Hemicellulose extraction and its effect on pulping and bleaching

TROY RUNGE AND CHUNHUI ZHANG

ABSTRACT: A potential biorefinery is envisioned to use the hemicellulose portion of biomass to create transportation fuels or chemicals and the cellulose portion for fiber to be used in papermaking. To understand the effect on hemicellulose removal to pulpability and bleachability, a liquid hot water extraction was performed on two types of biomass with high hemicellulose content: poplar and miscanthus. The resulting materials were pulped using either a soda anthraquinone or kraft process. The pulps were then oxygen delignified and bleached with an elemental chlorine free sequence. The results demonstrate that a significant portion of hemicellulose can be extracted using liquid hot water extraction conditions of 170°C, 60 min, and a 6:1 ratio, with minimal glucan degradation. These low hemicellulose-content pulps delignified similarly to the control pulp, but had lower oxidative demand because of the absence of hemicellulose degradation products. Oxygen delignification of the low hemicellulose-content pulps was enhanced, but so was cellulose degradation. The delignification gains resulted in higher brightness ceilings for the pulps when a D(EP)D sequence was used. Measured fiber morphology did not change significantly from extracting the hemicellulose. Overall, hemicellulose extraction before pulping improved the efficiency of pulping and bleaching materials to a high brightness, but increased cellulose degradation.

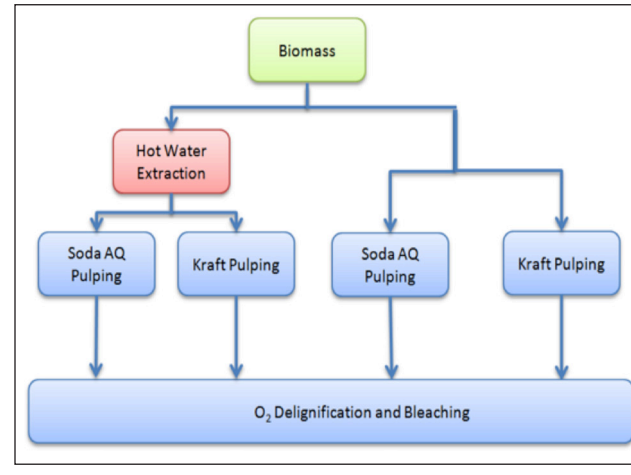
Application: Additional revenue might be available by extracting a portion of hemicelluloses before pulping and then converting the polysaccharide into a fuel or other products. This work suggests that hemicelluloses extraction improves bleachability of the resulting materials.

The Integrated Forest Products Biorefinery (IFPB) concept uses forest materials to produce bioenergy and bioproducts, in conjunction with manufacturing traditional forest products [1]. One of the early transformations imagined for pulp mills has been to extract hemicelluloses before pulping to convert into chemicals or fuels. Hemicelluloses, because of their branched nature, are fairly reactive and can be extracted through mild acidolysis or liquid hot water treatments and converted into fuels or chemicals [2,3]. Higher value can be envisioned for these materials, as the majority of hemicelluloses are degraded during the alkaline pulping and are removed from the pulp with the black liquor. Previous work has shown that overall yield might be reduced unless cooking modifications are made [4-7], but products such as furfural can be made from these extracted materials [8-10].

With any change, however, consideration must be given to primary pulp products to understand their quality and processability. This study investigates the possible effects of hemicellulose extraction on pulpability and bleachability of a woody and herbaceous biomass.

MATERIALS AND METHODS

Two biomass samples, hybrid poplar and miscanthus, representing woody and herbaceous biomasses, were acquired and used for these experiments. Both materials are high in xylan hemicellulose, which can be extracted easily with either hot water or acid extraction. NM-6 hybrid poplar trees (*Populus maximowiczii x nigra*) were harvested from northern Wisconsin after 10 years of growth and seasoned for 3 months before use. The pulp was hand-debarked, chipped and screened, air dried, and cold stored. Miscanthus (*Miscanthus giganteus*) was collected from agricultural stations in Arlington, WI, USA, and aged 3 months before being chopped and screened. **Figure 1** shows the experimental flow.



