

Continuous pH Monitoring During Pretreatment of Yellow Poplar Wood Sawdust by Pressure Cooking in Water

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ABSTRACT

Yellow poplar wood sawdust consists of 41% cellulose and 19% hemicellulose. The goal of pressure cooking this material in water is to hydrate the more chemically resistive regions of cellulose in order to enhance enzymatic conversion to glucose. Pretreatment can generate organic acids through acid-catalyzed degradation of monosaccharides formed because of acids released from the biomass material or the inherent acidity of the water at temperatures above 160°C. The resulting acids will further promote the acid-catalyzed degradation of monomers that cause both a reduction in the yield and the formation of fermentation inhibitors such as hydroxymethyl furfural and furfural. A continuous pH-monitoring system was developed to help characterize the trends in pH during pretreatment and to assist in the development of a base (2.0 M KOH) addition profile to help keep the pH within a specified range in order to reduce any catalytic degradation and the formation of any monosaccharide degradation products during pretreatment. The results of this work are discussed.

Index Entries: pH monitoring; aqueous pretreatment; pH control; hydrolysis; cellulose; hydrothermal.

INTRODUCTION

Cellulose is a linear polymer of glucose that is found in herbaceous and woody plants. It is associated with another polysaccharide, hemicellulose, and both are sealed with lignin, a complex three-dimensional polyaro-

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matic compound that is resistant to enzyme and acid hydrolysis (1). Another challenge to hydrolysis is the crystallinity of the cellulose itself. The β -1,4 orientation of the glucosidic bonds result in the formation of six hydrogen bonds per anhydro-glucose molecule, thus, allowing the cellulose to form a tight crystalline structure (2). One way to overcome these challenges is to pretreat the lignocellulosic material to increase the accessible surface area of the cellulose and enhance conversion of the cellulose to glucose. There are many methods of pretreating lignocellulosic material to this end (3). Recent work with aqueous pretreatment of yellow poplar wood sawdust have shown improved hydrolysis of the cellulose to glucose (4), and diminished formation of degradation products during pretreatment when the pH was controlled. Hydrolysis refers to the formation of monosaccharides from polysaccharides and oligosaccharides from hemicellulose and cellulose. Degradation refers to the formation of aldehydes such as hydroxymethyl furfural (HMF) and furfural, and organic acids such as levulinic and formic acid from monosaccharides. These aldehydes and organic acids are also referred to as degradation products.

The goal of aqueous pretreatment of lignocellulosic material is to hydrate the crystalline structure of the cellulose and modify it to a form that is more accessible and susceptible to enzyme hydrolysis, thereby enhancing conversion of cellulose to glucose (5). During the pretreatment, organic acids can form and dissociate hydrogen ions, which will promote acid-catalyzed hydrolysis of the cellulose to glucose and, also, the acid-catalyzed degradation of the glucose to HMF, and levulinic and formic acids. This process competes with the physical hydration of the cellulose by the water. Hydrogen-ion formation from water and from organic acids is an important factor during aqueous pretreatment of lignocellulosic material since the wood sawdust and water mixture will reach temperatures as high as 260°C and pressures as high as 700 psi during the pretreatment. These high temperatures and pressures will accelerate the acid-catalyzed hydrolysis of the cellulose and hemicellulose as well as the acid-catalyzed degradation of the glucose and xylose. The loss of substrate to degradation products will decrease the extent of enzymatic conversion of the polysaccharides and oligosaccharides to monosaccharides. Monitoring and control of the pH of this system is necessary to minimize the hydrogen-ion concentration during pretreatment and help prevent hydrolysis of the cellulose and hemicellulose to oligosaccharides and monosaccharides and, more importantly, the acid-catalyzed degradation of the monosaccharides to degradation products (5).

Because of the accumulation of organic acids and the liberation of hydrogen ions during pretreatment, pH is an important parameter to monitor. Conventional laboratory-scale pH probes are too delicate to read the pH of solutions at temperatures of 100°C or greater. These probes will lose their accuracy and will be permanently damaged. Probes for use at temperatures above 100°C are still experimental and internal referencing

does not give completely accurate results (6). One way to overcome this challenge is to continuously pull a stream of the pretreatment supernatant from the vessel, cool it down to room temperature where the pH probe is most accurate, read the pH, and then pump the supernatant back to the pretreatment vessel.

