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Hot Water Extraction: Short Rotation Willow, Mixed Hardwoods, and Process Considerations

Christopher D. Wood [1,*], Thomas E. Amidon [1], Timothy A. Volk [2] and Rachel M. Emerson [3]

[1] Applied Biorefinery Sciences, Syracuse, New York, NY 13212, USA; teamidon@absciences.com
[2] Department of Sustainable Resources Management, SUNY College of Environmental Science and Forestry, Syracuse, New York, NY 13210, USA; tavolk@esf.edu
[3] Chemical and Radiation Measurement Department, Idaho National Laboratory, Idaho Falls, ID 83415, USA; rachel.emerson@inl.gov
* Correspondence: cdwood@absciences.com; Tel.: +1-315-559-9431

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Abstract: Short rotation woody crops (SRWC) like shrub willow are highly productive biomass resources of interest for energy and fuel applications. Hot water extraction (HWE) as an upgrading tool to enable the use of willow biomass in pellet applications has been proposed, and is of increasing interest. This study treats willow and mixes of willow and conventional mixed hardwood feedstock with HWE in a tumbling laboratory reactor to elucidate the effects of time, temperature, feedstock mixes, and other process considerations (water:biomass ratio, presteaming, counter-current processing) on mass removals and other extraction outcomes (e.g., sugar, acetate, and furan yields). Results demonstrated alignment of extraction outcomes with P-factor from 155 °C to 175 °C, with a good compromise of removed mass and co-product potential in the range from 575–800 P-factor. The preferred condition was chosen as 575 P-factor. HWE of mixes of willow and hardwood feedstocks showed a linear response of extraction outcomes to willow:hardwood ratios. Testing of water:biomass ratios demonstrated that this is a significant consideration, with each outcome being affected somewhat differently, and indicating that HWE is more diffusion dependent than expected. Presteaming shows little to no effect on extraction outcomes, while multi-stage cooks simulating counter-current operation indicate a significant potential value in counter-current extraction.

Keywords: biorefining; biomass; short rotation woody crops; willow biomass; hot water extraction

1. Introduction

The interest in replacing non-renewable chemicals and fuels with renewably sourced products has continued to grow over the past decade. United States Department of Energy (DOE) has indicated that 1.2–1.5 billion tons (dry basis) of biomass could be available in the United States by 2040 to support the production of fuels, chemicals, and other products [1]. This study suggests that 411–736 Million Mg of this is expected to come from energy crops such as switchgrass, miscanthus, southern pine, hybrid poplar, and willow. Willow, or more specifically willow biomass crops (WBC), is of particular interest to the northeastern United States, being well adapted to the climate and soils, and managed using coppicing with short rotation times of 2–4 years. These biomass crops are highly productive, generating 4–16 Mg/ha/year of dry biomass [2]. This high productivity led the New York State Energy Research and Development Authority (NYSERDA) to state that 20% of a proposed 14.6 Million Mg/year biomass resource in New York State (NY) could be provided by WBC, with the remainder derived from hardwood and softwood forest resources and agricultural residues [3]. This indicates that WBC is likely to be a significant component of the northeastern US biomass resource in the future.

One fast growing area of renewable energy in the United States is the manufacture of fuel pellets for both residential heating and export, with exports primarily replacing coal in utility scale power generation. Fuel pellet production was 37 Million Mg/year worldwide in 2018 [4], and grew at 9–14%/year in the past decade [5], moving from a niche market to a large scale worldwide commodity. In the United States, the largest increases in capacity have been in the Southeast, where the focus has been on the export market [6]. This has left the northeastern US pellet industry primarily focused on local and regional markets, despite several efforts to engage with export markets [5,7], which have yet to succeed [6]. As demand continues to rise, new capacity in the northeast is likely to become attractive, with WBC being a component of the necessary biomass resource to enable large export plants to be built. Biomass willow is, however, challenged in the pellet market by its higher ash content, which is above the specification threshold conventionally acceptable in fuel pellets [8].

To address this challenge, Hot Water Extraction (HWE) has been proposed as a tool for upgrading biomass for a range of wood products. This upgrading can include reducing ash content in fuel pellets [8,9], making pellets water-resistant, making reconstituted wood products more water-resistant [10,11], and reducing energy consumption in pellet manufacturing [12], while simultaneously recovering a range of potential co-products [13]. HWE involves treating biomass in liquid water at elevated temperatures (140 °C–180 °C) for an extended period (usually 30–180 min), which solubilizes 15–30% of woody biomass [9,14], and up to 40% of some non-woody biomass [15]. The bulk of the extracted components are monomeric and polymeric hemicellulose-derived sugars, organic acids, and lignin. These are derived primarily from xylan, which makes up the bulk of hemicelluloses in hardwoods [16]. Extracted lignin appears to be in the form of lignin-carbohydrate complexes [17]. Furans and methanol are also generated, and a large portion of the ash (~60%) is removed [9].

As these reactions rely entirely on the inherent chemistry of the biomass, and consist heavily of hydrolysis reactions, they are also commonly referred to as autohydrolysis. These types of reactions have previously been elucidated by the study of water and steam prehydrolysis for the production of dissolving pulp [18]. These studies have demonstrated that the HWE reactions are primarily controlled by the rapid hydrolysis of xylan. A method for normalizing time (t, hours) and temperature (T, in Kelvin) for prehydrolysis has been developed that combines these terms into a single value, referred to as P-factor [19]. This method uses Arrhenius-type kinetics, and defines the reaction rate at 100 °C as having a value of 1. This technique has been used by others to describe HWE of biomass other than WBC [20] and is calculated as:

$$P = \int_{t_0}^{t} e^{(40.48 - \frac{15106}{T})} dt \quad (1)$$

The economic drivers for using HWE are the value derived from upgrading biomass, as noted above, and the value of the potential co-products. Maximizing the value derived from these product streams, along with minimizing energy and material inputs, is key to providing a strong business case for commercial applications of HWE. Value derived from the extracted components comes in the form of fermentable sugars (e.g., for ethanol), lignin (e.g., as a chemical feedstock [21]), acetic acid, formic acid, methanol (as commodity chemicals), and furfural (as a specialty chemical). Other extract components, such as hydroxymethylfurfural (HMF), occur in the extracts at very low concentrations, and thus may not be recovered unless high values per kg justify such recovery [13]. Minimizing energy inputs requires considerable re-use of the thermal energy required to heat water and wood to HWE reaction temperatures. To this end, it is expected that more energy efficient continuous extraction equipment will be used in industrial applications.

As the reaction conditions for HWE are similar to conventional kraft pulping, it is reasonable to assume the equipment for conducting HWE will be similar to that used for pulping. Several continuous pulping reactors, or digesters, have been developed over the past century, with the most common design being the Kamyr [22]. However, there are system design and process chemistry considerations that may be different between kraft pulping and HWE, and thus should be considered in the laboratory,

to the extent that they can be simulated. One such consideration is that all common continuous digesters utilize a presteaming stage to remove air from chips, aid in the impregnation of chemicals into the chips, and pre-heat the chips. A presteaming at 15 psig for 1 to 5 min is common. As presteaming could conceptually change the chemistry of the cook (e.g., through steam extraction of low-boiling compounds), it may be an important factor to consider in industrial applications.

Similarly, continuous processing opens an opportunity for counter-current reactions, where water and wood are fed in opposite directions through the extraction reactor. This should encourage the diffusion of extracted components out of the biomass, reducing either the carryover of potential products with the extracted biomass or the need for separate washing stages. This research team suspects that HWE is more diffusion-limited than the literature would indicate [23], and that by changing the effective chemical profile in the extractor, more high-value extractable components may be recovered. This change in chemical profile would be equivalent to the alkali profiling techniques that have become common in kraft pulping in recent years [24]. Some researchers have stated that dilution (through increasing water-to-wood ratio) has no effect [23]. However, work by Mittal [14] showed that reducing the particle size (from a chip to 30 mesh wood meal), resulting in an increased surface area, made a significant (e.g., 30% relative increase in mass removal) difference in how much, and what, was extracted, suggesting diffusion has a significant effect on HWE. Our research team has noted what appears to be the effects of water-to-biomass ratios in previous unpublished experiments. This indicates that both water-to-biomass ratio and potentially the chemical concentration/time profile during the reaction may significantly impact extraction performance, as these would drive a potentially large variation in diffusion pressures.

The goal of this work was to study the various aforementioned process conditions and considerations for HWE of WBC and mixed WBC/conventional hardwood feedstocks. This study maps various extraction outcomes (e.g., mass removal, sugar yield) to P-factor to determine if the relationships identified for other types of biomass also hold true for WBC feedstocks. This is used to identify preferred conditions for the extraction of WBC, to be used in the rest of the work. As mentioned above, there is an expectation that WBC is likely to be co-processed with conventional hardwood feedstocks. This too is tested to identify potential advantages and pitfalls of mixed WBC/conventional hardwood feedstocks. A study of the effect of changing the water-to-wood ratio is also included, to clarify what effects this specific variable has on its own. A test of an aggressive presteaming is also included to identify any considerations this might require in industrial practice. Finally, as there are no laboratory or small pilot scale test systems available for continuous counter-current reactions on biomass, laboratory simulations are necessary to study this concept. To simulate the reduced concentrations of extraction products late in an extraction when using counter-current processing, cooks are broken into two and three stages, intended to give 2-step and 3-step approximations of counter-current extraction.

