

AUTOHYDROLYSIS PRETREATMENT OF MIXED HARDWOODS TO EXTRACT VALUE PRIOR TO COMBUSTION

Yan Pu, Trevor Treasure, Ronalds Gonzalez, Richard Venditti,* and Hasan Jameel

Biomass pretreatment by autohydrolysis uses hot-water to extract soluble components from wood prior to converting the woody residuals into paper, wood products, or fuel, etc. Mixed hardwood chips were autohydrolyzed in hot-water at 150, 160, 170, and 180 °C, for 1 and 2 h. The tradeoff between fermentable sugar yield and caloric value of the residual solids was studied for a process that will be referred to as “value prior to combustion”. The extracted liquid was treated with dilute sulfuric acid to break down sugar oligomers into fermentable monomers. Material balances were performed around autohydrolysis to evaluate the role of temperature and residence time on sugar production and residual solid heating value. The composition (sugars and byproducts) of the extracted liquid was determined. As the autohydrolysis temperature increased, the material balance became less precise, presumably due to more volatile byproducts being formed that were not quantified. More hemicelluloses were extracted from the wood by the hot water extraction process under higher temperature and longer residence time, but a greater degree of sugar degradation was also observed. After hot-water extraction the heating value of the solid residues was higher than the original wood. The total energy content of the residual solid after extraction ranged from 74 to 95% of the original energy content of the feed.

Keywords: Hot water extraction; Sugar yield; Heating value; Bomb calorimeter; Value prior to combustion

Contact information: Department of Forest Biomaterials, College of Natural Resources, North Carolina State University, 1022F Biltmore Hall, Raleigh, NC 27695-8005. USA.

* *Corresponding author e-mail:* richard_venditti@ncsu.edu. Phone number: 919-515 6185

INTRODUCTION

Motivated by the urgency to discover alternative sources of sustainable and environmentally friendly energy, cellulosic ethanol has received increasing attention from private and public research sectors. Biofuels produce much lower greenhouse gas emissions and might potentially provide more employment in rural and industrial areas in comparison with fossil fuel products (Von Blottnitz et al. 2007; Bai et al. 2010; Cherubini et al. 2010). Conversion of biomass to ethanol and chemicals may be able to sustain our way of life, since woody biomass (lignocellulosic) can be replenished. Unlike fossil fuel energy sources whose natural replenishment is in the time scale of 200 million years (regarded as nonrenewable), biomass can be regenerated in the time scale ranging from 3 months to 80 years and is therefore considered renewable (Liu et al. 2006). Moreover, lignocellulosic biomass is the most abundant organic source on earth with approximately 170 billion metric tons annual production (Sticklen 2006; Kumar et al. 2009).

Lignocellulosic feedstocks are basically composed of three components: cellulose, hemicelluloses, and lignin (Amidon et al. 2008; Willför et al. 2008). Cellulose is a linear

homopolymer composed of D-glucose units connected by a $\beta(1,4)$ linkage. Cellulose provides structure and strength for the plant or tree. Hemicelluloses are heteropolymers composed of five- and six-carbon sugars with short branched side connections. Lignin is an amorphous heteropolymer with three-dimensional structure synthesized from three phenyl propylene alcohol units. Lignin has a carbon to oxygen atom ratio higher than 2:1 and is more energy-dense compared to cellulose (1:1) and hemicelluloses (1:1) (White 1987; Amidon et al. 2008).

In bioenergy conversion processes, biomass is the major cost driver, accounting for 35 to 50% of total production costs (Gonzalez et al. 2008, 2011b,d). Though technical/economic analyses of several bioenergy conversion processes (with special emphasis on cellulosic ethanol) have highlighted the importance of recovering all major lignocellulosic components to offset high feedstock cost (Gregg et al. 1996a,b; Gonzalez et al. 2011c), commercial byproducts of lignocellulosic ethanol processes are minimal thus far. Researchers are working to find possible uses of hemicelluloses in the manufacture of polymers (Salam et al. 2011) and identifying more profitable uses of lignin other than heat-steam-power generation (Pan et al. 2005a,b; Janssen et al. 2008, 2010; Gonzalez et al. 2011a,c). The production of marketable byproducts is of great importance for the economy of the biorefinery. The need to utilize all parts of the biomass is the basis for this study. The technology examined here could be deployed as a front end/pretreatment for many different pathways that use biomass to produce fuels, chemicals, and materials.

The hot-water extraction process, which is also known as autohydrolysis, can partially extract hemicellulose oligomers (mainly xylo-oligomers with different degrees of polymerization) from wood while leaving other components intact (White 1987; Amidon et al. 2008, 2009; Taherzadeh et al. 2008; Leschinsky et al. 2009). The extracted xylose and other hemicellulose sugars can undergo fermentation to ethanol and can be considered a potential renewable resource for bio-based fuels (Hess et al. 2007; Stoutenburg et al. 2008). Hemicellulosic sugars can also be used to produce biodegradable plastics and chemicals that are currently derived from petroleum (Amidon et al. 2008, 2009; Salam et al. 2011). The residues after hot water extraction can be burned to produce steam and electricity or alternatively can be used as a raw material for wood and paper products.

During the process of hot-water extraction, acids are produced by the hydrolysis of hemicelluloses (Amidon et al. 2009). These acids, coupled with the dissolution of extractives in the biomass, cause the liquor pH to drop and effectively self-catalyze the process. That is the reason why the hot-water extraction process is also known as auto-catalytic. Previous studies have demonstrated that hot-water extraction (160°C) of sugar maple wood chips largely removed extractives and hemicellulose, while most of the lignin and cellulose remained with the residual wood structure (Amidon et al. 2008). The residual solids are then processed for production of pulp and paper, wood products, or power.