This paper explains the method in which the pH was monitored and the procedure for which the pH was modified during the aqueous pretreatment of wood sawdust. This work will also discuss the effects of controlling pH on the polysaccharides in the wood sawdust and compare those results to the pretreatments in which the pH was not controlled.

MATERIALS AND METHODS

Materials

The yellow poplar wood sawdust was provided by National Renewable Energy Laboratory (NREL) in 1×5 -mm average particles. The untreated wood sawdust consisted of 41% cellulose and 19% hemicellulose that consisted of predominantly xylose (4). The wood sawdust was immediately frozen upon arrival and removed from the freezer as needed.

Pretreatment Reactor

A Parr, 304 SS reactor (Model 4843; Moline, IL) was used to pretreat yellow poplar wood sawdust in water at selected temperatures and pH values (Fig. 1). The reactor has a total volume of 2 L, with three turbine propeller agitators, and a proportional integral derivative (PID) temperature controller ($\pm 1.0^\circ\text{C}$). Cooling water was circulated through a serpentine coil to cool the reactor contents at the end of each run. A bottom port and two inlet ports allow sampling of the pretreated material and addition of reagents to the reactor.

Pretreatment Procedures

The wood sawdust was pretreated under six conditions. The three final set-point temperatures were 220, 240 and 260°C . Two runs were made at each set-point temperature. One run pretreated the sawdust with the addition of KOH to help control the pH, and another was carried out without any pH control.

The wood sawdust was first soaked in water at room temperature for approximately 14–18 h. The vessel loading for the wood sawdust was between 53 and 63 g/L (dry weight basis) depending on the dry weight of the wood sawdust. The working volume of the pretreatment vessel was 1.5 L for the 220 and 240°C pretreatments, and 1.0 L for the 260°C pretreatments. The volumes were selected to maintain adequate head space since pretreatment at these temperatures caused expansion of the liquid phase ($\rho = 0.845 \text{ g/mL}$ at 220°C vs $\rho = 0.785 \text{ g/mL}$ at 260°C). The ratio of solids to liquids was kept at a constant level.

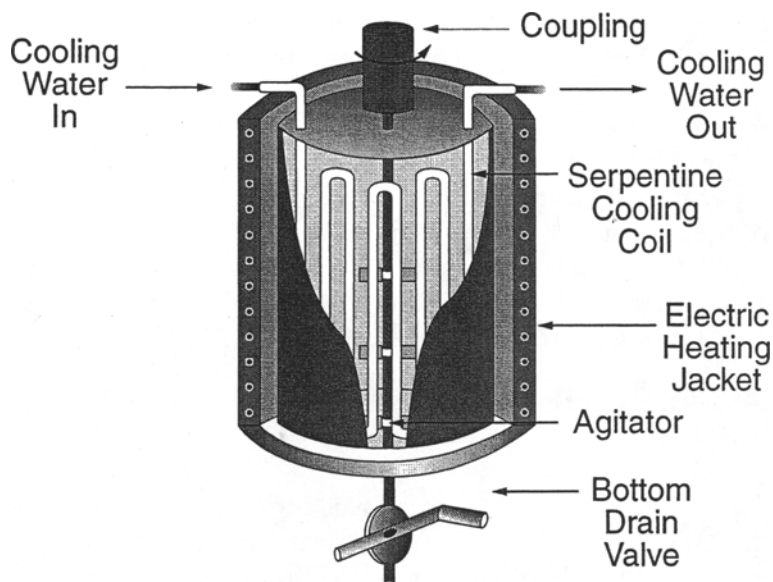


Fig. 1. Schematic diagram of the pretreatment vessel.