2. Materials and Methods

2.1. Raw Biomass

Willow biomass crop (WBC) feedstock was harvested and chipped as a whole-stem, bark-on material sourced from willow biomass crops at the State University of New York College of Environmental Science and Forestry (SUNY ESF) research station in Tully, NY, which included a mixture of cultivars. Harvesting was accomplished using a New Holland FR-9080 forage harvester equipped with a New Holland 130FB coppice header. The length of the cut selected by the operator was the largest setting ("33-mm"). Mixed northern hardwood chips (MHW) were also provided by SUNY ESF. Bark-on logs of maple, cherry, and ash from SUNY ESF's forest properties were chipped with a Morbark M-18-R drum-style chipper into a dump trailer. Samples were hand mixed as chips were transferred from the trailer to drums for storage. Both WBC and MHW chips were air dried and stored in sealed drums at an ambient temperature for the duration of the project. Moisture contents

were determined by oven drying samples of approximately 50 g at 105 °C (±2 °C) to constant mass (<1% relative change in measured moisture content). Moisture contents were run in at least triplicate with separate grab samples of ~50 g from the storage drum taken for each replicate. Moisture contents were taken from these drums five times for willow and three times for mixed hardwoods at different times during the project, with the most closely preceding moisture content being used to calculate oven dry weights of biomass for each extraction. Moisture contents ranged from 10.8% to 13.3% for willow and 7.6% to 9.0% for the mixed hardwood sample. No fractional screening of chips was done once the biomass was received; thus the biomass was used as-is, with fines and overs. Some gross oversized material that was physically too large to fit in the extraction reactors was removed; however, both willow and mixed hardwood feedstocks contained very few identifiable gross overs.

2.2. Hot Water Extraction Reaction System

Hot water extractions were conducted in a laboratory extraction reactor system built by Applied Biorefinery Sciences (ABS). This system consists of two mirror image 6.6 L (5.2 L working volume) 304 L stainless steel vessels (Feldmeier, Syracuse, NY, USA), arranged in frames to allow rotation perpendicular to their long axis on trunnions, as shown in Figure 1. Each vessel is heated by a 3 inch (~76 mm) wide 1800 W band heater (Nordic Sensors Inc., Mooers, NY, USA), roughly centered on the vessel. Rotation was provided by a combination motor/gear reducer and a variable frequency drive. Rotation was controlled to approximately 6 RPM, and was always in the direction toward the operator (top rotating forward and down) to facilitate discharge of solids. Temperature is measured by a 3-wire PT100 RTD (Nordic Sensors Inc., Mooers, NY, USA) in a $\frac{1}{4}$" (~6.4 mm) stainless steel sheath inserted from the bottom of the vessel, and centered in the vessel. Power for the heating elements and signal from the RTD are passed through slip-ring assemblies from the rotating vessel assembly to the stationary frame. Internal screens constructed of 304SS 200 mesh screen over thin plate with 1.6 mm perforations are provided, to prevent the biomass from entering the various vessel nozzles. Each vessel is equipped with a liquid-filled pressure gauge and spring-loaded pressure safety valve (Stra-Val, Elmwood Park, NJ, USA).

The paired vessels are controlled by a common process logic controller (PLC) (SNAP-PAC-R2, Opto 22, Temecula, CA, USA). Programming of this system provides a reasonable ramp to temperature (50 min to 160 °C), with minimal overshoot (<1 °C). P-factor is calculated by the PLC, as per equation 1, with a 2 s time step, allowing control of the extraction to a specific P-factor rather than to a specific time, if desired. No significant buildup of residue was seen on the walls of the vessels, suggesting that little or no extract or chip degradation occurred at the heater band, and thus that very limited heat concentration was seen, and that the mixing was effective. A heat exchanger for cooling liquid removed from the vessels was included, consisting of ~2m of $\frac{1}{4}$ inch (~6.4 mm) OD 304SS tubing bent into a coil, and enclosed in a flowing water bath. This cooler was connected to the vessels via a flexible stainless steel hose with quick connect fittings. A small gear pump was similarly connected to the top of the vessel by flex hose and quick connects, and was used to inject wash water and the later water additions in multi-stage extractions. Wash water was ejected from the vessels by compressed air.

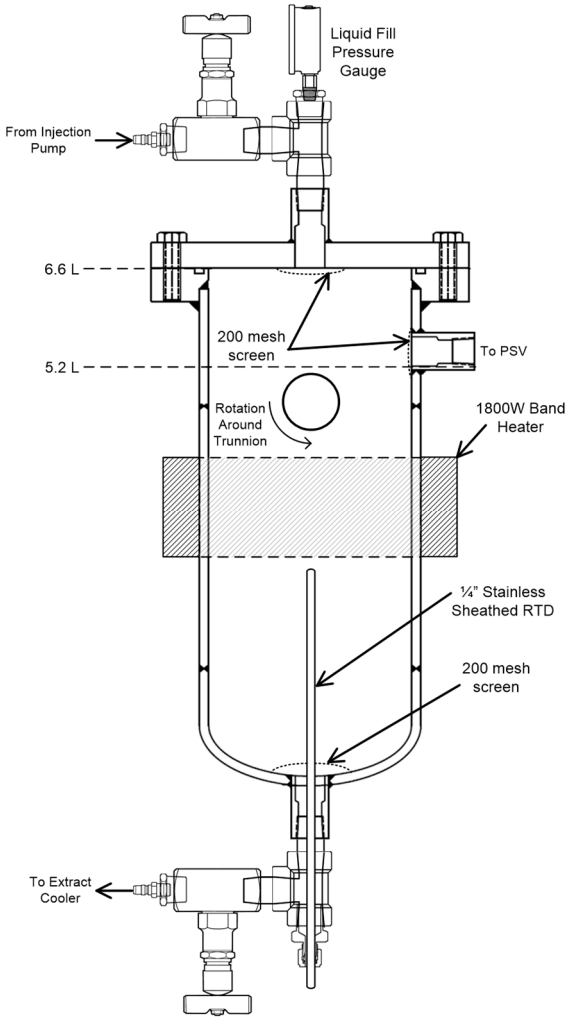


Figure 1. Laboratory extraction system for hot water extraction of biomass.

2.3. Hot Water Extractions

For each willow extraction approximately 850 g (dry basis) of WBC chips were weighed out, corrected to an as-received basis using the most recent moisture content. Water-to-wood ratio studies required varying chip masses, ranging from 440 g to 1050 g to match the total volume to reactor volume. Mixed hardwood reactions were conducted on approximately 1050 g (dry basis) due to the higher chip density. Chips were loaded into the vessels followed by water (reverse osmosis deionized water), which was weighed into the vessel. The water-to-wood ratio was calculated as:

Water:wood ratio = (added water mass + water in chips mass)/oven dried chip mass

The vessel was then sealed up and rotation started. The temperature was increased at the maximum rate provided by the heaters to the set point temperature and held to the desired time or P-factor. At the completion of each extraction, the vessel rotation was stopped, heaters turned off, and the cooling heat exchanger connected to the bottom quick connect of the extraction vessel. Extract vapor pressure was used to drive the extract through the heat exchanger into a tared vessel. A small volume of the total extract recovered from each extraction, coming off at the end of the liquid discharge, was clear (rather than the light brown of the bulk of the extract), and appeared to be the result of condensation of vapors generated by evaporative cooling of the chips and water remaining in the vessel. This volume was captured and included in the overall extract.

At the completion of the main portion of each extraction, two washes were conducted in series. Fresh water (reverse osmosis deionized water) was introduced into the vessel, with the volume

added for each wash being approximately equivalent to the volume of extract removed. Wash water was pumped into the vessel with a small gear pump to avoid the need to remove the tops of the vessels. Once wash water was loaded, rotation and heating were restarted. Each wash was run at approximately 80 °C (the first wash was commonly hotter than this due to residual heat in the vessel), for 20 min. Wash water was ejected from the vessel at the end of the wash by pressurizing the vessel with compressed air. Wash solutions were captured and weighed. This process was repeated for the second wash.

To study how the intensity in both time and temperature of the extraction impacted the extraction outcomes, extractions were run at conditions ranging from 155 °C to 175 °C, with P-factors ranging from 237 (155 °C, 60 min) to 1935 (175 °C, 120 min), as shown in Table 1. Generally, two cooks were run for each condition, usually as a pair (one in each of the two available vessels). As the 160 °C/120 min/575 P-Factor cook was chosen as the preferred condition for comparative work (based on data developed in this study), four cooks were conducted at this condition and used as part of the dataset. For studying severity, all cooks were conducted on WBC chips at 4:1 water:wood. The study of extraction of mixes of WBC/MHW was conducted at the 160 °C/575 P-factor condition, with a 4:1 water:wood ratio. Mixes of 0%/100%, 25%/75%, 50%/50%, 75%/25%, and 100%/0% WBC/MHW were extracted in duplicate.