1. Experimental flow.

Hemicellulose extraction was accomplished by hydrolyzing the biomass in a 20 L circulating digester with an indirect

heat exchanger. The time and temperature of the reaction was controlled according to previously described, optimized conditions [11-14], and the solids and liquor were filter separated. Control and extracted biomasses were then pulped using either a soda anthraquinone (AQ) or a kraft pulping process using the same 20 L liquor circulating digester. Several of the pulp samples were subjected to dilute acid hydrolysis per the experimental design to further reduce the hemicellulose content before oxygen delignification and bleaching. Moisture and ash from the biomass, extracted biomass, and pulp samples were determined according to ASTM Test Methods E 1756-08 "Standard test method for determination of total solids in biomass" and E 1755-01 "Standard test method for ash in biomass," respectively. Kappa numbers were measured using TAPPI T 236 cm-85 "Kappa number of pulp." Cellulose chain lengths in the pulps were approximated by measuring cupriethylenediamine (CED) viscosity using TAPPI T 230 om-99 "Viscosity of pulp (capillary viscometer method)" and using Eq. (1) to calculate a carbohydrate degree of polymerization [15]:

$$DP^{0.905} = 0.75[954 \log (X) - 325] \quad (1)$$

where X is the measured viscosity in cP.

Bleaching was performed using either a Quantum Technologies Mark IV reactor/mixer (Quantum Technologies; Akron, OH, USA) for oxygen and chlorine dioxide stages or bag bleaching in a water bath for alkaline extraction stages. Samples were thoroughly washed with distilled water, with no carryover. Chlorine dioxide for elemental chlorine free (ECF) pulping was prepared through sulfuric acid acidification of sodium chlorite and collection of the chlorine dioxide gas into chilled water after passing through a sodium chlorite solution trap.

Biomass, extracted biomass, and pulp samples were subjected to a two-step acid hydrolysis procedure described by the National Renewable Energy Laboratory (NREL) [16] to obtain Klason and acid soluble lignin measurements. Additionally, hydrolyzed samples were neutralized, centrifuged at 4000 rpm for 5 min, and filtered through a nylon filter to further remove any suspended material. The cleaned sample was then characterized for saccharides using a Dionex high performance liquid chromatography (HPLC) system (ICS-3000) equipped with integrated amperometric detector and Carbopac PA20 guard and analytical columns at 20C [17,18]. Eluent was provided at a rate of 0.6 mL/min, according to the following gradient: 0-20 min, 100% water; 20-30 min, 25% water, and 75% 0.1 mol/L sodium hydroxide (NaOH); 30-35 min, 100% water. As post-column eluent, 0.5 mol/L NaOH was used. References were purchased from Fischer Scientific and subjected to a one-step acid hydrolysis following the suggested NREL procedure [16].

RESULTS AND DISCUSSION

Hemicellulose extraction and biomass characterization

Samples from the biomass were analyzed for saccharides, lignin, and ash to characterize the material. Sugar analysis provides insights into the amount and type of hemicelluloses present, with arabinose, galactose, xylose, and mannose being found only in hemicelluloses, and glucose existing primarily as cellulose. The results were as expected for the two species, with higher saccharide content for the herbaceous biomass, primarily in the form of hemicelluloses (**Table I**).

Approximately 1.5 kg of each sample was extracted with distilled water at 170°C for 60 min with a 6:1 liquor-to-biomass ratio following optimization experiments [19]. The biomass was filtered and washed with deionized water at a 4:1 water-to-biomass ratio. Extraction yields were measured gravimetrically, with approximately 13% of the biomass solubilized and removed during this process (Table I). The resulting washed and extracted biomass was then characterized to ensure a significant amount of the material removed was hemicellulose. Comparing these results to the chemical composition of the initial biomass indicated that approximately half of the hemicelluloses were removed with minimal cellulose degradation. The extraction lignin content slightly increased for the extracted samples, as expected, because of the selective removal of hemicelluloses saccharides.