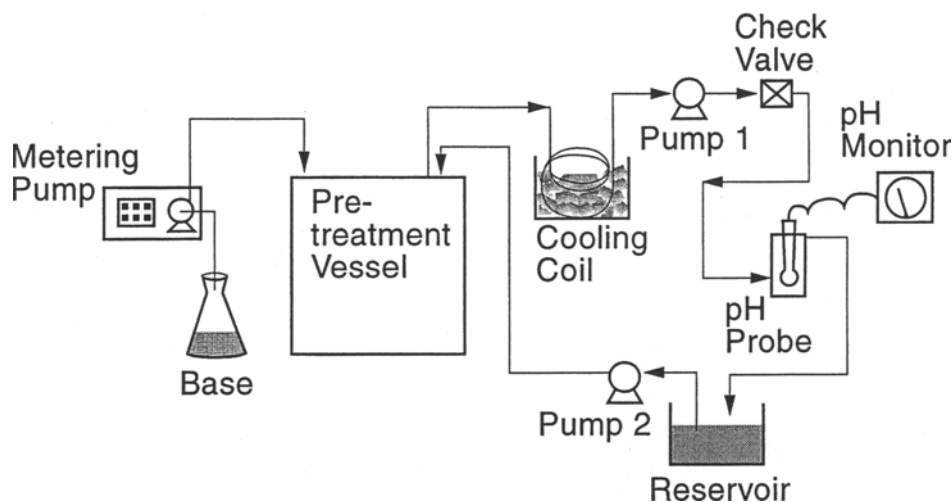


Fig. 2. Schematic diagram of the pH-monitoring system.

Prior to pretreatment, the pumps and tubing for the pH-monitoring system were primed with deionized water (Fig. 2). This was done to calibrate the two pumps to the same flow rate and to evaluate the system for leaks and for plugging.

The pretreatment slurry was agitated using 3 turbine impellers (1 cm wide by 6 cm diameter) set at 115 rpm. The reactor contents were initially at ambient temperature. The heater set-point temperature was set at 220,

240 or 260°C, and heat-up was initiated by turning the heat switch to high. The heat-up rate for the wood sawdust was between 3.5 and 4.0°C/min. The control of temperature and heat-up was achieved using the PID controller supplied by Parr (Moline, Illinois).

A continuous pH-monitoring system was developed to sample the supernatant without loss during the pretreatment. The system consisted of two Milton Roy pumps (Mini-pump; 46/460 mL/hr) (Fig. 2). pH monitoring was initiated when the pretreatment temperature reached 150°C, with a vessel pressure of 50 psi (\pm 3 psi). Pump 1 continually metered liquid supernatant from the reactor through a 0.2-micron filter stone (Alltech, Deerfield, IL.), then through 1/8-in od (0.085-in id) stainless-steel tubing. The vessel pressure ranged from 0 to 700 psi over the course of the pretreatment and hence, provided the back pressure required for the supernatant to pass through the filter stone. The supernatant passed through an ice bath, then through pump 1. From pump 1, the supernatant went through a water bath, at ambient temperature, and was pumped through a check valve (set at 750 psi) into a pH probe/flow cell at a rate of 8.5 to 9.0 mL/min. The total time for supernatant to travel from the filter stone in the pretreatment vessel to the pH flow cell was approx 1.5 min.

The flow cell, which housed the pH probe, was fabricated from a 50-mL graduated cylinder with two approx 1 mm id (3/8-in od) glass ports fitted at the top and bottom of the cylinder by the Purdue University Chemistry Glass Shop. The temperature of the supernatant entering the flow cell was 24°C. The fluid entered a port at the bottom of the cylinder and flowed out through a port at the top into a reservoir. The reservoir was a graduated beaker that held approx 40 mL of fluid. The volume of the reservoir was checked regularly to calibrate the flow rates of the two pumps in the monitoring line. A second Milton Roy pump (Mini-pump; 46/460 mL/h) then returned the supernatant from the reservoir to the pretreatment vessel at approximately the same flow rate as pump 1. The total time for supernatant to flow through this circuit was approx 10 min.

A Markson pH meter (Markson Science, Phoenix, AZ) and pH electrode (Markson V-830) were used to determine the pH of the supernatant in the flow cell. The pH electrode was calibrated using standardized buffer solutions (Fischer, Pittsburgh, PA) of pH 4.0 and 7.0. The electrode was stored in pH 4.0 buffer when it was not being used.

For the pretreatments in which the pH was controlled by the addition of KOH, the base was metered into the reactor by manual control using a third pump, Dynamax SD-200 (Woburn, MA), pumping at 10 mL/min, shown in Fig. 2. The base was added directly to the pretreatment vessel to reduce the time between reading the pH meter and the physical contact of the base with the contents of the pretreatment vessel. This minimized the possibility of alkaline degradation reactions that might otherwise occur if the base were added to the reservoir, where a small portion of the slurry can sit at a high pH (7.0–12.0) at room temperature for a period of 5 min.