Table 1. Times, temperatures, and P-factors for various hot water extractions run for comparison of P-Factor. Note times are the time at temperature in minutes. P-Factor is the average experimental value of the P-factor for the cooks in question.

155 °C		**160 °C**		**165 °C**		**175 °C**	
Time (min)	**P-Factor**	**Time (min)**	**P-Factor**	**Time (min)**	**P-Factor**	**Time (min)**	**P-Factor**
60	237	120	575	30	296	30	590
120	400	165	800	60	442	60	1010
210	686			120	943	90	1500
270	868			180	1370	120	1935

To study the effects of water-to-biomass ratio, extractions were conducted at water-to-biomass ratios of 3:1, 4:1, 7:1, and 10:1, with WBC chips at 575 P-factor (160 °C, 120 min). A ratio of 3:1 was the lowest that could be achieved in the laboratory extraction system while maintaining consistent coverage of the heating elements. Chip mass in the vessel was reduced to allow for the higher water-to-wood ratios. Three other trials were also conducted that resulted in different water-to-wood ratios. First, a pair of extractions was run to study the effect of presteaming chips to remove air. Chips were loaded into one of the two available digesters, while the other was loaded with water. Steam (30 psig building steam) was bubbled through the water filled vessel, to clean and de-superheat it, before being passed into the bottom of the chip filled vessel. Steam and non-condensables were purged from the vessel containing chips for 15 min (totaling ~750 mL of condensate), while the vessel pressure was maintained at approximately 15 psi. The extractions were then continued normally. It was determined through careful tracking of water additions and removals that this resulted in water-to-wood ratios of 4.5 and 5 to 1, with differing values being the result of differing amounts of condensate in each vessel.

As a stepped simulation of continuous counter-current, paired extractions were run in two stages at 160 °C, with a total P-factor of 575. This was done by stopping the extraction at 285 P-factor, discharging the extract from the vessel, and adding water back to 4:1 water-to-wood (adding water totaling the same mass as the extract removed). The extraction was then reheated to 160 °C, and the extraction continued to the 575 P-factor. Similarly, a pair of extractions was run at 160 °C to a P-factor of 575 in three stages, with stops at the 192 and 384 P-factor. Each extract was analyzed separately from these cooks, and the amounts of the components of interest totaled for comparison to the other cooks.

2.4. Extraction Product Analysis

After the removal of the extract liquid and washes, the extracted biomass from each experiment was rinsed out of the vessel and into a drying tray. This rinse water was captured in the drying tray. The entire chip mass from each cook was oven-dried at 105 °C (±2 °C) to constant mass. Wash water from each cook was filtered through pre-dried and pre-weighed Whatman #1 (qualitative, 11μm) filter paper to remove the fines and chip reside that passed around the internal screens. The filters and solids were oven-dried and weighed, with the resulting mass added to the mass of the oven dry chips for calculating total mass removal. An aliquot of filtrate was captured from each wash. The pH of this filtrate was measured with a Horiba (Kyoto Japan) Model F-72 pH meter, calibrated each day with pH 4, 7, and 10 buffers.

Extract from each cook was kept in a 4 L beaker with a magnetic stir bar for agitation. These were covered to avoid changes in concentration due to evaporation between removal from the extractor and the various measurements taken. Each of the measurements taken of the extract was made in duplicate for each extraction (e.g., two solids contents for conditions run in duplicate resulting in four measurements per condition). To determine extract solids content, 20 mL aliquots of extract from each extraction were pipetted into pre-dried, pre-weighed aluminum drying pans. These were weighed wet, then oven-dried to an effectively constant mass (small changes continued to occur even at 6–10 days drying, with the endpoint when there was a change of <1% in reading).

Sets of four 15 mL aliquots from each extraction were centrifuged at 3000 Gs for 20 min. Approximately 0.3 mL was taken from each centrifuged volume, combined, and filtered through 4 mm diameter, 0.2 μm pore size hydrophilic polypropylene syringe filters (Thermo Scientific) into HPLC vials. These filtered samples were used for HPLC analysis. For post-centrifugation solids content, 20 mL aliquots of centrifuged extract (10 mL from each of two of the 15 mL portions centrifuged) were pipetted into pre-dried, pre-weighed aluminum drying pans. These were also weighed wet, then oven-dried to an effectively constant mass (small changes continued to occur even at 6–10 days drying, the endpoint was generally a change of <1% in reading). To determine filterable solids content of the extracts, 50 mL aliquots of extract from each extraction were filtered through pre-dried, pre-weighed, Whatman #40 (Quantitative, 8μm) filter paper. Filters and solids were then washed with 50 mL of DI water to remove soluble material, before being oven-dried to a constant weight. To determine total titrable acid concentration, 20 mL aliquots of extract were titrated to pH 7.0 with sodium hydroxide solution (~0.075 N, made with 98.8% sodium hydroxide from BeanTown Chemical) with a pH meter as indicator. The pH of these extracts was also measured.

HPLC analysis was conducted, based on Ehrman [25], using a Waters 2695 combination controller, pump, vacuum degasser, and column heater and a Waters 2414 Refractive Index Detector with data collection via Waters Empower II software. A Waters IC-Pak ion exclusion column (7.8 mm × 300 mm) was used for separation at 55 °C. Eluent was 0.01 N sulfuric acid solution (in HPLC grade water), and eluent flow was 0.6 mL/min, giving a 1 hr run time for each sample. The detector was maintained at 50 °C. Method linearity was confirmed several times throughout this study with linear ranges as per Table 2. Linear correlations had R^2 values of at least 99.9% across the linear range for each analyte, with the exception of methanol which had R^2 measurements as low as 98%. Standards were run at the beginning of each set of samples, as well as after every 5th sample. The standards injected between samples were diluted to the middle of the linear range, as per Table 2, to be close to expected extract concentrations. Standards were kept frozen to avoid degradation between runs of samples. Averages of standards run before and after a given sample were used to calculate concentrations. Previous experience with this method [26] indicates that carbohydrates have similar detector responses using this technique, and that furfural and HMF have similar detector responses. Concentrations of polymers (compounds that eluted before cellobiose) were therefore estimated using the cellobiose calibration. Similarly, HMF concentrations were estimated using the furfural calibration. Methanol concentrations appeared to have suffered more noise than other compounds, likely due to small and inconsistent amounts of methanol carryover from pump seal wash solutions. It should be

noted that xylose and mannose are known to co-elute using this method, and thus xylose concentrations likely include some mannose.

Table 2. Range of linearity for various compounds for which standards were run. The upper linearity limit is the highest concentration tested, while the lower limit is the lowest concentration tested. The upper limit is also the stock solution prepared and used for references. The normal reference standard value is an example of the concentrations used for a reference standard between samples. Purity is the purity listed on the CoA for each standard compound. Source is the producer of the standard compound used.

	Cellobiose	Glucose	Xylose	Arabinose	Formic Acid	Acetic Acid	Methanol	Ethanol	Furfural
Upper Linearity Limit (g/L)	8.3	12.0	11.4	12.0	7.2	7.1	2.8	4.7	5.1
Lower Linearity Limit (g/L)	0.04	0.06	0.06	0.06	0.04	0.04	0.01	0.02	0.03
Normal Reference Std. (g/L)	2.8	4.0	3.8	4.0	2.4	2.4	0.9	1.6	1.7
Purity	99.9%	99.5%	98.9%	99.0%	99.6	100.0%	99.99%	95.01%	99.4%
Source	Acros	Baker	Alfa	Alfa	EMD	Baker	Pharmco-Aaper		Alfa

Samples from the P-factor trials used for HPLC were taken from extract stored at room temperature in sealed sample bottles (sealed hot to avoid biological growth). These were centrifuged before being filtered into sample vials. Samples for water-to-wood ratio, MHW/WBC mixes, presteaming, and multi-stage cooks were taken from the extract immediately after each cook, with samples frozen in their sample vials until being run on the HPLC.

To allow for the most consistent comparison, all concentrations were normalized to a g/100 g dry wood basis, effectively giving a yield of each component in the extract. This dampens out small differences in water-to-wood ratio for P-factor and WBC/MHW extraction data. It also removes the purely dilutionary effects of increased water:wood ratio. This correction was conducted by multiplying the concentration of each component by the total quantity of water in the vessel at the beginning of the extraction, including experimentally added water and moisture present in the wood chips. This effectively assumes that all fluid (both within and outside the wood) in the vessel have effectively identical concentrations, that the specific gravity is 1.0, and that the extracted material did not significantly increase the volume of liquid. The first two assumptions are likely to be reasonably accurate (no significant difference from a specific gravity of one was found) and the third is reasonable within limits (error of less than 5% of reading). No better basis for comparison was identified.