Next, extracted and nonextracted biomass samples were pulped with an AQ process. Previous work and smaller screening experiments were used to find appropriate conditions before the 1.0 kg cooks were performed. **Table II** shows the process conditions and **Table III** shows the yield, kappa, and viscosity results from the pulping experiments. Yield numbers are displayed from each step, including the liquid hot water

	Extraction Yield (wt%)	Ara (wt%)	Gal (wt%)	Glu (wt%)	Xyl (wt%)	Man (wt%)	KL (wt%)	ASL (wt%)	Ash (wt%)	Total (%)
Poplar	n/a	0.41	0.64	42.1	16.8	3.67	30.1	3.63	1.22	98.6
Miscanthus	n/a	3.3	1.4	38.6	19.2	0.69	25.2	3.06	5.65	97.2
Water extraction: poplar	88.0	0.09	0.17	51.30	8.58	2.16	31.8	2.73	0.96	97.8
Water extraction: miscanthus	87.5	0.91	0.50	49.49	12.37	0.70	29.2	2.88	2.62	98.6

Abbreviations: Ara = arabinan; Gal = galactan; Glu = glucan; Xyl = xylan; Man = mannose; KL = Klason lignin; ASL = acid soluble lignin; n/a = not applicable.

I. Biomass characterization.

	Temp (°C)	Time (min)	Liquor (ratio)	AA (% as Na_2O)	AQ (%)	Sulfidity (%)
Poplar soda pulp	165	150	6	20	0.02	n/a
LHW poplar soda pulp	165	150	6	20	0.02	n/a
Poplar kraft pulp	165	110	6	20	n/a	25
LHW poplar kraft pulp	165	120	6	20	n/a	25
Miscanthus soda pulp	155	90	6	20	0.02	n/a
LHW Miscanthus soda pulp	155	90	6	20%	0.02	n/a
Abbreviations: LHW = liquid hot water extracted; AA = active alkali; AQ = anthraquinone; n/a = not applicable.						

II. Pulping conditions.

	LHW Ext Yield (%)	Cook Yield (%)	Overall Yield (%)	Kappa (No.)	CED Visc. (cP)	Calculated DP
Poplar soda pulp	n/a	48.7	48.7	24.1	17.0	1292
LHW poplar soda pulp	82.4	49.8	41.1	19.1	18.5	1351
Poplar kraft pulp	n/a	50.4	50.4	23.3	19.7	1395
LHW poplar kraft pulp	82.4	50.7	41.8	18.5	21.0	1440
Miscanthus soda pulp	n/a	43.6	43.6	18.6	10.9	986
LHW miscanthus soda pulp	73.0	45.7	33.4	14.5	11.9	1046
Abbreviations: LHW = liquid hot water extraction; CED = cupriethylenediamine; DP = degree of polymerization; n/a = not applicable.						

