 4 also shows that the kinetic models fit well with the measured values, which indicate that the kinetic models developed for the acids are reasonable. Table 1 shows parameters in Equations (4)–(10). The formation rate constant of acetates is higher than dissolution rate constant of bound acetyl and formic acid, which can explain the sharp increase of free acetate. b_{HAcOH} and b_{HF} are much larger than b_{HAcOP}, which indicate the proton has greater effect on formation of acetic acid and formic acid. In addition, Table 1 shows that the maximum number of acetyl groups in a solubilized oligosaccharide is 3.16 which is lower than the acetyl substitution rate in the hardwood which are seven per 10 xylose units. One can infer that the hydrolysis reaction of bound acetyl occurs quickly in the liquor.

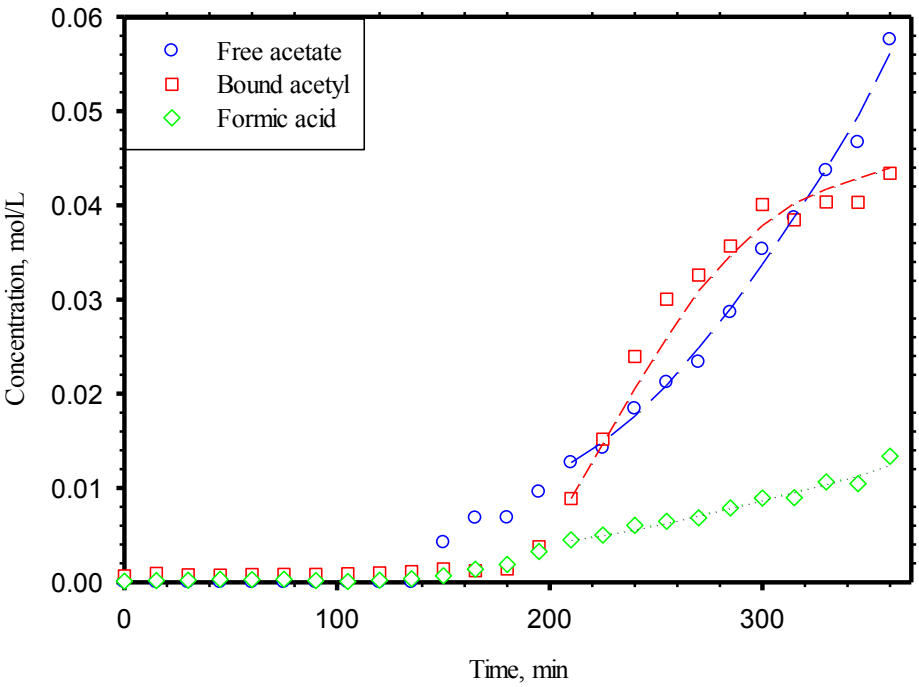

Figure 4. Acids variations as a function of extraction time.

Table 1. Parameters of Equations (8)–(10) for acids.

Parameters	Temp = 160 °C
k_{EAcOP}, min^{-1}	1.17×10^{-4}
b_{HAcOP}	10
k_{HAcOH}, min^{-1}	1.49×10^{-4}
b_{HAcOH}	1.03×10^{5}
k_{EFOH}, min^{-1}	1.7×10^{-6}
b_{HF}	9.29×10^{4}
C_{+0}	1.27×10^{-3}
K_{W}	2.84×10^{-12}
N_{OAC}	3.16