3. Results and Discussion

3.1. Study of Time/Temperature Effects

To develop an understanding of how WBC responds to hot water extraction, and enable comparison to other biomass types, extractions were conducted at a range of times and temperatures given in Table 1. Higher temperatures (155 °C, 165 °C, 175 °C) were used compared to some other work [9], as WBC has, in our experience, shown a less strong response to extraction. One of the clearest indicators of the extraction effect is the mass removal or yield. Plotted as mass removal versus time for each temperature, a set of parallel curvilinear trends are exhibited (Figure 2a).These trends are quite similar in shape to those seen in the literature for other biomass types (e.g., sugar maple [16]), but show a noticeably lower mass removal than seen for maple in previous studies (20.6% mass removal versus 22.3% for maple at 160 °C/120 min), or for mixed hardwoods in this study (22.4%, Table 4). It should be noted that lower mass removal for WBC compared to other hardwoods is most likely related to the lower average hemicellulose content (contributed to primarily by xylan), as indicated in Table 3.

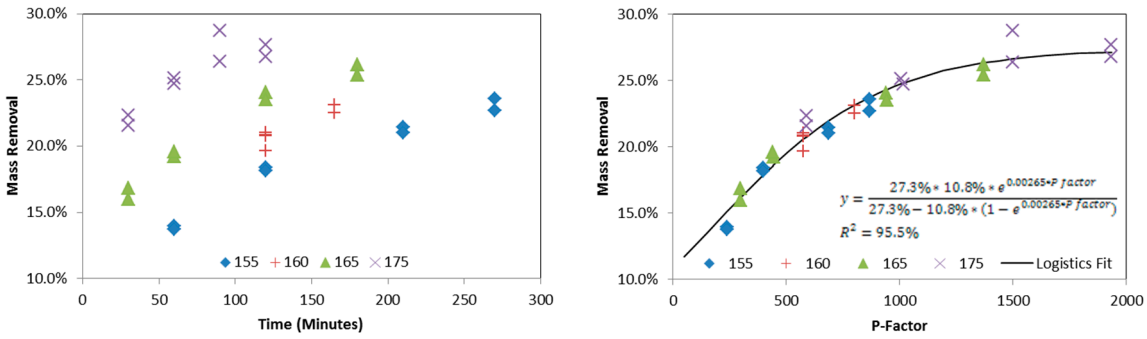


Figure 2. (**a**) (left). Mass removal against time at temperature for willow biomass crops (WBC). (**b**) (right). Mass removal against P-factor for WBC. Symbols in both plots represent differing extraction temperatures (°C).

Table 3. Composition of willow feedstock (WBC) as per [27], averaging 5 samples from Tully, NY, and estimated composition of mixed hardwood feedstock (MHW) as per [28], assuming $^1/_3$ each of *Prunus serotina*, *Acer saccharum*, and *Fraxinus americana*. All values are presented as percent of moisture free wood. The total value for willow is the average mass closure, not the sum of the values, as this would result in double counting (e.g., proteins would likely be included in extractives). The values here for MHW are from debarked wood, so some small difference would be expected for bark-on material such as that used in this study. Note uronic acids were not measured for the willow sample. Glucan is primarily from cellulose, with a small amount of glucomannan derived glucose.

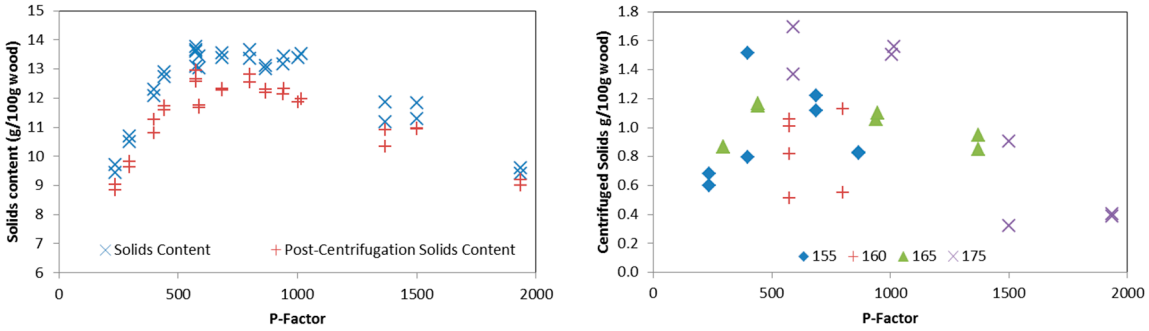
Wood	Glucan	Lignin	Xylan	Arabinan	Galactan	Mannan	Uronic Acids	Acetyl	Extractives	Protein	Ash	Total
WBC	39.6	25.9	14.0	0.6	1.6	1.9	n/a	3.9	9.5	0.9	1.2	98.3
WBC (S.E.)	0.9	0.4	0.9	0.1	0.1	0.1		0.1	0.9	0.1	0.2	
MHW	39.8	26.2	17.1	0.5	1.4	1.8	3.0	3.2	6.2	0.2	0.2	99.6

The mass removal data generated for WBC shows more cook to cook variability than was expected. This is likely due to the higher variability seen in the WBC, as compared to clean, debarked, and screened maple chips. As found with prior work and through analyzing data from Mittal [14], the time/temperature data consolidates cleanly into a single curve with P-factor allowing for comparison across all conditions simultaneously (Figure 2b), and thus all further data will be normalized to P-factor rather than to time and temperature. As HWE is generally accepted to be autocatalytic, a logistic regression (Equation (2)), as suggested by Chaffee [9] and Cramer [29], and is appropriate for mass removal, as well as methanol, acetic acid, and formic acid yields. These three compounds are believed to be stable under HWE conditions, and thus only formation reactions need to be considered. Loss reactions, such as those that effect furfural, would make the logistics fit inappropriate. This model has fitting parameters of X_{inf} and X_0 with units of the dependent variable (e.g., g/100 g wood for acetic acid), and r with units of inverse hours (inverse P-factor). The logistic fit for mass removal is shown in Figure 2b and does appear appropriate with an R^2 of 95.5%. Additionally, residual plots (not shown) support this fit as appropriate.

$$y = \frac{X_{inf} * X_0 * e^{r * P-factor}}{X_{inf} - X_0 * \left(1 - e^{r * P-factor}\right)} \quad (2)$$

The solid content of the extract is shown in Figure 3. Some components (acetic and formic acids, furfural, methanol) are not accounted for in this measurement as they evaporate during drying. Acid salts (e.g., sodium formate), however, do remain in the extract. Figure 3a exhibits increasing

solids content to around 575 to 800 P-factor. This indicates an increase in extracted sugar and lignin in solution. At higher P-factors, the solids content begins to fall. This suggests the rate of losses to components not recovered here outpaces the rate of extraction. The losses have historically been assumed to be to low molecular weight components, particularly furans and related low molecular weight degradation products that are likely to evaporate (e.g., methylglyoxal, glycolaldehyde, etc. as per Antal [30]). At very high P-factors, it was noted that some material coalesced and dropped out of solution as the extract cooled. While it was not possible to quantify this completely, on the cook conducted at 1500 P-factor, 1.2 g/100 g wood of this material was recovered. This indicates that losses to non-soluble precipitation—which is assumed to be due to polymerization of furans and lignin—were significant, as this is over half the total losses of solids content when comparing the 1500 P-factor and 575 P-factor data points.

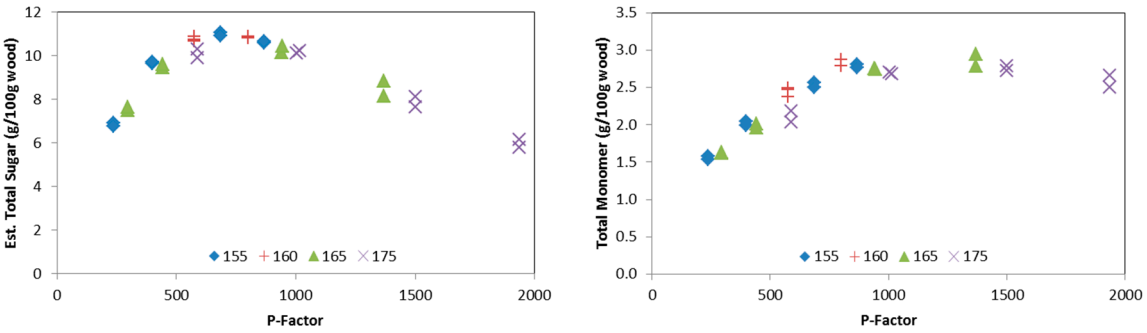


(**a**) (**b**)

Figure 3. (**a**) (Left). Extract solids content and post-centrifugation solids content against P-factor for WBC. Note the difference is that the extract in B has been centrifuged at 3000 Gs for 20 min, removing lignin and lignin-carbohydrate complexes. (**b**) (Right). Solids removed by centrifugation from WBC extract (difference between plots in A), against P-factor, with each temperature outlined individually.