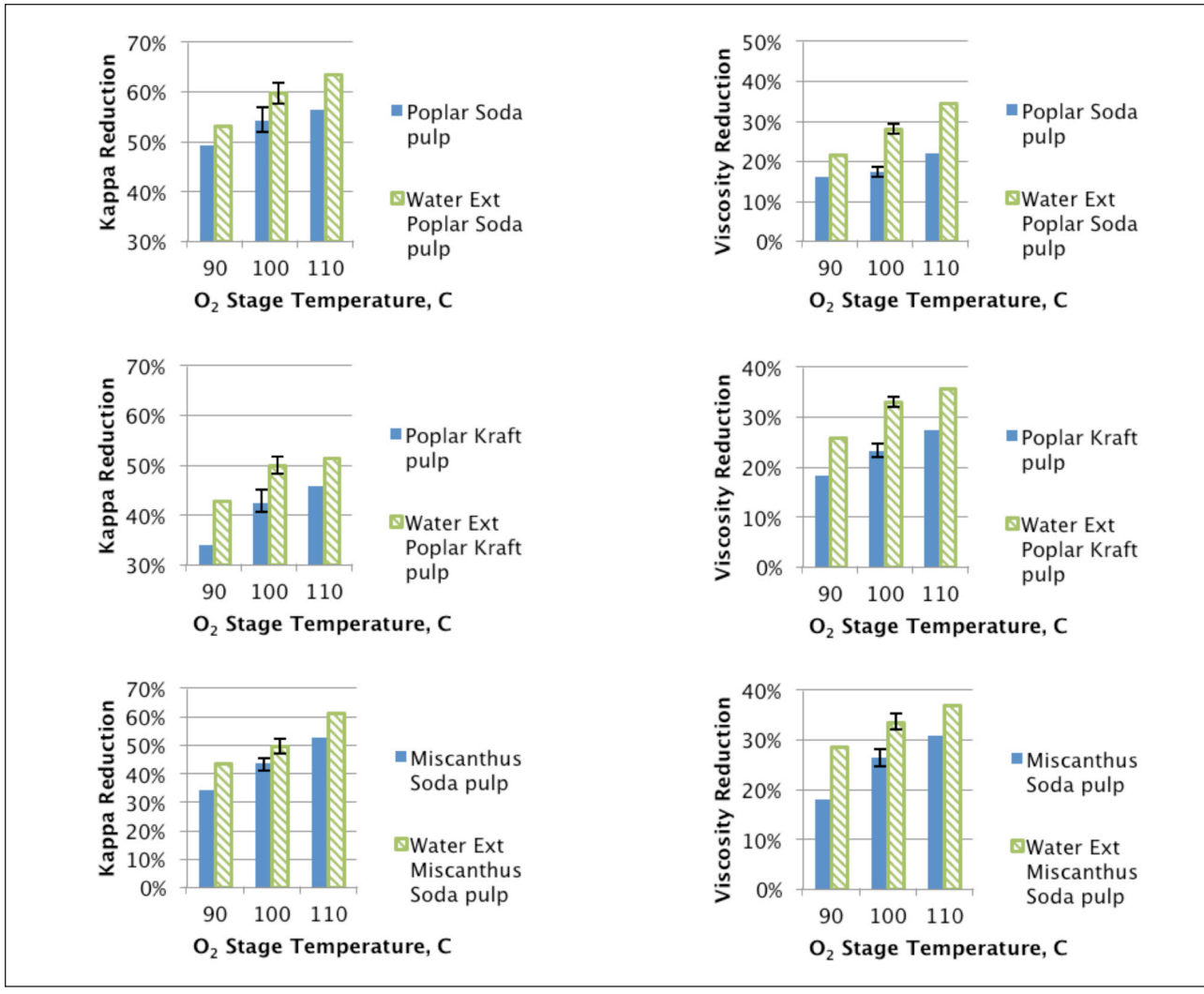
III. Pulping results.

	Ara (%)	Gal (%)	Glu (%)	Xyl (%)	Man (%)	KL (%)	ASL (%)	Total (%)
Poplar soda	0.05	0.05	74.2	18.0	1.59	2.45	0.60	96.9
LHW poplar soda pulp	0.00	0.03	87.8	5.02	1.03	2.45	0.51	94.9
Poplar kraft	0.00	0.00	77.3	17.3	1.42	2.13	0.67	98.9
LHW poplar kraft pulp	0.04	0.00	91.0	4.39	1.04	2.31	0.59	99.3
Miscanthus soda	2.12	0.35	70.6	20.0	0.65	2.44	0.55	96.7
LHW miscanthus soda pulp	0.28	0.00	83.4	6.49	0.35	2.54	0.43	93.5
Abbreviations: LHW = liquid hot water extraction; Ara = arabinan; Gal = galactan; Glu = glucan; Xyl = xylan; Man = mannose; KL = Klason lignin; ASL = acid soluble lignin.								

IV. Pulp characterization.

Stage	Conditions
O_2	Sparged reactor with O_2 for 5 min, pressurized with O_2 to 80 psig, 10% csc, 2.5% NaOH, 60 min, varying temperatures
D	0.20 kappa factor, 3.5% csc, 50°C, 45 min, pH adjustment to achieve final pH of 2.0-2.5 with 10% H_2SO_4
EP	0.5% H_2O_2, 10% csc, 70°C, 60 min, 2.5% NaOH, terminal pH ~ 11.0
D	Varying % ClO_2, 10% csc, 80°C, 120 min, pH adjustment to achieve final pH of 4.5-5.5 with 10% H_2SO_4

V. Bleaching conditions.



2. O_2 stage delignification and CED viscosity loss. Error bar depicts standard error done on three replicates for 100°C stage only.