Table 1
pH Results for Wood Sawdust Pretreatment Without pH Control

Temperature (°C)	Initial pH	Final pH
220	5.14	3.03
240	5.27	2.81
260	5.30	2.91

Once the predetermined set-point temperature was obtained, the heater was turned off and cooling water was charged through the serpentine cooling coil. The contents of the reactor cooled down to 180°C in approx 2 min, and to 150°C in approx 5 min. The reactor was kept sealed, and the slurry agitated until the reactor headplate had cooled to approx 50°C. The agitator drive was then disconnected and the reactor was then physically removed from the heating jacket and placed on the bench. The reactor was then opened, and the contents removed for further analysis and testing.

RESULTS AND DISCUSSION

Pretreatments of Wood Sawdust Without pH Control

The pH ranges for the wood sawdust pretreatments in which pH was not controlled are summarized in Table 1. The initial pH of the wood sawdust and water slurry after sitting 16 h was between 5.14 and 5.30. The pH reaches a final reading between 2.8 and 3.0 upon the completion of pretreatment and cool-down of the slurry to room temperature. There does not appear to be a strong correlation between final pretreatment temperature and the final pH. For the 240 and 260°C pretreatments, the final pH approached 2.8, where autohydrolysis of the cellulose may occur (7).

A typical pH profile that occurs during pretreatment to 240°C without pH control is illustrated in Fig. 3. Between 180 and 200°C, the pH decreased significantly from 5.0 to 3.5. From the 200°C point to the end of the pretreatment, where the slurry was cooled to 180°C, the pH continued dropping to approx 2.8.

Wood Sawdust Pretreatments with pH Control

Table 2 shows the experimental pH ranges observed for the wood sawdust pretreatments with KOH added to help control the pH. Before pretreatment, the pH of the slurry was measured directly from the vessel before pretreatment and was approx 5.2 for all three pretreatments. Approximately 0.3 mL of 2.0 M KOH were added to the vessel to bring the

Table 2
pH Results for Wood Sawdust Pretreatments with pH Control

Temperature (°C)	Initial pH	Final pH	pH range	KOH added (mls)
220	7.10	5.91	4.50 - 7.10	88.6
240	8.20	5.71	5.02 - 8.20	80.4
260	7.02	6.13	4.95 - 7.02	108.0

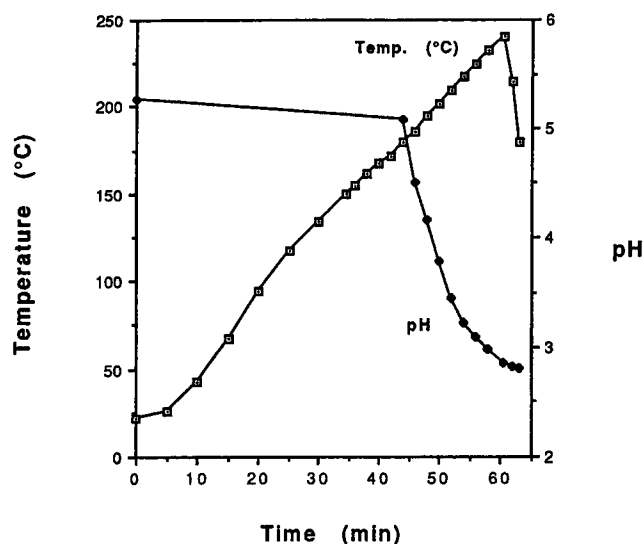


Fig. 3. pH profile for wood sawdust pretreated to 240°C without pH control.

pH to more neutral values, between 7.0 and 8.2, before the start of the pretreatment, Table 2. The target range for the pH was calculated to be between 5.0 and 7.0 and the volume of KOH added to control the pH was not to exceed 10% of the working volume. For the pretreatments to 220 and 240°C, the volume of 2.0 M KOH added was between 80 and 90 mL. A more significant volume of 2.0 M KOH, 108 mL, was needed to keep the pH between 5.0 and 7.0 for the pretreatment to 260°C.