Similar overall trends were present for the post-centrifugation solids concentration (Figure 3a). This is believed to represent the solids content with most high molecular weight lignin and lignin-carbohydrate complexes removed. The post-centrifugation measurement should leave mostly sugars, ash, and organic acid salts, along with some soluble low molecular weight lignin. The difference (shown in Figure 3b) provides an idea of the colloidal, and/or partially soluble lignin and lignin-carbohydrate complexes. The data in Figure 3b shows significant apparent scatter. Some of this is due to the amplifying effects of the different scale, while some is likely due to the compounding of the scatter in the data for the solids content and post-centrifugation solids content. A very rough but similar trend to the solids contents can be seen regardless of this noise. The amount of centrifugable solids rises to the 500–1000 P-factor range, before falling at higher P-factors. As this material is believed to be lignin related, polymerization and loss of stability in solution is a more likely loss pathway than degradation to volatiles. This may indicate that these centrifugable components are a large source of the material noted above that dropped out of solution before solids content could be measured, and was thus not captured in the solids content.

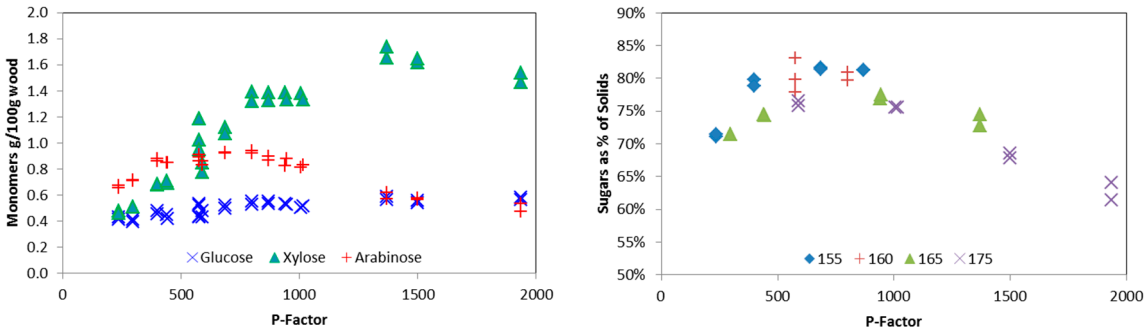
The bulk of the solids in solution (61–83%, see Figure 5b) are in the form of sugars, which were measured using HPLC. As shown in Figure 4a, the total sugar yield (including monomers and estimated polymer content) rises to a peak between 575–800 P-factor and then decreases, likely as the loss reaction rate increases compared to the rate of sugar release. The rate of sugar release would be expected to drop as the potentially available sugars from the hemicellulose fraction become depleted. Monomer yield peaks closer to 1000 P-factor, as shown in Figure 4b. Monomeric sugar yield does not drop significantly at higher P-factors, suggesting hydrolysis of polymers to monomers and losses to furans potentially balance out to the highest P-factor used in this study (1935).



(**a**) (**b**)

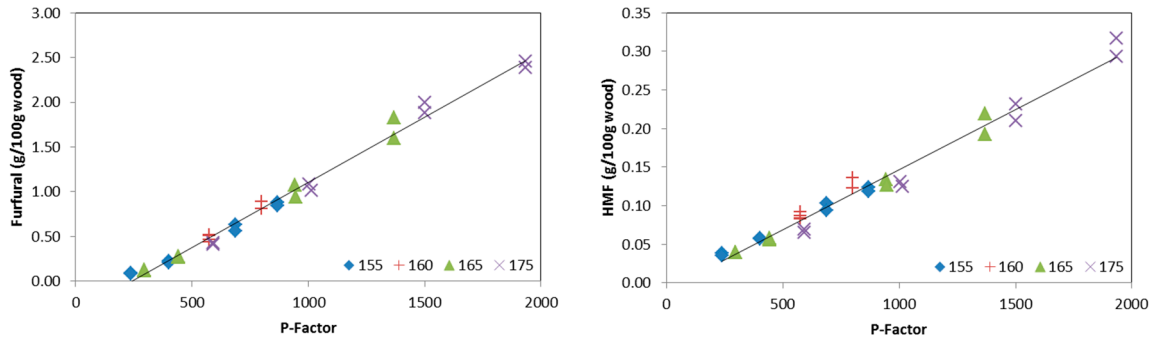
Figure 4. (**a**) (Left). Total sugar content in WBC extract based on HPLC analysis against P-factor. (**b**) (Right). Total identified monomer (xylose, glucose, and arabinose) content from WBC extract against P-Factor.

Breaking the total monomer plot from Figure 4b into individual sugars provides some further information, as shown in Figure 5a. It is clear that xylose rapidly becomes the dominant monomer, as would be expected, as the WBC hemicelluloses are composed primarily of xylan (Table 3). Arabinose yields initially rise quickly compared to xylose then drop off, suggesting the arabinose in the willow is more readily hydrolysable from the hemicelluloses than the xylan, and that the reservoir of hydrolysable arabinose units in the polymers is rapidly depleted. The glucose yields start close to their peak (about 0.4 g/100 wood) and plateau at 0.55 g/100 g wood beginning at around the 600 P-factor. HMF generation (shown in Figure 6b) suggests that there is some degradation of glucose and mannose. The relatively small amount of glucose (even including that converted to HMF) indicates that cellulose degradation is minimal with glucose likely being derived from glucomannan, as seen by Mittal [14] in work on maple. It is also instructive to compare the total sugar (Figure 4a) and solids contents (Figure 3a) data trends. This comparison, displayed as total sugar as a percentage of total solids, is shown in Figure 5b. The resulting plot shows that, despite similar curve shapes, there is a significant swing in what portion of the solids in solution is sugars. As sugars are a preferred product, Figure 5b indicates a preferred P-factor range of 575–900, with some indication that lower temperatures (155 °C and 160 °C) may provide a small but significant advantage.



(**a**) (**b**)

Figure 5. (**a**) (Left). Individual identified monomers in WBC extract against P-factor. Note the xylose value likely includes a small amount of mannose. (**b**) (Right). Percentage of the solids in solution of WBC extract accounted for by sugars (total sugar divided by solids content).



(**a**) (**b**)

Figure 6. (**a**) (Left). Furfural yield in WBC extract against P-factor. (**b**) (right). Hydroxymethylfurfural yield in WBC extract against P-factor. Both plots call out the temperatures of the extractions that each data point represents in degrees Celsius. R^2 for the furfural linear correlation shown is 98.9%, and for HMF is 97.6%.

In HWE, furan generation is a factor needing consideration, as past work has shown a positive correlation of furan generation with HWE severity [14], and furan production affects process value. Though they have considerable commercial value, furans are not an ideal product to generate during HWE, as the conditions prevalent in HWE are likely to result in selectivity under 50% (high losses) [31]. As shown in Figure 6, both furfural and HMF generation show a positive and linear response to P-Factor (R^2 of 98.9% for furfural, and 97.6% for HMF). As furfural is likely to be fairly stable once formed under these conditions [32], the furfural yield likely represents primarily formation, with losses after formation being less than 20%, even at 1900 P-Factor. The HMF generation represents more of a balance of loss and generation reactions. The linearity in HMF yield is surprising, considering that it comes from hexose sugars (with relatively flat concentrations, as per Figure 5a) and that it degrades much more rapidly than furfural.

Three other compounds of note are generated during HWE: acetic acid, formic acid, and methanol. Organic acids were measured both by HPLC (formic and acetic acids, specifically) and by direct titration (all free acids totaled). As shown in Figure 7, both formic and acetic acid yields rise before plateauing, with a logistic (autocatalytic) model explaining the patterns effectively (R^2 of 98.2% for acetic acid and 92.5% for formic acid). Acetic acid is known to come from acetate groups on the hemicelluloses, and is thus a limited reservoir of acetate is available for release, with the logistics fit suggesting a value of 3.8 g/100 g wood being the total reservoir. This would be on the high side of average for a range of hardwoods (3.6 g/100 g, [18]), but is reasonable and compares well with the slightly higher acetate content for WBC, as shown in Table 3.