3.3. Xylose, Xylooligomer, and Furfural

As the main components of hemicellulose, most of the xylan was extracted during the hot water pretreatment. The extraction process could be described by [25]:

$$\mathrm{R–X}_n\mathrm{OH\ (s)} + \mathrm{H^+\ (aq)} \rightleftharpoons \mathrm{R–X}_n\mathrm{OH{\cdot}H^+\ (s)} \quad (15)$$

$$\mathrm{R–X}_n\mathrm{OH{\cdot}H^+\ (s)} + \mathrm{H_2O\ (aq)} \rightarrow \mathrm{R–X}_m\mathrm{OH{\cdot}H^+\ (s)} + \mathrm{HX}_s\mathrm{OH\ (aq)} \quad (16)$$

$$\mathrm{HX}_n\mathrm{OH\ (aq)} + \mathrm{H^+\ (aq)} \rightleftharpoons \mathrm{HX}_n\mathrm{OH{\cdot}H^+\ (aq)} \quad (17)$$

$$\mathrm{HX}_n\mathrm{OH{\cdot}H^+\ (aq)} + \mathrm{H_2O\ (aq)} \rightarrow \mathrm{HX}_m\mathrm{OH{\cdot}H^+\ (aq)} + \mathrm{HX}_s\mathrm{OH\ (aq)} \quad (18)$$

where $m + s = n$, R is the cellulose and/or lignin bonding connected with the fibers, X_n represents an n-xylo-polymer middle group. The extraction starts with the transport of hydrogen ion from the liquor to the surface of woody biomass. When the active proton attached to the surface of the woody biomass, a surface reaction occurred. Then, dissoluble segments transferred from woody biomass to the liquor. Xylooligomers in the hot water extract continue to break down and form xylose. With the extended extraction time, part of the xylose was further degraded into furfural. Liu proposed kinetic models for the extraction rate of sugars which were shown by Equations (19)–(29) with the assumption that condensation reactions are negligible, the breakage of glycosidic bonds has an equal rate, and the affinities of glycosidic bonds to hydrogen ions are the same. The overall extraction rate of sugars (s-xylo-oligomers) is given by:

$$r_E = k_{DX}C_1 + \sum_{s=1}^{N_0} sr_s = \frac{k_E}{2}a_s\left[P_1\left(1+\frac{1}{DP_0}\right) + (N_0+1)\sum_{n=N_0}^{N}\theta_n\right] \quad (19)$$

where r_E is the overall extraction rate of sugars; r_s is the net reaction rate of s-oligomer (or oligosaccharides contain "s" units); k_{DX} is the rate constant for the degradation of monomeric sugar; C_1 is the mole concentration of monosaccharides in the liquor; N_0 is the maximum length of oligosaccharides can be cleaved off and dissolved in the liquor; k_E is the rate constant of dissolution for each extractable macromolecule; a_s is the specific surface area or m^2-furface area of biomass per m^3-liquor volume; P_1 is the total units of xylose residues in the solid for xylan which has a degree of polymerization less than N_0; DP_0 is the average degree of polymerization for xylan in the solid which has a chain shorter than N_0; $\Sigma\theta_n$ is the total concentration of xylan on the biomass solid surface. Initially, the concentration of small xylan molecules on the solid surface is very low, which could be negligible. $P_1 \approx 0$. Total mole concentration of xylan on solid surface is nearly constant, which leads to:

$$r_E \approx \frac{k_E a_s}{2}(N_0+1)\sum_{n=N_0}^{N}\theta_n = \text{constant} \quad (20)$$

The formation rate of the s-xylo-oligomer in the liquor is given by:

$$r_s = \sum_{n=s+1}^{N_0} 2k_{HX}C_n + a_s\sum_{n=s}^{N}\frac{k_E\theta_n}{\min[n, N_0]} - (s-1)k_{HX}C_s \quad (21)$$

where $s = 2, N_0$. For $s = 1$,

$$r_1 = \sum_{n=2}^{N_0} 2k_{HX}C_n + a_s \sum_{n=1}^{N} \frac{k_E \theta_n}{\min[n, N_0]} - k_{DX}C_1 \tag{22}$$

where k_{HX} is the rate constant of breaking one single β-1,4-O bond. Based on Equation (20) through Equation (22), one can obtain the initial sugar extraction rate:

$$r_1 \approx 2k_{HX}(C_{\Sigma 0} - C_1) + \frac{2r_E}{N_0(N_0+1)} - k_{DX}C_1 \tag{23}$$