The KOH addition profile was developed from the trend of the pH during pretreatment in the absence of pH control as well as the observation of the instantaneous change in pH caused by the addition of KOH during that particular pretreatment. The KOH addition profile for the pretreatment to 240°C with pH control is shown in Fig. 4. Prior to the pretreatment, 0.3 mL of 2.0 M KOH were added to the pretreatment vessel and changed the pH from approx 5.2 to 8.2. Typically, an addition of 0.3 mL 2.0 M KOH added prior to the pretreatment would raise the pH from 5.0 to approx 7.0 (Table 2, initial pH). As the pretreatment temperature rose to 200°C,

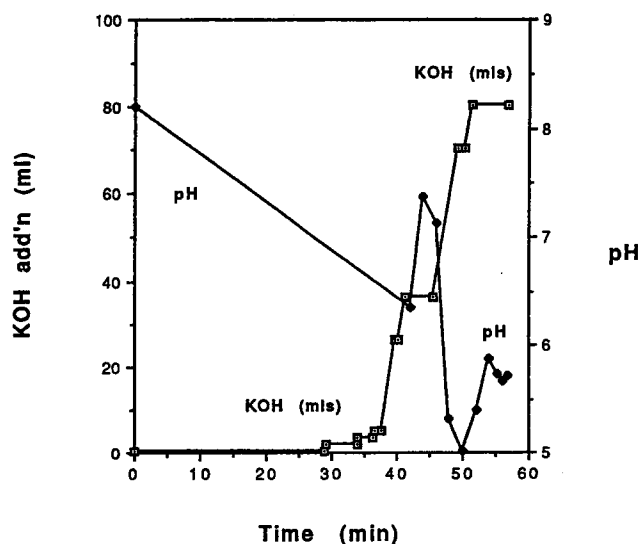


Fig. 4. pH profile for wood sawdust pretreated to 240°C with KOH added to help control the pH.

corresponding to 42 min into the pretreatment, 40 mL 2.0 M KOH were added to bring the pH from 6.5 to 7.5. As the pretreatment temperature rose from 200 to 240°C, another 40 mL 2.0 M KOH were added to keep the pH from dropping below 5.0. The pH profile and volume of KOH added over this temperature are consistent with the release of an acidic component from the sawdust, and may include significant quantities of acetic acid. Overall, the pH remained between 5.0 and 7.5 with the final pH being 5.7 during the hottest parts of the pretreatments, where temperatures ranged from between 170 and 240°C, Fig. 4.

Effects of Aqueous Pretreatment on Polysaccharides in Wood Sawdust Total Solids

The material balances for each pretreatment are shown in Table 3. From the overall material balance, the amount of solid retention was determined by comparing the amount of dry material remaining after the pretreatment to the amount of dry material initially being pretreated. The quantity of solid material remaining after pretreatment ranged from 56 to 84% with the assumption that the solid material not accounted for was solubilized during pretreatment, Table 3 and Fig. 5. The solubilization process may include the partial hydrolysis of the cellulosic and hemicellulosic polysaccharides into soluble oligosaccharides and their corresponding monosaccharides, glucose and xylose.

The addition of KOH helps to control the pH during the pretreatment of wood sawdust as well as reduce the quantity of total solids being solubilized. The range of solid solubilization for the three pretreatments with

Table 3
Material Balances for Each Pretreatment Condition

	220°C	220°C KOH	240°C	240°C KOH	260°C	260°C KOH
Material In:						
Dry	86.3	80.6	88.2	63.8	60.8	63.2
Liquid	1513.7	1519.4	1511.8	1003.2	1006.2	1003.8
KOH	0.00	88.6	0.00	80.5	0.00	107.9
Total In	1600.0	1688.6	1600.0	1147.5	1067.0	1174.9
Material Out:						
Dry	62.2	67.9	58.2	53.7	33.8	44.3
Liquid	1425.9	1559.5	1453.0	1012.8	998.7	899.5
Samples	20.1	20.4	25.1	25.3	30.2	30.5
Losses	30.1	10.2	20.1	20.2	10.1	173.1
Total Out	1538.3	1658.0	1556.4	1112.0	1072.8	1147.4
% Recovery	96.1	98.2	97.3	96.9	101.0	97.7

KOH addition was from 16 to 30%. This is less than the extent of solubilization for the pretreatments carried out in the absence of pH control where the solid solubilization was between 28 and 44%, depending on the temperature (Fig. 5). The greatest solubilization of solid material occurred at 240 and 260°C, both in the absence of pH control, where 34 and 44% of the original material was solubilized, respectively, Table 3 and Fig. 5. For the pretreatments that use KOH to control pH, both the 220 and 240°C pretreatments solubilized only 16% of the original material, whereas the 260°C pretreatment solubilized 30% of the original material, Fig. 5. For the pretreatments with and without the addition of KOH, the quantity of solid material solubilized increases as the final pretreatment temperature increases. This trend is more apparent for the pretreatments in which the