In this study, hot-water extraction was used to pretreat mixed hardwood chips at 150, 160, 170, and 180 °C and two residence times (1 and 2 hours) to obtain an understanding of the extraction of hemicelluloses and other components under different conditions. The heating value measurements of original wood and solid residues obtained for each treatment were also determined to evaluate the amount of heat in the wood that could be recovered after the autohydrolysis treatment. The objective was to understand

the tradeoff between fermentable sugar yield and caloric value of the residual solids. This process layout will be referred to as “value prior to combustion” or VPC. The study aims to develop a clear understanding of some of the tradeoffs that occur under different temperature, time conditions, and can be used for economic modeling of the proposed process.

MATERIALS AND METHODS

Feedstock

Hardwood chips (obtained from a local North Carolina pulp and paper mill) with dimensions of 30 mm length, 20 mm width, and 3 mm thickness were used as raw material for hot-water extraction. This feedstock is composed of several hardwood species naturally growing in the Southeastern U.S. Some of the species commonly found in this mix are maple, birch, and oak (USDA 2011). Wood chips were stored in a cold room at 4 °C and air dried for two days prior to use. Moisture content of the air-dried chips was measured by oven drying at 105 °C until constant weight was achieved. The composition of the original biomass, which was determined using the Klason lignin assay, acid hydrolysis, and HPLC, was determined to be: lignin 27%, glucan 41%, hemicellulose 20%, and unidentified components 12%.

Hot-Water Extraction

Hot-water extraction was performed in a pulp digester (M/K Systems Inc., Danvers, MA). Batches of ca. 800 grams air dry wood chips were used for each trial. The oven-dry weight of these chips was calculated based on the moisture content obtained from parallel chip moisture measurements. A water to solid ratio of 4:1 was used in all trials. Pre-treatment conditions differed in temperature (150, 160, 170, and 180 °C) and residence time (1 and 2 hours). After the extraction, filtrate was released from the bottom of the digester and collected after going through a water-cooling system. No difficulty was observed for the separation of the filtrate and solid residues. The remaining solid residues after extraction were washed and then centrifuged to achieve relatively uniform moisture content. Some of the obtained wet residual chips were subjected to moisture content measurement: some were air-dried before performing heating value measurements, and others were used for composition analysis. The wash water was not analyzed for sugars and other compounds.

Potential Process Configuration

The overall process flow is illustrated in Fig. 1, where an integrated hemicellulose extraction is envisioned as being part of an ethanol biorefinery and a power plant. In this system, wood chips are fed into a digester for hot-water extraction, then the slurry is screw pressed such that two streams are generated, one stream with low solid content (filtrate) and one stream with high solid content (extracted residues). Another alternative for the screw press can be a washing system to reduce sugar carryover with residues. The extracted solid residues are sent to combustion for generation of power and process steam. The filtrate needs to be cleaned up to remove agents that might interfere with hydrolysis and fermentation (White 1987; Amidon et al. 2008, 2009). After stream clean-up, the

stream is hydrolyzed (by means of acid or enzymes) in order to convert sugar oligomers into fermentable monomeric sugars. Then fermentation and distillation processes take place for alcohol production. With respect to oligomer hydrolysis, as previously noted, it can be done by means of acid or enzymes. Acid hydrolysis will require addition of more capital investment for chemical recovery so that the process can be profitable and also avoid downstream contamination problems in fermentation; also additional cost is required in equipment for acid-resistant metallurgy. An economic analysis comparing clean-up options may assess the economic potential and risk of the different options.

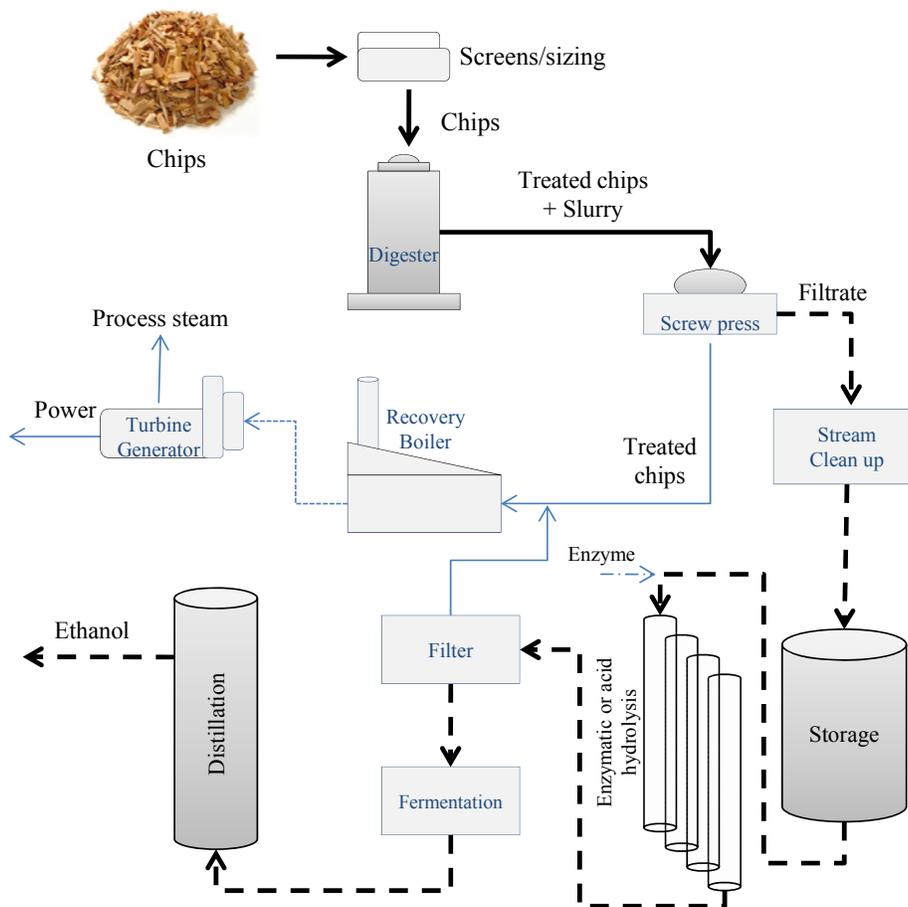


Figure 1. Autohydrolysis extraction integrated in a facility coproducing power and ethanol