$$r_s \approx \sum_{n=s+1}^{N_0} 2k_{HX}C_n + \frac{2r_E}{N_0(N_0+1)} - (s-1)k_{HX}C_s \tag{24}$$

where $C_{\Sigma 1}$ is the concentration of total xylo-units ($\sum_{n=1}^{N_0} nC_n$). $C_{\Sigma 0}$ is the total xylo-oligomer and xylose monomer mole concentration ($\sum_{n=1}^{N_0} C_n$). Summing up Equations (23) and (24):

$$r_{\Sigma 0} = k_{HX}(C_{\Sigma 1} - C_{\Sigma 0}) + \frac{2r_E}{1+N_0} - k_{DX}C_1 \tag{25}$$

where $r_{\Sigma 0}$ is the formation rate of the sum of mono- and oligo-saccharides measured based on number of moles. Considering the effect of proton, and proton effect factors were added into the xylose prediction equations, one obtains:

$$r_E = 0.5k_{EX}\,(1 + b_{EX}\mathrm{C}_{\mathrm{H}^+}) \tag{26}$$

$$r_{DX} = k_{DX}(1 + b_{DX}\mathrm{C}_{\mathrm{H}^+})C_1 \tag{27}$$

where r_{DX} is the formation rate of degradation products. b_{EX} and b_{DX} are the proton effect factor during sugar extraction and degradation process, respectively. k_{EX} is the modified rate constant of dissolution for each extractable macromolecule.

The formation rate of the sum of mono- and oligo-saccharides measured based on total number of monomeric units, $r_{\Sigma 1}$, is obtained by:

$$r_{\Sigma 1} = r_E - r_{DX} \tag{28}$$

The formation rate of oligo-saccharides based on number of moles is given by:

$$r_0 = r_{\Sigma 0} - r_1 = k_{HX}(C_{\Sigma 1} - 3C_0 - C_1) + \frac{2r_E(N_0 - 1)}{N_0(N_0+1)} \tag{29}$$

where $C_0\,C_0$ is the xylo-oligomer mole concentration. Figure 5 show the variations of xylose, xylooligomer, total xylose units, and furfural during the hot water extraction.