Formic acid yields show a similar trend to acetic acid (Figure 7b), though unlike acetic acid, its source is not well understood. Some is certainly the result of the losses associated with degradation of hexoses to HMF and subsequent degradation of HMF [33]. Other sources are currently unknown. The shape of the formic acid plot and reasonable fit with a logistics model suggests that some reservoir or source of formic acid exists that is being depleted, which does not clearly fit with the source of this material being hexose sugars and related degradation. Some un-identified secondary source of formic acid seems likely. An illuminating point becomes apparent when comparing the total of the acetic and formic acids with apparent quantity of acid indicated by titration (converted to mol/100 g wood, Figure 7c). There appears to be a consistent gap between the titrated and HPLC acid concentrations, which is in fact the case, as shown in the "difference" series in Figure 7c. This difference averages 0.017 mol/100 g wood, and has a coefficient of variation of only 9%. As the HPLC method would convert any acid salts (e.g., potassium acetate) to free acid (potassium sulfate and acetic acid), it seems that this difference is likely due to soluble acetate and formate salts of ash removed from the wood (e.g., sodium, potassium, calcium, magnesium, etc.). This constant quantity of organic acid salts suggests that effectively all ash removal (a known effect of HWE, though not one measured here) occurs before 230 P-factor. Finally, methanol is a known product of HWE, and is generally assumed to be lignin or glucuronic acid derived. Methanol generation in HWE

also appears to fit a logistic model, as shown in Figure 7d. The plateau at higher P-factors, along with the logistic fit, seems to indicate a reservoir of methanol source material that is depleted by the extraction, with a maximum available quantity of 0.83 g/100 g wood.

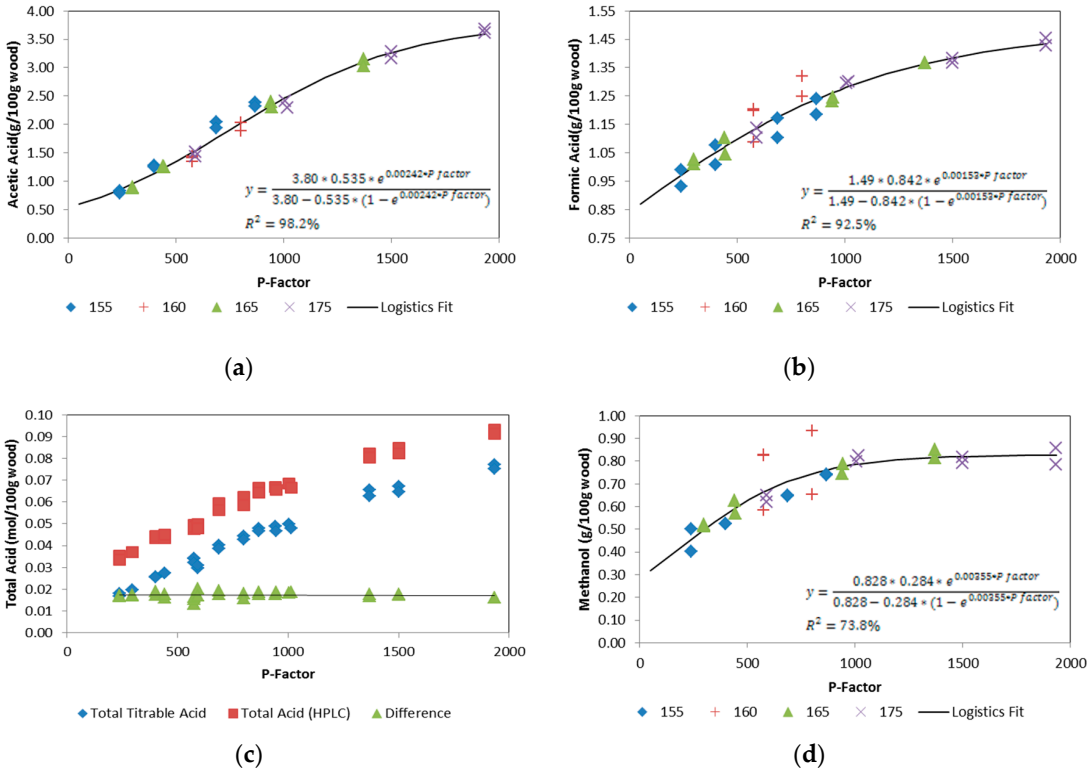


Figure 7. (**a**) (Upper left). Acetic acid concentration in willow biomass extract against P-factor, along with the logistic model. (**b**) (Upper right). Formic acid concentration in willow biomass extract against P-factor, along with the logistic model. (**c**) (Lower left). Acid concentrations (by HPLC and titration) in willow biomass extract against P-factor. The difference values indicate acid that appears in the HPLC but not in the titration data. This is believed to indicate acid salts (e.g., potassium acetate). (**d**) (Lower right). Methanol concentration in willow biomass extract against P-factor with logistics model.

As the primary purpose of HWE is to extract valuable products and upgrade and reduce the variability of the quality of the biomass, the preferred conditions for HWE are those that recover the most value across the processed biomass and the recoverable products. Sugars, lignin, acetic acid, formic acid, furfural, and methanol are all intended products of HWE biorefining. To maximize sugar recovery, a P-factor in the 575–800 range appears to be preferred. At the 575 P-factor, 85% of the potential methanol, 77% of the potential formic acid, and 37% of the available acetic acid are already in the solution. The maximum quantity of sugar (or very close to it) and overall solids are in solution, and losses of sugars to furans and other compounds is low. Further mass removal beyond 575 P-factor likely does not result in increased sugar yield and will overall reduce the mass available in the biomass stream for other products, suggesting the lower end of the 575–800 P-factor range is preferable. Reduced P-factor also has the advantage of reducing extractor vessel size or lowering reaction temperature, either of which has value in industrial practice. The 575 P-factor condition appears to be a reasonable maxima for overall value, and aligns with the 160 °C/120 min at temperature condition used as a preferred condition in other work [9]. It should also be noted that, though the acetic acid recovery is low at this condition, work by Mittal [14] suggests that a considerable portion of the available acetate may in fact be in bound form still attached to polymeric hemicellulose sugars in solution. The 575 P-Factor (160 °C, 120 min) condition is used for the experiments in Sections 3.2 and 3.3 as being representative of likely industrial conditions.

3.2. Short Rotation Willow and Mixed Hardwood Combined Extraction

As it is generally expected that biorefineries and other biomass consuming facilities would use a mix of WBC and conventional wood chips from forestry operations, the effect of mixing these raw materials is potentially quite important. To study this, extractions were conducted on three mixes of WBC and mixed hardwoods, as well as pure samples of WBC and pure MHW. The 575 P-Factor (160 °C, 120 min) condition was used, as noted above. These extractions were compared to determine if there were unexpected advantages or disadvantages as a result of the mixed feedstock. It is instructive to begin with a comparison of the pure WBC and pure MHW samples, as shown in Table 4. Most values, including mass removal, solids content, and sugar yield, were noticeably lower for WBC than for MHW, as would be expected from the estimated compositions given in Table 3. Organic acids, methanol, and HMF yields all were higher for WBC. The higher acetic acid yield is consistent with the higher average acetate content of WBC compared to the MHW feedstocks, as shown in Table 3. Formic acid yield rises similarly, though to a larger extent than for acetic acid. The source of this is unclear, but parallels an increase in HMF yield. This may indicate that, counter to the indications discussed earlier, the main source of formic acid may in fact be hexose sugar degradation. The higher pH combined with the higher acid content suggests more buffering, likely from dissolved ash in the extract. Overall, this suggests somewhat less value could be derived (in sugars and lignin) from willow than for mixed hardwoods, though more processed biomass is available for other applications (e.g., pellets), along with more value from acetic acid, formic acid, and methanol.

Table 4. Comparison of extractions of willow (n = 4) and mixed hardwood chips (n = 2) conducted at 575 P-factor (160 °C, 120 min). Values in parentheses are standard error.

Extraction Outcome	WBC Willow		Mixed Hardwoods	
Mass Removal	20.6%	(0.3%)	22.4%	(0.3%)
Extract pH	3.79	(0.02)	3.54	(0.02)
Solids content (g/100g wood)	13.5	(0.2)	15.9	(0.0)
Post Centrifugation Solids (g/100g wood)	12.7	(0.1)	14.8	(0.0)
Est. Total Sugar (g/100g wood)	11.0	(0.1)	15.4	(0.1)
Polymer (g/100g wood)	8.2	(0.1)	11.6	(0.0)
Glucose (g/100g wood)	0.48	(0.03)	0.44	(0.00)
Xylose (g/100g wood)	1.09	(0.06)	2.01	(0.08)
Arabinose (g/100g wood)	0.88	(0.01)	1.04	(0.02)
Acetic Acid (g/100g wood)	1.40	(0.02)	1.25	(0.02)
Formic Acid (g/100g wood)	1.14	(0.03)	0.50	(0.02)
Methanol (g/100g wood)	0.70	(0.07)	0.44	(0.00)
Furfural (g/100g wood)	0.48	(0.02)	0.47	(0.03)
HMF (g/100g wood)	0.086	(0.002)	0.046	(0.002)
Total Titrable Acid (mol/100g wood)	0.034	(0.000)	0.029	(0.000)
Total Acid (HPLC) (mol/100g wood)	0.048	(0.000)	0.032	(0.001)

While HWE of feedstocks containing increasing quantities of WBC yields lower quantities of sugar and lignin, the potentially lower value of the co-product suite needs to be viewed in its overall context. A potential advantage of willow biomass crops is their high yields, very short rotations, and coppice management, where the plants resprout and grow after each harvest. Yields can be an order of magnitude greater than natural forests in the region and can use a wide range of open land. This creates opportunities for feedstock for a given size of biorefinery to be generated on a much smaller land base, and in much closer proximity to the facility. Both of these could contribute to lower feedstock costs. In addition, the biomass produced from willow crops can have a negative carbon footprint [34], which would impact the overall carbon footprint of this system. Ultimately, the economic and environmental impact of different proportions of willow in the feedstock should be assessed using tools like life cycle assessment and techno-economic analysis across the entire system.