Analysis of Original Wood and Extracted Wood Residues

Original wood chips and air-dried extracted wood residues were ground to pass through a 40 mesh screen and be retained on a 60 mesh screen. A certain amount of such ground wood powder (0.300 g) was subjected to acid hydrolysis by adding 1.5 mL of 72% sulfuric acid and thoroughly stirring every 15 minutes at room temperature. After 1.5 hours, the resulting sample was carefully transferred to a serum bottle by washing with 56 mL DI water. The serum bottle was sealed and autoclaved for 90 minutes at 122 °C. The autoclaved hydrolysis solution was vacuum-filtered through a previously weighed filtering crucible and collected. This sample was used to determine acid soluble

lignin as well as structural sugars (original sugars found in the biomass), as described above. Deionized water was used to quantitatively transfer all remaining solids in the serum bottle into the filtering crucible (medium porosity) after the filtrate had been collected. The crucible accompanied with acid insoluble residue was oven dried at 105 °C until a constant weight was achieved. Acid insoluble lignin (AISL), which is also known as Klason lignin, was calculated after the gravimetric analysis as described above (NREL 2005).

Analysis of Extracts

The solid content of the extract was determined gravimetrically by oven drying at 105 °C to a constant weight. Triplicate measurements were carried out for each sample. Sugar monosaccharides of the extract were determined with an ion chromatography system (Dionex ICS-3000, Sunnyvale, CA) before and after acid hydrolysis (sulfuric acid, 122°C, 1.5 hour autoclaved). The monomeric sugar content difference before and after the acid hydrolysis represents the oligo- and polysaccharide content in the sample (Andersson et al. 2007; Persson et al. 2007). The chromatograph was equipped with an auto sampler, a dual pump (model DP-1), an eluent generator (model EG-2), and a detector/chromatography module (model DC-1). Milli-Q water and 400 mN sodium hydroxide (NaOH) solution were used as the eluents at the flow rate of 1.1 mL/min. Fucose was added to each sample as an internal standard. D-fucose, D-arabinose, D-rhamnose, D-galactose, D-glucose, D-xylose, and D-mannose were used as calibration standards to make the sugar calibration curve (Pettersen 1991).

Acid-soluble lignin (ASL) in the extract was measured by UV absorption at a wavelength of 205 nm (Gatenholm 2008). A 3% sulfuric acid solution was employed as the baseline for comparison. The extracted sample was diluted with deionized water to appropriate levels (10-500x) to bring the absorbance into the range of 0.1 to 1. The quantity of ASL was calculated by the following equation:

$$ASL (g) = \frac{A \times t \times V}{b \times a \times 1000} \quad (1)$$

where A is the absorbance obtained by the UV measurement, b is the light path (cm), a is the absorptivity ($L g^{-1}cm^{-1}$), t is the times dilution relative to the original sample, and V is the total volume of sample (mL)

Furfural, hydroxymethyl furfural (HMF), formic acid, and acetic acid were determined by a Dionex HPLC system, (Dionex, Sunnyvale, CA), which consisted of an ASI-100 automated sample injector, Solvent Rack SOR-100 module, P680 HPLC pump, and UVD170U multi wavelength ultraviolet detector. Chromatographic separation was achieved using a 4.0 mm x 250 mm Acclaim® Organic Acid column (5 mm, Dionex, Sunnyvale, CA) coupled to an Acclaim Organic Acid-Guard column (5 mm, Dionex, Sunnyvale, CA). Non-linear gradient separations were carried out using 2.5 mmol L⁻¹ methanesulfonic acid and water/acetonitrile (10:90, v/v) as the Mobile phase A and Mobile phase B solvents, respectively. Concentrations of formic acid and acetic acid of samples were measured at 210 nm and HMF and furfural at 277 nm. 4-tert-butylphenoxyacetic acid (Alfa Aesar, Ward Hill, MA) was used as an internal standard

(Chen et al. 2006; Lee et al. 2010). Standard curves were made for each byproduct by using a 6-point calibration. All the standard samples were dissolved in the ACS grade methanol, and 4-tert-butylphenoxyacetic acid was used as the internal standard. Methanesulfonic acid and acetonitrile were used as the two eluents, with a flow rate of 1mL/min.

Standard Bomb Calorimeter Method for Heat Content of Samples

All samples were subjected to a standard bomb calorimeter (1341 Oxygen Bomb Calorimeter, Parr Instrument Company, Moline, IL) measurement. Samples were first ground to pass a 20 mesh screen and then compressed into pellets using a pellet press (Perkin Elmer 15.011, Britain) prior to being weighed.

Heat content was determined by burning the samples with excess of oxygen at a pressure of 30 atmospheres in a sealed steel bomb, which is regarded as a near-adiabatic system. The steel bomb was submerged in a certain amount of water, whose temperature changes during the combustion process were monitored by a thermometer. Time versus water temperature over the entire combustion process was recorded. The total temperature rise and other pertinent thermochemical corrections, which included correction for heat in formation of nitric acid, sulfuric acid, and heat of combustion of fuse wire, were determined and used in the final heating value calculations.

Before the heat of combustion measurement, four trials were carried out combusting standard benzoic acid pellets provided by Parr Instrument Company to obtain the energy equivalent of the calorimeter (ASTM 2011). The procedure was strictly performed following the procedure from the Instruction Sheet No. 204M (Operating Instruction Manual, Parr Instrument Company). All samples were first ground into powder form by Wiley Mill and then pressed into pellets, to facilitate a slow and complete combustion in the bomb.