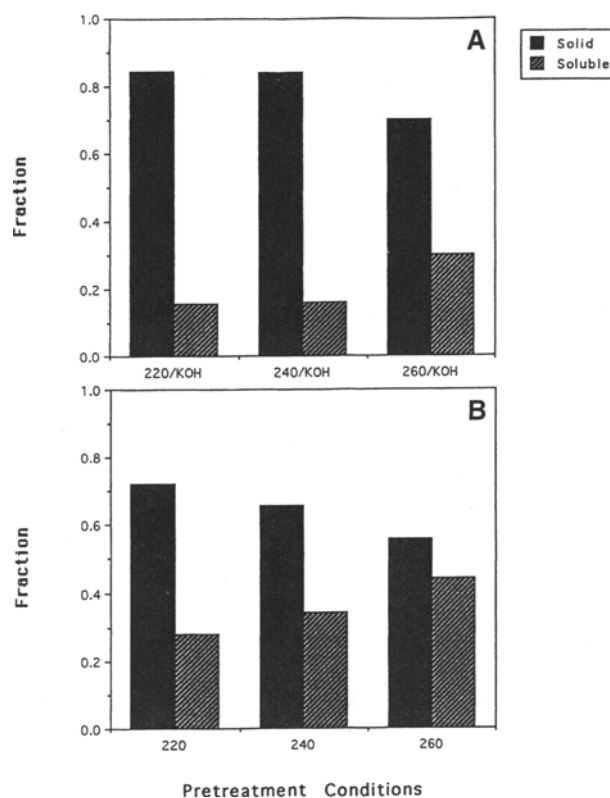


Fig. 5. Fraction of the wood sawdust remaining in the solid phase and that which has been dissolved based on pretreatment conditions; (A) with KOH added to control pH; (B) without pH control.

pH is not controlled, where the extent of solubilization increases with final pretreatment temperature, Fig. 5.

Cellulose

Significant hydrolysis of cellulose and degradation of the glucose occurs if the pH is below 3.5 and the temperature above 200°C (7–9). Released organic acids may facilitate polymeric hydrolysis and degradation of hemicellulose and cellulose fractions, whereas hydroxyl-mediated degradation of the released saccharides leads to low yields. Therefore a goal of this study was to maintain pH in a range in which the production of organic acids from degradation of monosaccharides are minimized and organic acids are in a salt form that minimizes their activity as acid catalysts and thereby keeps the carbohydrates in an oligomer form at conditions whose goal is to hydrate the cellulose fraction.

Treatment of wood sawdust using water at high temperatures and pressures and the addition of KOH for pH control may help the conversion

Table 4
Composition of Treated and Untreated Solid Wood Sawdust
(% Basis)

	220°C	220°C KOH	240°C	240°C KOH	260°C	260°C KOH	Untreated
Cell.	65.6 (± 1.2)	47.0 (± 1.3)	60.9 (± 1.2)	66.3 (± 1.7)	54.8 (± 1.8)	67.6 (± 2.0)	41.0 (± 0.3)
Xylans & Arabans	0.00	0.00	0.00	0.00	0.00	0.00	19.4 (± 0.1)
Klason Lignin*	29.4 (± 1.6)	25.3 (± 0.1)	32.8 (± 0.5)	24.0 (± 0.3)	38.1 (± 0.6)	19.7 (± 0.7)	22.7 (± 0.3)
Acid Lignin	9.0 (± 0.9)	13.9 (± 0.8)	12.7 (± 0.4)	1.9 (± 0.0)	3.2 (± 0.5)	1.7 (± 0.3)	4.3 (± 0.0)
Ash	0.2 (± 0.0)	2.9 (± 0.1)	0.2 (± 0.0)	3.8 (± 0.0)	0.3 (± 0.2)	5.3 (± 0.1)	0.5 (± 0.0)
Total	104.2	89.1	106.4	96.0	96.4	94.3	87.9

* Contains components other than Klason Lignin (possibly some protein).