Extractions of mixes of MHW and WBC generally showed the expected linear relationship between the WBC fraction and each outcome, as shown in the plots in Figure 8. While noisy, mass removal (Figure 8a) is roughly linear with willow percentage. Most other outcomes have less variation, with the linearity of the extract solids and sugar contents suggesting the roughness in the mass removal is probably noise. While linearity seems to be lacking in the methanol plot (Figure 8e), methanol was generally the noisiest of the HPLC measurements, due to a combination of low concentrations and non-zero baseline. As seen in the P-factor studies in Figure 3b, centrifugable solids (solids content minus post-centrifugation solids content) data had considerable scatter, but for the WBC/MHW extractions shows a slight downward trend in centrifugable solids with increasing WBC. The average lignin content of the WBC is slightly lower than that of the MHW feedstock (Table 3), indicating the likely source of this difference.

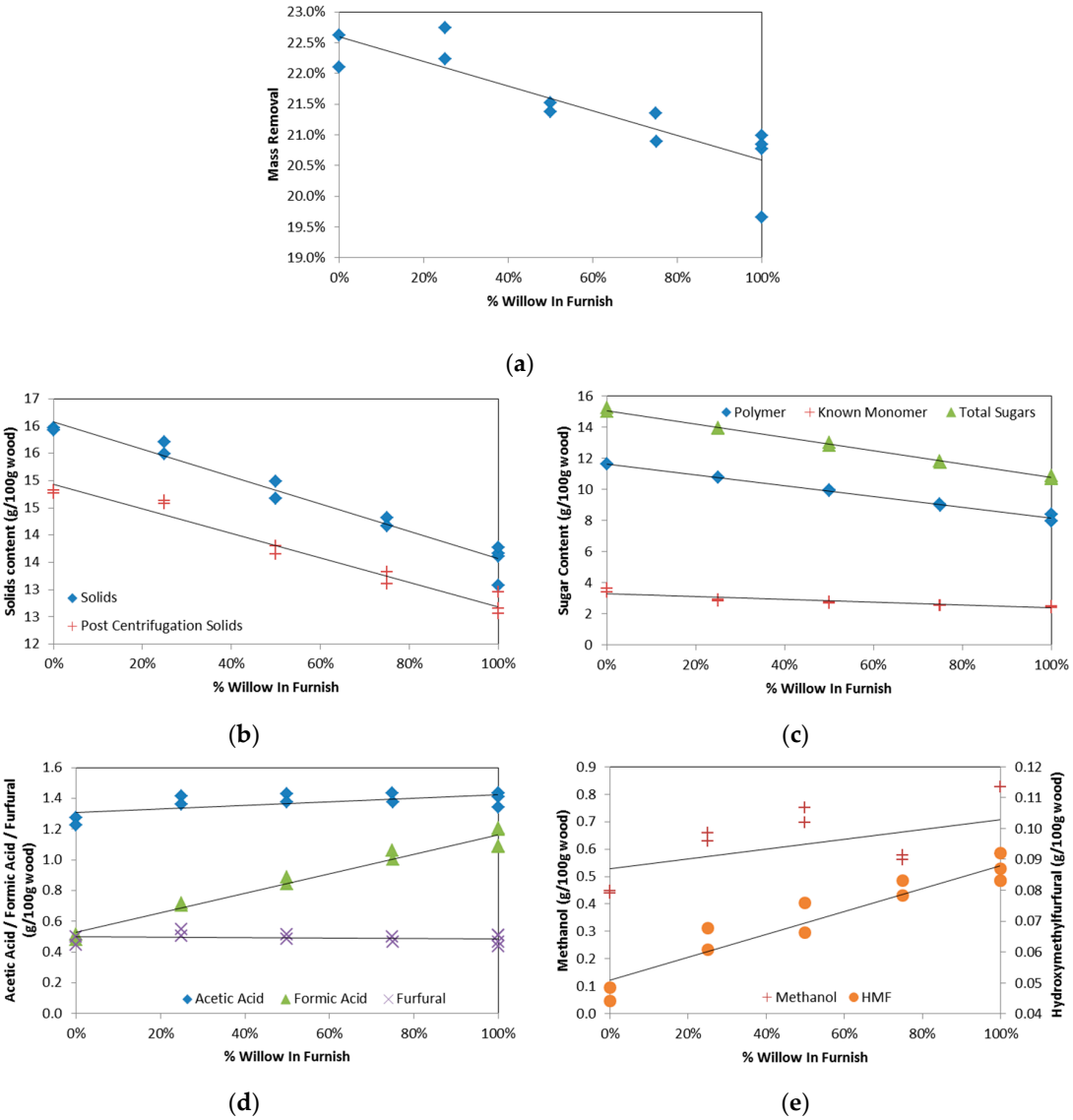


Figure 8. (**a**) (Top Center). Mass removal against % willow in feedstock. (**b**) (Mid Left). Solids contents and post-centrifugation solids content against % willow in feedstock. (**c**) (Mid Right). Polymer, monomer, and total sugars against % willow in feedstock. (**d**) (Lower Left). Acetic acid, formic acid, and furfural yield against % willow in feedstock. (**e**) (Lower Right). Methanol and hydroxymethylfurfural (HMF) yield against % willow in feedstock. All data from extractions conducted to 575 P-factor (160 °C/120 min).

3.3. Water-To-Wood Ratio and Other Variables

HWE processing has historically been assumed to be unaffected by the water-to-wood ratio, in terms of mass removal and yield of recovered products [23]. However, unpublished research on extraction of non-woody materials suggests that the water-to-wood ratio may affect multiple extraction outcomes. Additionally, developing a better understanding of the effects of presteaming and counter-current extraction are of significant interest for industrial applications. As laboratory analyses of these techniques result in water-to-wood ratios that are not consistently 4:1, these tests will be compared with the water-to-wood ratio trends, rather than the base 4:1 data points. To enable these comparisons, logarithmic curve fits have been used to approximate the diffusion effects of higher water-to-wood ratios, and 95% confidence intervals have been plotted around them (Figure 9). This is intended to give an approximate indication of the significance of any differences between the base water-to-wood ratio data set and the presteamed extractions and the counter-current simulation extractions.

As in the P-factor studies presented above, mass removal and solids content are the first indicators of the effect of water-to-wood ratio. Figure 9a demonstrates that changes are clear, with mass removal rising considerably as water-to-wood ratio is increased, from an average of 19.1% at 3:1, through 20.6% at 4:1, to 23.3% at 10:1. This is a considerable range (equivalent to decreasing P-factor by 100 points, and increasing it by 240 points respectively) around the 4:1 base value and indicates that there are important changes resulting from differing water-to-wood ratios. This indication is supported by a similar rise in extract solids yield across this range (Figure 9b), from an average of 12.7 g/100 g wood at 3:1 to 16.2 g/100 g wood at 10:1. The increase in solids yield is more rapid than the increase in mass removal, with the recoverable solids (solids content/mass removed) increasing from 66% to 70%. Total sugar yields (Figure 9c) also rise with increasing water-to-wood ratio, as do monomer yields (Figure 9d), with monomers increasing as a proportion of total sugars. This increased percentage may be due to lower furan generation, as shown in Figure 9e. This shows a 33% reduction in furfural generation, compared to the 24% increase in monomer yield. In absolute terms, the furfural not generated accounts for approximately 50% of the increase in monomer yield. Under the conditions of HWE, 50% selectivity (molar yield) would not be surprising, indicating that reduced losses may be the primary source of the extra monomer.

HMF yields showed the opposite trend (Figure 9f), rising with increasing water-to-wood ratio. While this would seem directly counter to the discussion above, this may suggest that HMF concentrations are more controlled by loss reactions than by formation reactions. Loss reactions would be slowed significantly by the reduced acid concentrations and reduced HMF concentration resulting from the dilution effects of increased water-to-wood ratio. This appears to have a larger effect than the lower formation rates that would be expected from the lower absolute (g/L) hexose sugar concentrations. Acetic acid recoveries responded unexpectedly as well, staying effectively flat across the range of water-to-wood ratios tested. This indicates that diffusion pressures are rather un-important in the reactions generating acetic acid, also suggesting that acid concentration is less important than acetate available for hydrolysis. Formic acid recoveries follow the same trend as monomeric sugar yield, and rise by an almost identical proportion (23.3% for formic acid, 24% for monomer sugars). This may indicate that the main source of formic acid is in fact hexose sugar degradation. Methanol yield did decrease ~27% across this range, but with so much noise that it is difficult to clearly interpret.