RESULTS AND DISCUSSION

Solid Content of Extracts and Residues

The solid yield after the autohydrolysis treatment decreased from 90% to 70% as the treatment temperature increased from 150°C to 180°C and the residence time increased from 1 to 2 hours (Table 1). The effect of residence time on yield was greater at lower temperatures. At higher temperatures and longer residence times the moisture content of wet residues after centrifugation was higher. A possible explanation for this may be a more open structure of the wood chips, which absorbs and holds more water. This phenomenon may have implications for subsequent pressing or drying operations if the chips are used for fuel. The residues obtained by harsher conditions will need more pressing or drying operations in order to maximize the efficiency of the heating generation.

The dissolved solid content of the extract solution increased with increasing temperature from 150°C to 160°C and by increasing the residence time from 1 to 2 hours (Table 2). However, yet higher temperature (greater than 170°C) and longer residence times resulted in lower sugar recovery in the extract solution. This can be explained by higher temperature and longer extraction times promoting the formation of furfural and

hydroxyl-methyl furfural (HMF) when pentose and hexose sugars are degraded by the elevated temperatures (Jeoh 1998; Jeoh et al. 2001; Sun et al. 2002; Yang et al. 2007). When the solid content was measured by atmospheric oven drying, the volatile components such as furfural, HMF, methanol, and other light organics were evaporated, resulting in a lower solid content measurement.

Table 1. Autohydrolysis Solid Yield at Various Temperatures and Residence Times *

Temp (°C)	Time (hour)	Original Wood (OD g)	Solid Residue after Autohydrolysis (OD g)	Yield (%)	Moisture Content (%)
150	1	721.0±1.6	658.6	91.3	54.7±0.6
	2	721.0±1.6	625.7	86.8	55.4±0.9
160	1	713.7±1.1	557.1	78.1	58.9±0.7
	2	721.0±1.6	539.4	74.8	60.0±0.8
170	1	713.7±1.1	540.9	75.8	60.8±0.3
	2	713.7±1.1	520.5	73.0	62.4±0.9
180	1	713.7±1.1	504.6	70.8	62.0±0.9
	2	713.7±1.1	501.4	70.3	63.7±1.0

* The mean value and deviation of duplicate experiments are reported

Table 2. Solid Content in the Extract after Auto-Hydrolysis Treatment under Each Condition *

Temp (°C)	Time (hour)	Original o.d wood ^a (g)	Total extract ^b (g)	Total extract ^c (ml)	Solid content ^d (%)	Oven dried solids ^e (g)	Yield ^f (%)
150	1	721.0±1.6	2,911.4	2,850.1	1.9±0.0	53.8	7.5
	2	721.0±1.6	2,944.3	2,910.1	2.8±0.0	84.4	11.7
160	1	713.7±1.1	3,007.9	2,904.7	3.7±0.1	111.1	15.6
	2	721.0±1.6	3,030.6	2,992.8	4.7±0.0	142.1	19.7
170	1	713.7±1.1	3,027.3	2,993.9	4.0±0.0	120.2	16.8
	2	713.7±1.1	3,047.8	2,961.1	3.4±0.1	102.2	14.4
180	1	713.7±1.1	3,060.4	2,973.6	2.7±0.0	83.3	11.7
	2	713.7±1.1	3,066.9	3,006.7	2.1±0.1	63.4	8.9

^a Calculated by weight of air-dried wood chips times consistency measured gravimetrically

^b Calculated by subtracting OD solids of the residue from total raw material (wood + water)

^c Calculated from extract weight with known volume

^d Weight percentage, measured gravimetrically, calculated by (oven dried solid weight in the filtrate / weight of extract*100)

^e Total solids in the extract, calculated by (solid content (w/w%) times total grams of extract)

^f Weight percentage, calculated by (total solids in the extract / total original solid weight*100)

* The mean value and deviation of duplicate experiments are reported.

Autohydrolysis Byproducts

Other byproducts identified in the extract solution were quantified using HPLC. The amount of acetic acid, which is produced from the degradation of the acetyl groups in the hemicelluloses, increased with temperature and residence time (Table 3) (Amidon et al. 2008). Furfural and HMF exhibited the same increasing trends with increasing extraction temperature and time.

Table 3. Acetic Acid, Furfural, HMF and Formic Acid in the Filtrate Measured by HPLC (based on 100 grams of original OD wood)

Temperature (°C)	150		160		170		180	
Time (hour)	1	2	1	2	1	2	1	2
Acetic Acid (g)	1.3±0.1	1.5±0.2	1.5±0.1	3.1±0.4	2.7±0.0	4.0±0.4	5.4±0.0	6.2±0.6
Furfural (g)	0.1±0.0	0.2±0.0	0.2±0.0	0.6±0.0	0.4±0.0	1.0±0.1	1.1±0.1	1.2±0.0
HMF (g)	0.0±0.0	0.0±0.0	0.0±0.0	0.1±0.0	0.1±0.0	0.2±0.0	0.4±0.0	0.5±0.0
Formic acid (g)	2.5±0.0	1.4±0.1	1.7±0.2	1.7±0.2	1.5±0.1	1.4±0.3	1.7±0.0	1.8±0.2

Table 4 summarizes the solid recovery yield of both solid residues and extract solutions after auto-hydrolysis. As temperature increased, the total solid recovery yield was consistently decreased from nearly 99% at 150°C to about 80% at 180°C. There was a similar solid yield decrease tendency with the extension of residence time, if the temperature was above 170 °C. The increasing loss of total solids is associated with the increasing volatile components formed during the extraction (Table 3). Even when the byproducts in Table 3 are accounted for, the material balance becomes more open when the temperature is greater than 170°C. The opening of the material balance is likely due to the formation of other sugar degradation byproducts that are not being quantified.