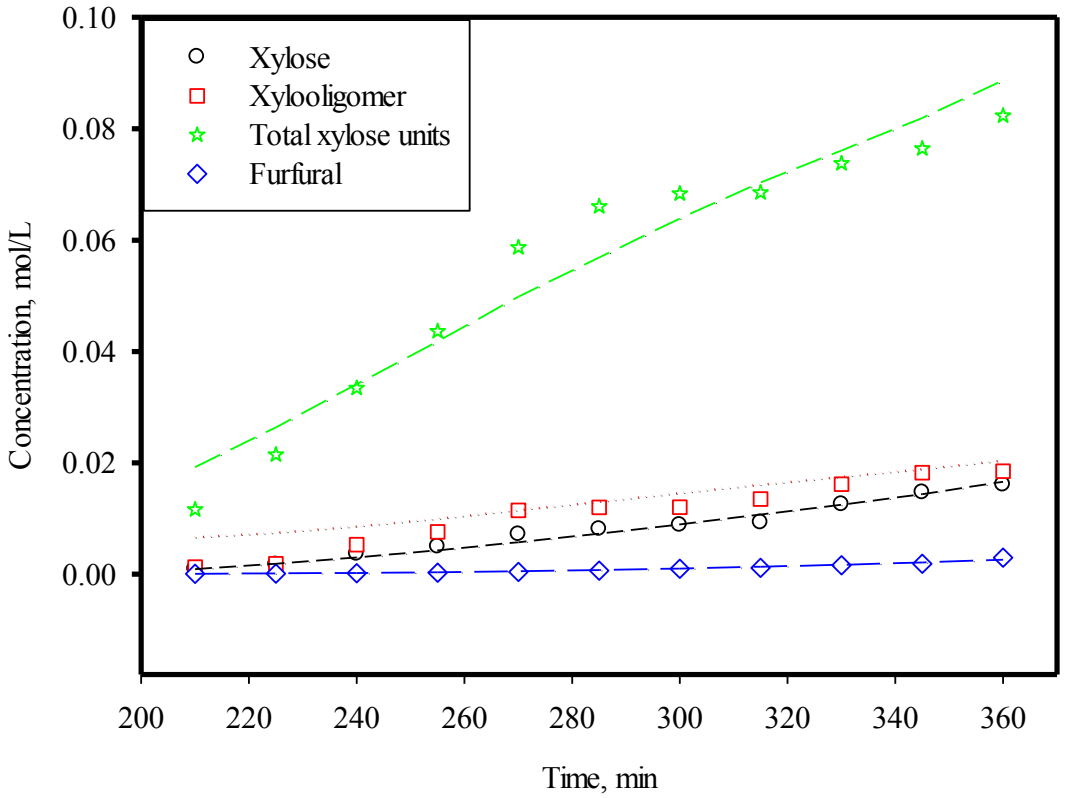

Figure 5. Variations of xylose, xylooligomer, total xylose units, and furfural as a function of extraction time. The lines are based on Equations (19)–(29).

Figure 5 shows that concentration of xylose, xylooligomer, total xylose units, and furfural increase with the increasing of extraction time and reach maximum value at 360 min, which are 0.016 mol/L (2.4 g/L), 0.018 mol/L, 0.08 mol/L (12 g/L), and 0.0029 mol/L (0.28 g/L), respectively. Compared to Lu's work, the xylose and furfural concentration was lower in the big digester than the M/K digester [15,27]. Besides the low concentration of furfural, no sharp increase of concentration was observed after 150 min at 160 °C, which was noted by Lu *et al.* during the hot water extraction in M/K digester [15]. One can infer that degradation reaction is limited due to the low concentration of xylose and acetyl groups. By comparing the concentration of xylose and furfural, one can conclude that about 5% of xylose was degraded into furfural in the second stage of extraction (210–300 min). In the last stage (300–360 min), about 12% of xylose was degraded into furfural. One can infer that xylose tends to degrade with a long extraction time, which also explains the low accumulation rate of dissolved solid by the end of the extraction. The total xylose units shown in Figure 5 refer to the sum of xylose units in both xylose monomers and oligomers contained in hot water extract. One can also observe that the concentrations of total xylose units are much higher than that of xylose and xylooligomer, which indicates that most xylose units in the liquor are contained in xylooligomer [24]. In order to increase the conversion of oligomers to the monomers, a higher extraction temperature and a longer reaction time were preferred [33]. Figure 5 also shows that the lines built based on the kinetics models fit well with the test values. However, one may notice that the concentration of xylooligomers is over-estimated by the kinetic model. One possible reason was that some of the xylooligomers with high molecular weight precipitated during the cool down process. Table 2 shows the parameters in the kinetic models for xylose, xylooligomers, and furfural.

Table 2. Parameters in xylose, xylooligosaccharide and furfural kinetic models.

Parameters	Temp = 160 °C
k_{EX}, min^{-1}	1.07×10^{-3}
k_{HX}, min^{-1}	4.95×10^{-3}
k_{DX}, min^{-1}	2.4×10^{-3}
b_{EX}	100
b_{DX}	2.86×10^{-9}
N_0	15

One can observe from Table 2 that b_{EX} is much larger than b_{DX}, which indicates that the protons have greater effect on the xylose extraction than the xylose degradation. Table 2 also shows that the maximum length of the oligosaccharides that can be cleaved off into the liquor is 15, which indicates that only a short chain of oligosaccharides can be removed from the aspen woody biomass.

3.4. Minor Monosaccharides

Besides xylose and xylooligomers, other monosaccharides were found in the liquor which resulted from the degradation of hemicelluloses. There are both five-carbon and six-carbon sugars which could be used to produce high value products. Figure 6 shows these variations of monosaccharides as a function of extraction time.