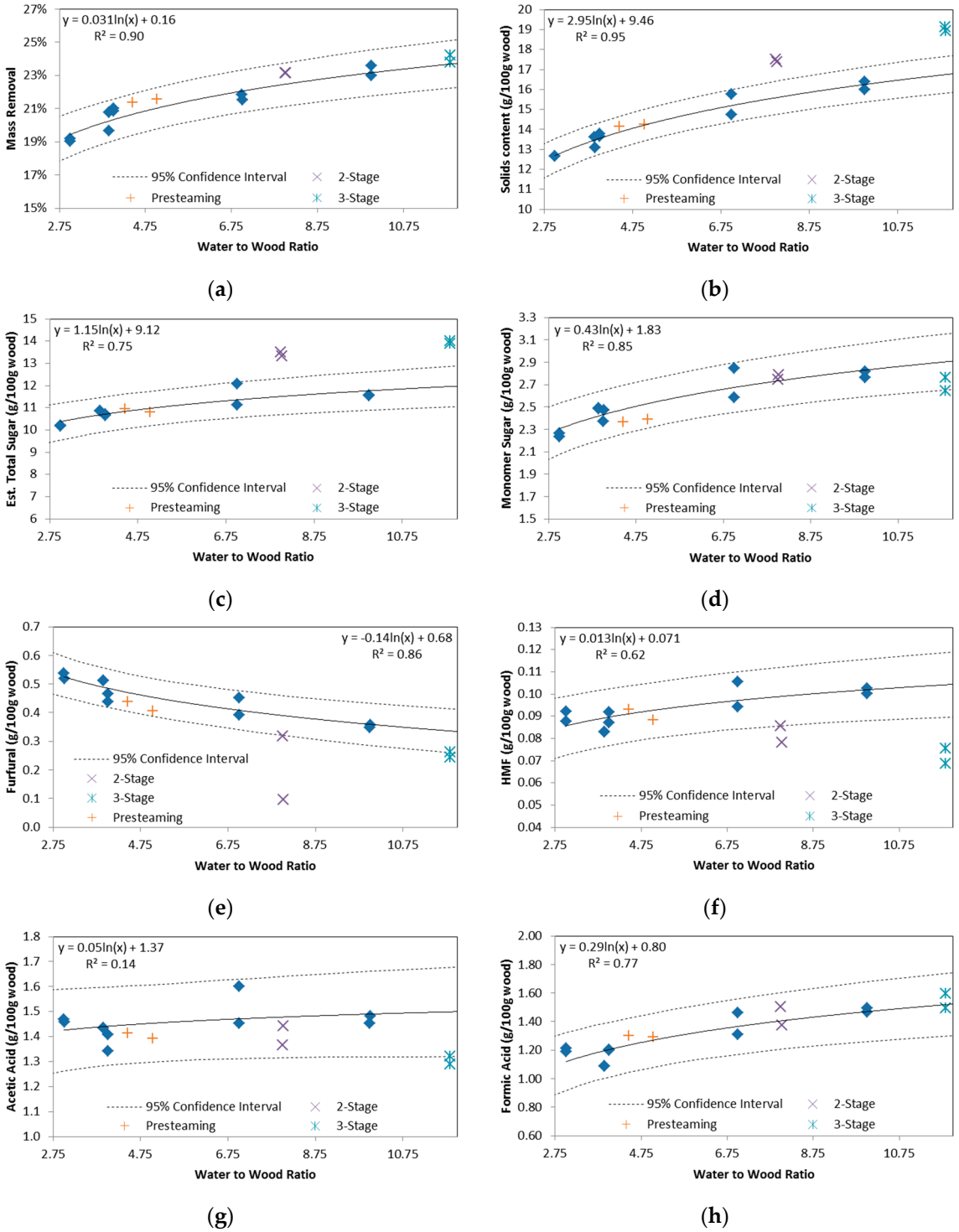


Figure 9. Response of different parameters to changes in the water-to-wood ratio used in the hot water extraction of willow biomass. Blue diamonds represent the water-to-wood ratio dataset to which the logarithmic curve is fit. Parameter responses reported are: (**a**). mass removal, (**b**). total extract solids content, (**c**). total sugar (monomer and polymers), (**d**). total monomer (total of xylose, arabinose, glucose), (**e**). furfural, (**f**). hydroxymethylfurfural (HMF), (**g**). acetic acid, and (**h**). formic acid. In each plot cooks conducted using presteaming or in 2 or 3 stages are plotted for comparison. Confidence intervals were determined for a linear regression in log/linear coordinates, before being converted back to linear/linear coordinates. Points outside the confidence interval indicate a difference that is likely to be significant.

The other modified extractions tested all resulted in varying effective water-to-wood ratios. As the water-to-wood ratios seen in these extractions did not align directly with the water-to-wood ratios used in the water-to-wood ratio study, comparisons are to the trend lines identified (and their 95% confidence interval) to indicate if differences are significant. Presteaming is an important tool in industrial pulping practice to remove air from chips, pre-heat them, and improve penetration of pulping chemicals. As shown in Figure 9 (the orange + symbols) presteaming seems to have neither significant advantages nor disadvantages for HWE. This is also true with methanol (not shown), for which no change is apparent. The presteaming utilized here (15 min at 15 PSI) is quite aggressive, with 1–5 min at 15 psi being a common range in this team's experience. This indicates that for industrial applications presteaming can be tailored to operating needs (e.g., air removal and preheating) without concern for changing downstream process chemistry.

Continuous counter-current extraction appears to be a highly attractive technique for commercial applications: providing washing and potentially yield improvements if advantageous diffusion pressures can be harnessed. While laboratory scale testing cannot accurately duplicate the chemistry in a continuous extractor, by breaking a cook into stages, we can to some extent simulate the stronger diffusion effects (lower product concentrations) that would be seen in this format, as compared to batch cooking. The 2 and 3 stage cooks were intended to simulate this effect to different extents, giving a two-tier indication of the scale of this effect. As demonstrated in Figure 9a, the mass removal is not significantly impacted by multi-stage cooking (beyond the simple dilution effect), while solids (Figure 9b) and sugar yields (Figure 9c) rise significantly. The rise in sugars was primarily due to an increase in polymeric sugars, with monomeric sugar yield (Figure 9d) not changing significantly. Furan generation drops significantly (Figure 9e,f), likely due to the lesser maximum time ($\frac{1}{2}$ or $^1/_3$ that of a batch cook to the same P-factor), and an average quantity of monomeric sugar was held at temperature. Acetic acid yields (Figure 9g) may have dropped slightly, though not enough to be clearly differentiated from background noise. A drop in free acetic acid (as compared to bound acetate, which was not measured in this study) would make sense, paralleling the effect seen with monomer above. Formic acid yield did not change at all with the multi-stage cook, and as with presteaming, no change in methanol yield could be clearly separated from noise. The changes in solids, sugars, and furans all suggest significant potential benefits to counter-current extraction.

4. Conclusions

This work has clearly demonstrated that the HWE of WBC is overall quite similar to the HWE of other woody biomass, with some changes in extract composition and somewhat lower mass removals. The changes in extract composition indicate that commercial extraction of WBC can be expected to generate less sugars and lignin, but more acetic acid, formic acid, and methanol, when compared to conventional hardwood feedstock. Major extraction outcomes track well to P-factor across a range of temperatures, indicating that time and temperature can be traded off against one another as needed to match the desired processing conditions with available equipment. A preferred P-factor range of 500–800 P-factor has been identified, with the data presented here indicating a preferred point around the 575 P-factor. This P-factor provides a high recovery of products and maximizes recoverable mass. Ash removal, of interest for upgrading biomass, appears to occur at low P-factors. Mixed biomass feedstocks (WBC and MHW) have been demonstrated to pose no challenges for HWE, with linear responses to changes in feedstock composition.

Considerable effects of changing water-to-wood ratio were found. Noticeably, increasing the water-to-wood ratio increased mass removals, sugar yields, and formic acid yields. No clear effect on acetic acid or methanol yields was found. Furfural production fell (likely associated with lower concentrations of acids and monomeric sugars), while HMF recovery rose, indicating HMF recovery is controlled more strongly by loss reactions than formation reactions. Differences were large enough to clearly indicate that water-to-wood ratio is a parameter worth tracking carefully in future work. Presteaming showed no effects on extraction outcomes, indicating that decisions on presteaming use

and conditions can be made entirely on the need for air removal and preheating, without concern for extraction outcomes. Finally, testing for potential effects of continuous counter-current extraction showed no clear change in mass removals, but did produce clear increases in polymeric sugar yield and extract solids yield, while reducing sugar losses to furans. This indicates that continuous counter-current extraction could provide significant improvements in product yields without increasing extraction cost.

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