Table 4. Summarized Solid Content in the Solid Residue and Extract after Auto-Hydrolysis Treatment under Different Conditions as Grams based on 100 Grams of OD Original Wood

Temp (°C)	150		160		170		180	
Time (hour)	1	2	1	2	1	2	1	2
Solid in residue (g)	91.3	86.8	78.1	74.8	75.8	73.0	70.8	70.3
Solid in filtrate (g)	7.5	11.7	15.6	19.7	16.8	14.4	11.7	8.9
Total (g)	98.8	98.5	93.7	94.5	92.6	87.3	82.5	79.2

Sugars in the Extract Solution

During the auto-hydrolysis process, water under high temperature and high pressure penetrates into the wood, causing partial hydrolysis of cellulose, dissolving part of the hemicelluloses, and removing a portion of lignin (Taherzadeh et al. 2008). The hemicellulose is extracted from the wood chips in the form of liquid-soluble oligosaccharides with various degrees of polymerization. The oligosaccharides can be further hydrolyzed to monosaccharides by using acid or enzymes. The monomeric sugars formed during the auto-hydrolysis can be degraded at the extraction temperatures into furfural and HMF (which are not desirable for the overall process). In the present study, monomeric sugars, formed during auto-hydrolysis and after acid hydrolysis (using 3%

H₂SO₄), were analyzed with a Dionex ICS 3000 system (Table 5). For the 170 °C and 2 hours residence time condition, the total extracted carbohydrates amounted to almost 10 grams out of 100 grams (oven dried) of starting material. Carbohydrate yields decreased as the extraction temperature increased to 180 °C. The decrease was extensive for arabinose and xylose under severe conditions that went beyond 170 °C, 2 hour, mainly due to their acidic degradation to furfural (Jeoh et al. 2001; Yang et al. 2007; Amidon et al. 2008, 2009).

Arabinose was mostly extracted in the monomeric form under all the conditions, while rhamnose was in the form of monomer only under higher temperatures (170 °C and 180 °C). A major portion of xylose was extracted in the polymeric form except for the 180 °C extraction. Xylose in the auto-hydrolysis filtrate was at a maximum level of 4.1g at 180 °C, 1 hour. This was the highest yield of mono-sugar in the filtrate compared to all other sugars. Glucomannan was detected mostly in the polymeric form even under higher temperatures and longer residence times. This is revealed by the fact that after the acid treatment, monomeric glucose and mannose amount increased even for the trials at severe conditions. Most of the glucose formed in the extract was derived from glucomannan, while an unknown amount may have originated from the hydrolysis of cellulose.

Table 5. Sugar Composition in the Autohydrolysis Extracts under Each Condition Before (Mono) and After Acid-hydrolysis (Total) by 3% H₂SO₄ as Grams of Mono-sugar Recovered from 100 grams of OD Original Wood

Temp		150 °C		160 °C		170 °C		180 °C	
Time (hour)		1	2	1	2	1	2	1	2
Arabinose (g)	Mono ^a	0.27	0.34	0.55	0.37	0.33	0.32	0.27	0.13
	Total ^b	0.37	0.40	0.54	0.40	0.29	0.26	0.15	0.04
Rhamnose (g)	Mono ^a	0.04	0.05	0.14	0.17	0.13	0.24	0.22	0.12
	Total ^b	0.11	0.16	0.28	0.28	0.20	0.24	0.16	0.10
Galactose (g)	Mono ^a	0.07	0.11	0.21	0.30	0.30	0.49	0.55	0.41
	Total ^b	0.34	0.51	0.61	0.58	0.69	0.63	0.46	0.34
Glucose (g)	Mono ^a	0.03	0.04	0.05	0.07	0.02	0.20	0.34	0.43
	Total ^b	0.15	0.19	0.25	0.24	0.33	0.42	0.44	0.54
Xylose (g)	Mono ^a	0.11	0.24	1.10	2.10	2.61	3.84	4.10	2.40
	Total ^b	1.90	3.76	7.56	7.84	7.26	7.45	5.29	2.54
Mannose (g)	Mono ^a			0.05	0.09	0.10	0.33	0.52	0.46
	Total ^b	0.24	0.31	0.57	0.63	0.59	0.83	0.76	0.60
Sum (g)	Mono ^a	0.52	0.78	2.10	3.09	3.49	5.42	6.00	3.93
	Total ^b	3.10	5.34	9.81	9.96	9.35	9.82	7.27	4.15
Yield (%)	Extract ^c	41.48	45.67	62.95	50.57	55.51	68.62	62.22	46.66
	Lost ^d	35.78	40.43	44.66	40.53	38.64	36.26	24.77	13.92

^a The amount of monosaccharides formed in the extracts during auto-hydrolysis

^b The total amount of monosaccharides in the extracts after acid-hydrolysis by 3% H₂SO₄

^c Sugar yield per solid in the extract, calculated by (total sugar / total solid yield in the extract *100)

^d Sugar yield out of solid loss of original OD wood material, calculated by (total sugar / (100 – solid recovery yield of solid residue after hot-water extraction)*100)

After 1 hour pretreatment at 180 °C, 6.0 g of mono-sugars per 100 g of feed were contained in the autohydrolysis filtrate. All the filtrate was subjected to acid hydrolysis at 3% H₂SO₄, and after that a total of 9.9 g sugar was recovered from the extracted solution (170 °C for 2 hours), which accounted for 68.6% of the total solid recovered from the extracted solution and 36.3% relative to the total solid lost during the extraction. Hot-water extraction at 160 °C for 1 hour had the highest sugar recovery yield relative to the total solid lost: in total 9.8 g sugar was recovered, which is 62.9% of the total solid in the extract and 44.7% of the solid lost.