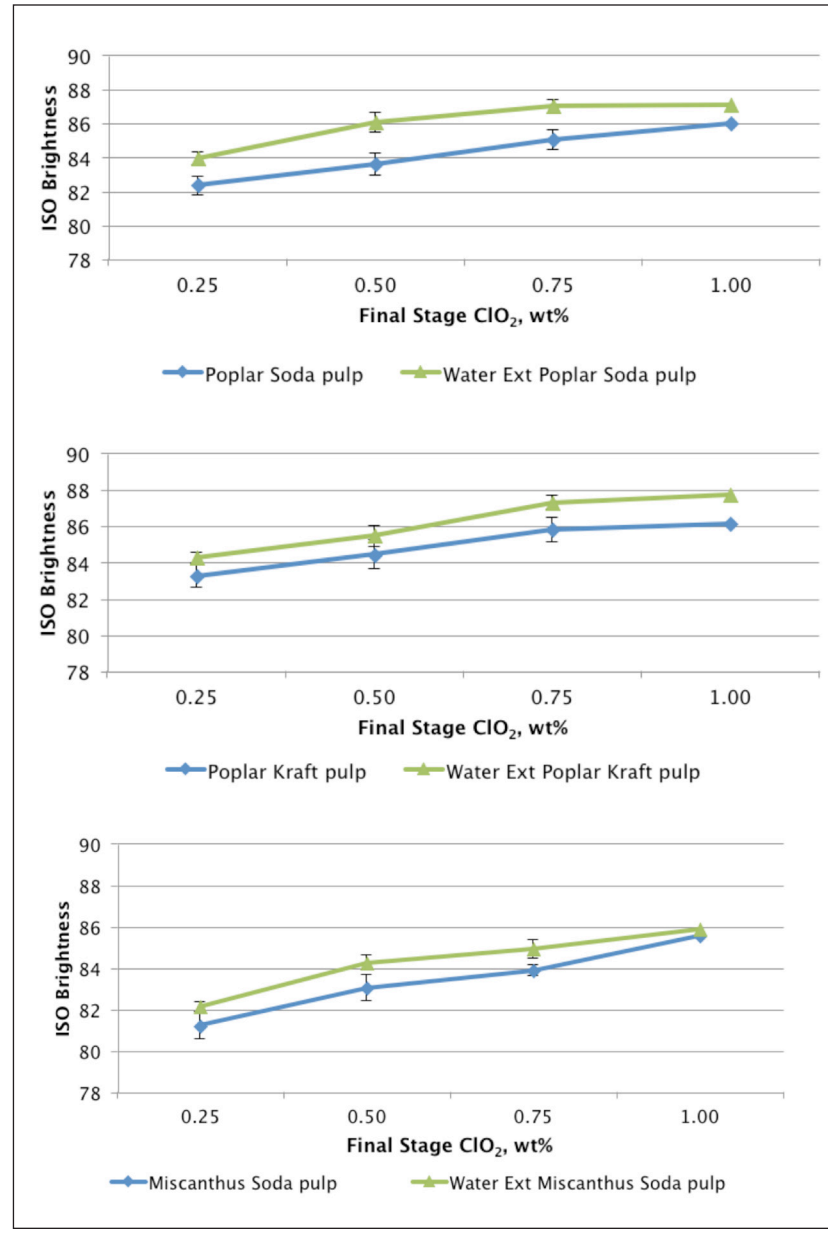
(LHW) extraction and pulping. These yields are on an individual process basis and may be multiplied together to calculate a total yield of the process.

The data indicate that the extracted biomass had similar pulping yields as the nonextracted biomass, based on material entering the digester. Compared with the original biomass, however, the LHW extraction and cooked pulp had an overall lower yield (considering both processes) of approximately 8%-10%. The miscanthus had slightly higher losses than hybrid poplar, and the soda AQ and the kraft processes were similar in yield loss. LHW extraction before pulping also appears to reduce lignin, as measured by the kappa number, either because of an opening of the lignocellulose matrix through hemicellulose removal or removal of carbohydrate degradation products acids, such as hexenuronic acids, that consume permanganate in the kappa number test [20,21]. Slightly higher viscosities and corresponding degrees of polymerization of the extracted pulps were measured, and presumed to result from the loss in low molecular weight hemicelluloses from extraction.