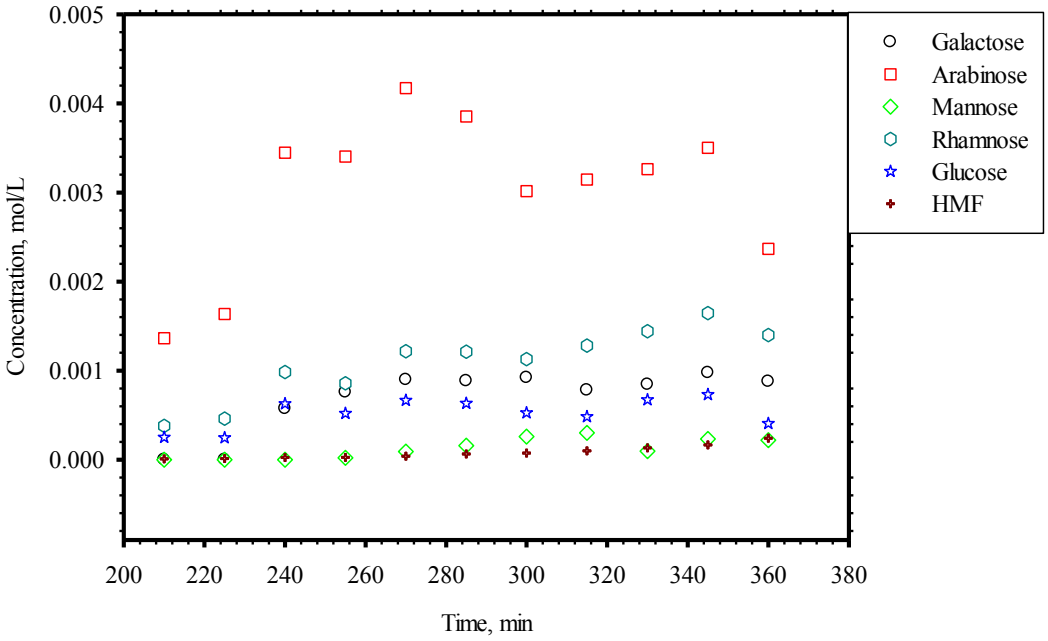

Figure 6. Variations of monosaccharides as a function of extraction time.

Figure 6 shows that the concentrations of galactose, rhamnose, glucose, and HMF increase slowly with the increase of extraction time, and reach maximum value at 340 min. The concentration of arabinose increased gradually and reached a maximum value at 270 min, which is 0.0042 mol/L (0.63 g/L). The maximum concentration of mannose was obtained at 315 min. By comparing the concentrations of minor monosaccharides, one could notice that arabinose is the secondary five-carbon sugar while rhamnose is the main six-carbon sugar in the hot water extract, which is different from the results

reported in former research [24,34,35]. The concentration of minor sugars obtained from pilot digester is much lower than M/K digester especially for glucose and mannose. One possible reason is that the acids' concentration is relatively low, which was the extraction catalyst and is shown in Figure 4. The relatively higher concentration of arabinose could be explained by the fact that arabinose side chains are easily hydrolyzed due to their furanosidic structure [36].

4. Conclusions

Xylose and xylooligomer are the main five-carbon sugars in the hot water extract, which reach a maximum concentration of 0.016 mol/L, 0.018 mol/L, respectively, at 360 min. The maximum concentration of total xylose unit is 0.08 mol/L. Rhamnose is the main six-carbon sugar in the liquor, which has a maximum concentration of 0.0042 mol/L at 270 min. The concentrations of monosaccharides and oligosaccharides increase with the increase of extraction time during the bulk extraction period. However, the degradation of monosaccharides also benefits from the extended extraction time. By the end of the extraction, furfural and HMF reached a maximum value of 0.0029 mol/L, and 0.00024 mol/L. Kinetics models fit well with the experimental data and show that extraction reactions are zero-order in the bulk extraction period.

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Author Contributions

The authors contributed equally to this work.

Conflicts of Interest

The authors declare no conflict of interest.

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