Table 6. Sugar Composition of the Raw Material and of the Auto-hydrolysis Residue from Each Condition as Grams Recovered from 100 Grams of OD Original Wood

Temp		150°C		160°C		170°C		180°C	
Time (hour)	Raw	1 hour	2 hour						
Arabinose (g)	0.8	-	-	-	-	-	-	-	-
Rhamnose (g)	0.5	-	-	-	-	-	-	-	-
Galactose (g)	1	0.5	0.4	-	-	-	-	-	-
Glucose (g)	41.2	43.8	42.6	38.4	43.1	42	42.3	39.3	40.1
Xylose (g)	16.2	12.7	11	7.4	5.1	5.1	3.7	3.1	2.4
Mannose (g)	1.6	1.2	1.2	1.1	0.6	0.8	0.5	0.3	0.2
Sum (g)	61.2	58.3	55.2	46.9	48.8	47.8	46.6	42.7	42.6
% of sugar ^a		63.8	63.6	60	53.5	63	63.9	60.3	60.7

^a Percentage of total sugar out of solid recovery yield of solid residue after auto-hydrolysis

The high yield of xylose in the extract was in agreement with the analysis of sugar content in the solid residues after extraction. The amount of xylose in the solid residues decreased from almost 13 g at 150 °C for 1 hour to only 2.4 g at 180 °C for 2 hours, which means that more xylose was removed under higher temperatures and longer retention time.

A majority of the arabinose, rhamnose, and galactose were removed under higher reaction temperature and longer reaction time, while there was a significant amount of glucose found in the residues, suggesting very little cellulose degradation (Song et al. 2008).

Heat Content of Residues

The heating values of all the residues from different auto-hydrolysis treatment conditions as well as from the original wood sample were determined by a standard bomb calorimeter method. The heating value determined was the “high heating value” (HHV), which includes the latent heat given up when newly formed water vapor condenses and cools to the temperature of the bomb (Thipse et al. 2002). Table 7 shows all the heating value results obtained in duplicate for each sample.

Table 7. High Heating Value of the Original Wood and of the Residues under Each Condition

		Heat of combustion (calories/gram)		
		Exp. 1	Exp. 2	Mean
From Reference		n/a	n/a	4,630 ^a
Original wood		4,391	4,363	4,377
150°C	1 hour	4,566	4,549	4,557
	2 hour	4,627	4,629	4,628
160°C	1 hour	4,400	4,420	4,410
	2 hour	4,500	4,503	4,502
170°C	1 hour	4,480	4,508	4,494
	2 hour	4,533	4,534	4,534
180°C	1 hour	4,628	4,626	4,627
	2 hour	4,656	4,576	4,616

^a Data obtained from a reference (Thipse et al. 2002).

The heating value of the original wood sample was about 4,376 calories per gram (oven dry), which was the lowest value compared with all other extracted samples. As the extraction temperature increased, the corresponding heating values of the residues steadily increased. This is a reasonable tendency, since the higher the temperature the more extensive the hemicellulose and cellulose extraction. As a result, the residues after the hot-water extraction had a higher concentration of lignin (Table 8), which has a higher heating value than the carbohydrates in woody material (White 1987; Demirba 2001, 2002). However, this did not mean that a higher extraction temperature will always achieve a higher total energy content, since higher temperatures resulted in a dramatic weight loss of the solid residues (Table 4). Figure 2 shows the percentage of total energy remaining in the solid residues, compared with the original starting material. At 150 °C and 1 hour treatment the energy content of the solid residues was 95% of the original wood. As the extraction temperature increased to 160 °C, 75% of the total energy was retained in the residue.

Table 8. Lignin Content in the Residues (Based on oven dry residues)

Temp (°C)	Residence time (hours)	Lignin ^a (%)
150	1	26.8
	2	27.0
160	1	27.8
	2	27.9
170	1	28.9
	2	29.7
180	1	34.4
	2	34.5

^a Including both acid soluble lignin and acid insoluble lignin

When considering the use of the solid residues for energy content in a combustion process and the use of the extracted carbohydrates as feedstock for ethanol production, a careful analysis of the overall net benefit of the system versus extraction temperature and time needs to be carried out. A subsequent paper on the relative economics of the proposed “value prior to combustion” process will use these results as modeling inputs.