of cellulose to glucose by concentrating the cellulose found in the treated solid material by removing other components. The pretreatments with KOH addition have the highest percentage of cellulose in the remaining solids. The cellulose content of the remaining solids for the pretreatment to 260°C with KOH addition was approx 68% and for the 240°C pretreatment with KOH the percentage of cellulose in the remaining solids was 66%, Table 4. Pretreatments to 240 and 260°C without KOH addition showed a lower cellulose content in the remaining solid material at 61 and 55%, respectively, Table 4. The pretreatments to 220°C were the exception in this case. The cellulose content for the remaining solids after pretreatment to 220°C with no KOH was approx 66%, whereas the cellulose content for the remaining solids pretreated to 220°C with KOH was 47%. These values compare to a cellulose content of 41% for untreated wood sawdust, Table 4.

The prevention of cellulose solubilization by controlling the pH with KOH may be one way to increase the cellulose content after pretreatment. The most notable indication that the addition of KOH helps prevent cellulose solubilization can be shown by the pretreatments to 260°C. Pretreatment to 260°C without KOH solubilized the most cellulose, approx 26%, whereas the pretreatment to 260°C with KOH addition showed all of the cellulose remained with the solids after pretreatment conditions were removed, Fig. 6.

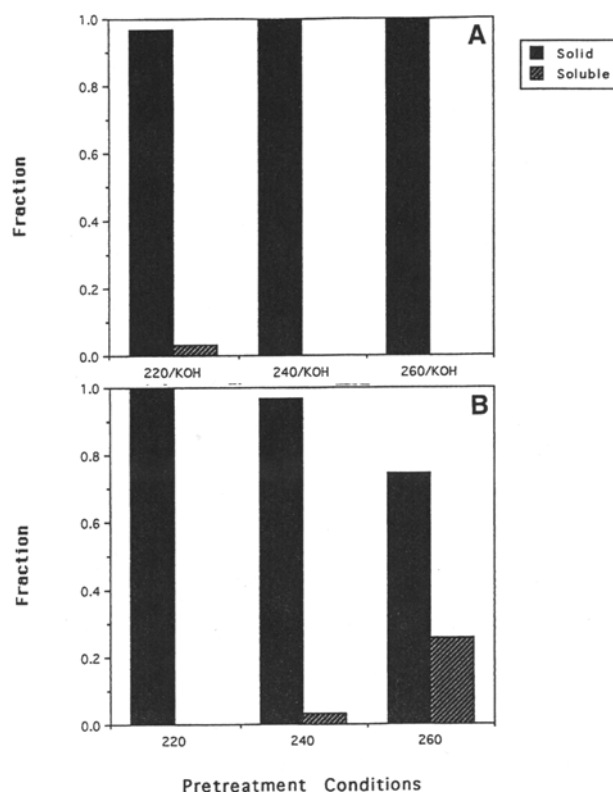


Fig. 6. Fraction of cellulose remaining in the solid and that fraction solubilized based on pretreatment conditions; (A) with KOH added to control pH; (B) without pH control.

Hemicellulose

Another polysaccharide present in the wood sawdust is hemicellulose, and is composed of xylose, a small amount of arabinose, and acetate. The xylan and araban polysaccharide composes approx 20% of the dry-wood sawdust. The hemicellulosic polymer was completely dissolved from the solid at all the pretreatment conditions. Xylans and arabans were not detected in the remaining solids from any pretreatment, Table 4. Liquid chromatography analysis indicates that the majority of the solubilized hemicellulosic material appeared as oligosaccharides. Xylose was found in quantities that corresponded to less than 10% of the total xylan balance for the 240 and 260°C pretreatments with no pH control. Furfural was only found in trace quantities, less than 0.3 g/L, in the supernatant of the 260°C pretreatment carried out in the absence of pH control. There were no detectable quantities of xylose or furfural in the supernatant for all of the pretreatments where KOH was used to control pH.

CONCLUSIONS

pH control is necessary for aqueous pretreatment of yellow poplar wood sawdust, especially at the high temperatures and pressures used for treating the sawdust. The addition of base to the pretreatment vessel prevents the accumulation of acids that will promote the hydrolysis of the cellulose to soluble oligosaccharides and glucose, and the degradation of the glucose to HMF and levulinic and formic acid. The pH monitoring system described here, when combined with a previously determined, well-characterized, pH profile enables the development of a base addition profile that will keep the pH within a specified range.

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