Samples were taken and analyzed for saccharide content to distinguish differences between standard pulps and LHW extracted and then cooked pulps. The results (**Table IV**) demonstrate that the nonextracted pulps had significant hemicelluloses content left after pulping, as evidenced by the presence of sugars other than glucose. In comparing the standard pulps to the LHW extracted and cooked pulps, it is evident that the hemicelluloses of the final pulp are significantly depleted, with about 12%-14% more glucan and a corresponding decrease in the other measured carbohydrates. This supports the hypothesis that the degree of polymerization was higher for the LHW extracted pulps because of hemicellulose depletion. Klason and acid soluble lignin measurements indicate that the LHW extracted and standard pulps had similar lignin contents. These data support the hypothesis that the decrease in kappa number observed from the LHW treatment is likely the result of carbohydrate degradation products.

Samples from the LHW/cooked and standard cooking chemistries were delignified with an O_2 stage in a pressurized reactor under the conditions listed in **Table V**, with a 150 g

sample used for each reaction. Three O_2 delignification reactions were conducted, with temperatures varying from 90°C to 110°C, to provide a measure of sensitivity of the pulps to reaction conditions. Additionally, three replicates were performed at 100°C to obtain a measure of error and provide enough pulp to complete subsequent bleaching steps. The resulting pulps were well washed with deionized water using a centrifuge outfitted with a nylon woven fabric to assist dewatering. The results display the delignification and the change in CED viscosity for each pulp (**Fig. 2**). The data show that oxygen delignification is improved with extraction of hemicellulose with liquid hot water before cooking or with dilute acid after cooking. This can be attributed to opening of the fiber super molecular structure through hemicellulose removal, allowing the lignin to be more easily reacted and removed. The additional extraction might also remove a portion of the transition metals, which can reduce the oxygen delignification efficiency through the formation of radicals [22]. The ash data support this idea, with a reduction seen from LHW extraction.



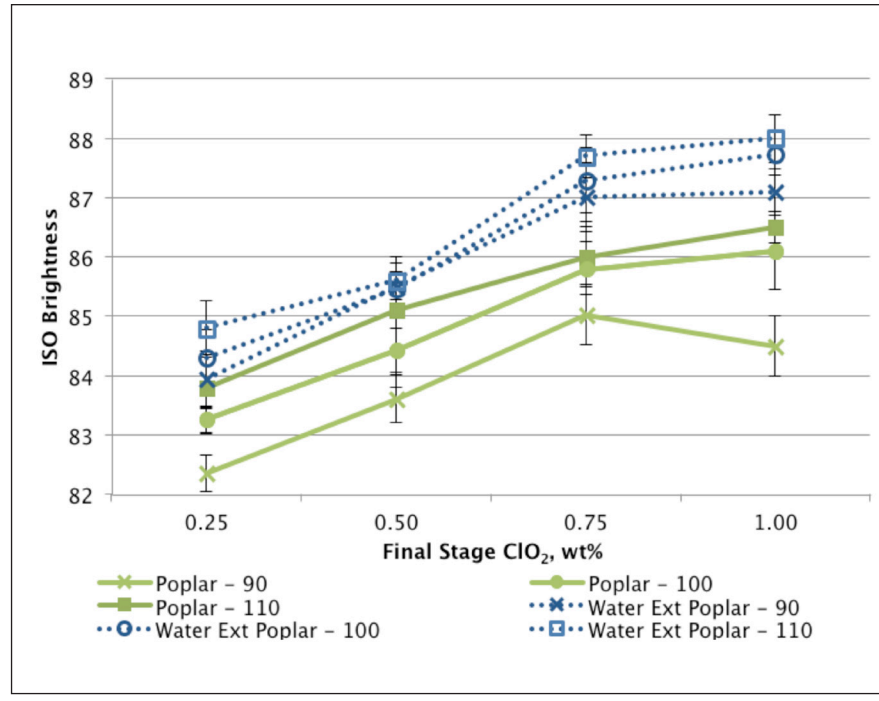
3. D-stage ISO brightness of 100°C O_2 delignified pulps with standard error bars. Connecting lines are to assist demarcation between data and are not correlations.