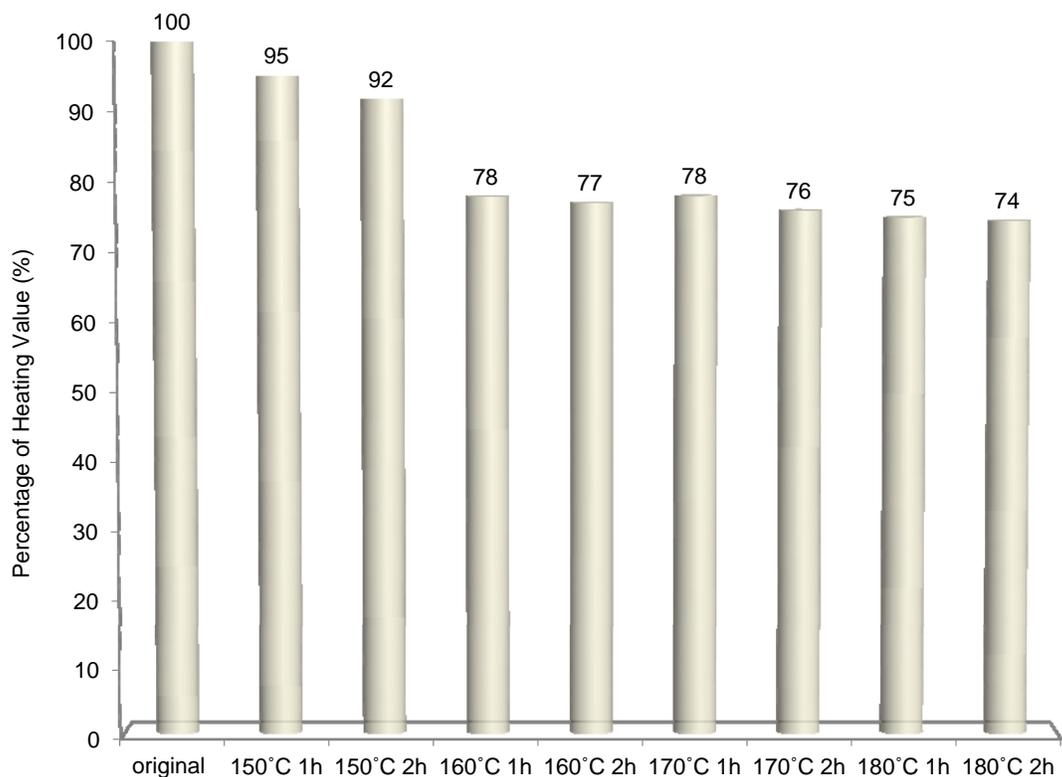


Figure 2. Percentage of total energy left in the solid residue

CONCLUSIONS

The hot-water extraction of mixed hardwood was carried out from 150 °C to 180 °C, with 1 and 2 hours residence time. By examining the solid content in both the extraction liquid and solid residues, a significant weight loss was found for the higher temperature and longer reaction time treatment, which correlated to a greater amount of volatile byproducts formed during the extraction process. Acetic acid, furfural, and HMF formed during the hot-water extraction were found to steadily increase with increasing extraction temperature and reaction time. There were four “optimal” conditions found for sugar extraction, in terms of different criteria: 180 °C, 1 hour had the highest mono-sugars (6.00 grams) in the filtrate without acid hydrolysis treatment; 160 °C, 2 hours had the highest sugar monomers after breaking down all the oligo-sugars to mono-sugars (9.96 grams); 170 °C, 2 hours resulted in the highest yield of sugar per unit of solid in the extract (68.6%); and 160 °C, 1 hour ended up with the highest sugar yield per unit of solid that supposed to be dissolved in the filtrate (44.7%). Xylose had the highest yield out of all extracted sugars. Xylose was primarily extracted in a polymeric form. The

composition analysis of the solid residues verified that most of the hemicelluloses were effectively extracted into the liquid, while the cellulose remained in the residue. As the extraction temperature increased, more material was dissolved, leaving higher proportions of lignin in the residues and thus higher heating values of the residues. The total energy that could be recovered in the residue after the hot-water extraction was approximately 75% after extraction of the hemicelluloses.

REFERENCES CITED

- Amidon, T., and Liu, S. (2009). "Water-based woody biorefinery," *Biotechnology advances* 27(5), 542-550.
- Amidon, T., Wood, C., Shupe, A., Wang, Y., Graves, M., and Liu, S. (2008). "Biorefinery: Conversion of woody biomass to chemicals, energy and materials," *Journal of Biobased Materials and Bioenergy* 2(2), 100-120.
- Andersson, A., Persson, T., Zacchi, G., Stålbrand, H., and Jönsson, A. (2007). "Comparison of diafiltration and size-exclusion chromatography to recover hemicelluloses from process water from thermomechanical pulping of spruce," *Applied Biochemistry and Biotechnology* 136(140), 971-983.
- ASTM (2011). "Standard test method for gross calorific value of coal and coke by the adiabatic bomb calorimeter," Retrieved 06/17, 2011, from <http://www.astm.org/Standards/D2015.htm>.
- Bai, Y., Luo, L., and van der Voet, E. (2010). "Life cycle assessment of switchgrass-derived ethanol as transport fuel," *The International Journal of Life Cycle Assessment* 15(5), 468-477.
- Chen, S. F., Mowery, R. A., Castleberry, V. A., Walsum, G., and Chambliss, C. K. (2006). "High-performance liquid chromatography method for simultaneous determination of aliphatic acid, aromatic acid and neutral degradation products in biomass pretreatment hydrolysates," *Journal of Chromatography A* 1104(1-2), 54-61.
- Cherubini, F., and Jungmeier, G. (2010). "LCA of a biorefinery concept producing bioethanol, bioenergy, and chemicals from switchgrass," *The International Journal of Life Cycle Assessment* 15(1), 53-66.
- Demirba, A. (2001). "Relationships between lignin contents and heating values of biomass," *Energy conversion and management* 42(2), 183-188.
- Demirba, A. (2002). "Relationships between heating value and lignin, moisture, ash and extractive contents of biomass fuels," *Energy, Exploration & Exploitation* 20(1), 105-111.
- Gatenholm, P. (2008). "Fractionation and characterization of xylan rich extracts from birch," *Holzforschung* 62, 31-37.
- Gonzalez, R., Jameel, H., Chang, H., Treasure, T., Pirraglia, A., and Saloni, D. (2011a). "Thermo-mechanical Pulping as a Pretreatment for Agricultural Biomass for Biochemical Conversion," *BioResources* 6(2), 1599-1614.
- Gonzalez, R., Phillips, R., Saloni, D., Jameel, H., Abt, R., Pirraglia, A., and Wright, J. (2011b). "Biomass to energy in the Southern United States: Supply chain and delivered cost," *BioResources*. 6(3), 2954-2976.
- Gonzalez, R., Saloni, D., Dasmohapatra, S., and Cubbage, F. (2008). "South America: industrial roundwood supply potential," *BioResources* 3(1), 255-269.

- Gonzalez, R., Treasure, T., Phillips, R., Jameel, H., and Saloni, D. (2011c). "Economics of cellulosic ethanol production: Green liquor pretreatment for softwood and hardwood, greenfield and repurpose scenarios," *BioResources* 6(3), 2551-2567.
- Gonzalez, R., Treasure, T., Phillips, R., Jameel, H., Saloni, D., Abt, R., and Wright, J. (2011d). "Converting Eucalyptus biomass into ethanol: Financial and sensitivity analysis in a co-current dilute acid process. Part II," *Biomass and Bioenergy* 35(2), 767-772.
- Gregg, D., and Saddler, J. (1996a). "Factors affecting cellulose hydrolysis and the potential of enzyme recycle to enhance the efficiency of an integrated wood to ethanol process," *Biotechnology and Bioengineering* 51(4), 375-383.
- Gregg, D., and Saddler, J. (1996b). "A techno-economic assessment of the pretreatment and fractionation steps of a biomass-to-ethanol process," *Applied biochemistry and Biotechnology* 57(1), 711-727.
- Hess, J., Wright, C., and Kenney, K. (2007). "Cellulosic biomass feedstocks and logistics for ethanol production," *Biofuels, Bioproducts and Biorefining* 1(3), 181-190.
- Janssen, M., Chambost, V., and Stuart, P. (2008). "Successful partnerships for the forest biorefinery," *Industrial Biotechnology* 4(4), 352-362.
- Janssen, M., and Stuart, P. (2010). "Sustainable product portfolio and process design of the forest biorefinery," Proceedings of the Canadian Engineering Education Association.
- Jeoh, T. (1998). "Steam explosion pretreatment of cotton gin waste for fuel ethanol production," Master Thesis. Virginia Polytechnic Institute and State University.
- Jeoh, T., and Agblevor, F. (2001). "Characterization and fermentation of steam exploded cotton gin waste," *Biomass and Bioenergy* 21(2), 109-120.
- Kumar, S., Singh, S. P., Mishra, I. M., and Adhikari, D. K. (2009). "Recent advances in production of bioethanol from lignocellulosic biomass," *Chemical Engineering & Technology* 32(4), 517-526.
- Lee, J., Venditti, R., Jameel, H., and Kenealy, W. (2010). "Detoxification of woody hydrolyzates with activated carbon for bioconversion to ethanol by the thermophilic anaerobic bacterium *Thermoanaerobacterium saccharolyticum*," *Biomass and Bioenergy* 35(1), 626-636.
- Leschinsky, M., Sixta, H., and Patt, R. (2009). "Detailed mass balances of the autohydrolysis of Eucalyptus globulus at 170 C," *BioResources* 4(2), 687-703.
- Liu, S., Amidon, T., Francis, R., Ramarao, B., Lai, Y., and Scott, G. (2006). "From forest biomass to chemicals and energy... Biorefinery initiative in New York State," *Industrial Biotechnology* 2(2), 113-120.
- NREL (2005). "Biomass analysis technology team laboratory analytical procedure." US Department of Energy, National Renewable Energy Laboratory.
- Pan, X., Arato, C., Gilkes, N., Gregg, D., Mabee, W., Pye, K., Xiao, Z., Zhang, X., and Saddler, J. (2005a). "Biorefining of softwoods using ethanol organosolv pulping: Preliminary evaluation of process streams for manufacture of fuel-grade ethanol and co-products," *Biotechnology and Bioengineering* 90(4), 473-481.
- Pan, X., Xie, D., Gilkes, N., Gregg, D., and Saddler, J. (2005b). "Strategies to enhance the enzymatic hydrolysis of pretreated softwood with high residual lignin content," *Applied Biochemistry and Biotechnology* 124(1), 1069-1079.

- Persson, T., Nordin, A., Zacchi, G., and Jönsson, A. (2007). "Economic evaluation of isolation of hemicelluloses from process streams from thermomechanical pulping of spruce," *Applied Biochemistry and Biotechnology* 136(140), 741-752.
- Pettersen, R. (1991). "Wood sugar analysis by anion chromatography," *Journal of Wood Chemistry and Technology* 11(4), 495-501.
- Salam, A., Venditti, R., Pawlak, J., and El-Tahlawy, K. (2011). "Crosslinked hemicellulose citrate-chitosan aerogel foams," *Carbohydrate Polymers* 84(4), 1221-1229.
- Song, T., Pranovich, A., Summerskiy, I., and Holmbom, B. (2008). "Extraction of galactoglucomannan from spruce wood with pressurised hot water," *Holzforschung* 62(6), 659-666.
- Sticklen, M. (2006). "Plant genetic engineering to improve biomass characteristics for biofuels," *Current Opinion in Biotechnology* 17(3), 315-319.
- Stoutenburg, R., Perrotta, J., Amidon, T., and Nakas, J. (2008). "Ethanol production from a membrane purified hemicellulosic hydrolysate derived from sugar maple by *Pichia stipitis* NRRL Y-7124," *BioResources* 3(4), 1349-1358.
- Sun, Y., and Cheng, J. (2002). "Hydrolysis of lignocellulosic materials for ethanol production: A review," *Bioresource Technology* 83(1), 1-11.
- Taherzadeh, M., and Karimi, K. (2008). "Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: A review," *International Journal of Molecular Sciences* 9(9), 1621-1651.
- Thipse, S., Sheng, C., Booty, M., Magee, R., and Bozzelli, J. (2002). "Chemical makeup and physical characterization of a synthetic fuel and methods of heat content evaluation for studies on MSW incineration," *Fuel* 81(2), 211-217.
- USDA (2011). "Forest Inventory and Analysis National Program," Retrieved 06/14, 2011, from <http://fia.fs.fed.us/>.
- Von Blottnitz, H., and Curran, M. A. (2007). "A review of assessments conducted on bio-ethanol as a transportation fuel from a net energy, greenhouse gas, and environmental life cycle perspective," *Journal of Cleaner Production* 15(7), 607-619.
- White, R. (1987). "Effect of lignin content and extractives on the higher heating value of wood," *Wood and Fiber Science* 19(4), 446-452.
- Willför, S., Sundberg, K., Tenkanen, M., and Holmbom, B. (2008). "Spruce-derived mannans-A potential raw material for hydrocolloids and novel advanced natural materials," *Carbohydrate Polymers* 72(2), 197-210.
- Yang, H., Yan, R., Chen, H., Lee, D. H., and Zheng, C. (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel* 86(12-13), 1781-1788.

Article submitted: August 17, 2011; Peer review completed: September 29, 2011;
Revised version received and accepted: October 6, 2011; Published: October 10, 2011.