Figure 2 also displays the change in CED viscosity, which is used as a proxy for cellulose degree of polymerization, with higher CED viscosities corresponding to higher chain lengths and less cellulose damage. LHW extraction resulted in pulps that had higher initial viscosity, but experienced a greater CED viscosity loss during the oxygen stage, as seen from the effect of the oxygen delignification stage on CED viscosity. This is thought to be primarily the result of a difference in hemicellulose level, with the LHW extracted pulp being significantly lower before the oxygen stage. With less low molecular weight hemicellulose initially, its removal during the oxygen stage does not provide an increase in the saccharide average MW or the measured CED viscosity. The other possibility is that the hemicellulose provides protection for the cellulose during the oxygen delignification stage. A similar phenomenon is seen during the alkaline soda or kraft pulping step. The LHW extracted pulps with lower hemicellulose content see a marked reduction in glucan content as a result of cellulose degradation. These data suggest that the hemicellulose presence inhibits cellulose degradation.

The oxygen delignified pulps from the 100°C condition were further bleached using a D(EP)D sequence under the conditions listed in Table V. The ClO_2 was varied in the final stage to provide a measure of brightness potential. Brightness pads were made and used to measure ISO brightness, which was plotted for the LHW extracted and control pulps (**Fig. 3**). The results demonstrate that the control and the LHW extracted pulps could be bleached to greater than 85% ISO brightness with a O_2D(EP)D sequence, with the extracted pulps demonstrating higher brightness values for all three pulps. It is hypothesized that the improved delignification during the oxygen delignification continues into the D(EP)D stages, resulting in higher brightness values. Higher brightness values typical for market pulps (>90 ISO brightness) were

not targeted to allow bleachability differences to be more easily seen between the pulps.

To test the hypothesis, samples from the hybrid poplar kraft O_2 delignification experiment at the three temperatures (90°C, 100°C, and 110°C) were bleached with a D(EP)D sequence using the same conditions listed in Table V. The results indicate that, although higher ClO_2 was used in the first stage for the higher starting kappa numbers (a constant 0.2 kappa factor was used), higher brightness values were achieved with more delignified pulps (**Fig. 4**). This supports the hypothesis that the hemicellulose extraction assists bleaching by improving delignification pulping.



4. D-stage ISO brightness at different O_2 temperature conditions with standard error bars. Connecting lines are to assist demarcation between data and are not correlations.

The highest brightness pulps from 1% D1 stage were characterized for morphology to understand their usefulness as a papermaking raw material and to be sure the extraction did not create any significant changes. The results indicate that all of the biomasses had relatively short fiber lengths, with the length-weighted average fiber length in the 0.7-0.8 mm range, which is similar to a hardwood such as eucalyptus (**Table VI**). From a coarseness standpoint, the poplar was markedly lower than miscanthus, whereas miscanthus had significantly higher fines material than the poplar, presumably because of a higher amount of parenchyma cells. The morphology of the LHW extracted pulps and the control pulp were statistically not different, suggesting that cellulose degradation was not excessive after LHW extraction.

CONCLUSIONS

A biorefinery concept of extracting hemicelluloses from herbaceous biomass before making pulp from the remaining materal was further developed by understanding the effect of hemicellulose removal on pulpability and bleachability. In this work, a hot water extraction was performed on two biomass samples to deplete a significant portion of the hemicellulose before pulping and bleaching. Results showed that approximately half of the hemicellulose could be extracted under conditions of 170°C, 60 min, and a 6:1 ratio, which resulted in pulps with significantly depleted hemicellulose. Oxygen

	LWA Fiber Length (mm)	Coarseness (mg/100 m)	Fines (%)
Poplar soda	0.81±0.04	7.9±0.09	6.1±0.5
LHW poplar soda pulp	0.77±0.03	7.6±0.09	6.5±0.5
Poplar kraft	0.85±0.06	8.1±0.08	5.5±0.7
LHW poplar kraft pulp	0.88±0.05	8.0±0.11	5.5±0.4
Miscanthus soda	0.85±0.04	16.2±0.14	9.1±0.6
LHW miscanthus soda pulp	0.80±0.05	15.2±0.10	10.1±0.8

Abbreviations: LHW = liquid hot water extraction; LWA = length weighted average.
Note: The ± amount refers to the standard error of three measurements.

VI. Fiber morphology.

delignification and ECF bleaching of these pulps suggested that this removal enhanced delignification and brightening, but also cause additional cellulose degradation. This might be a result of the reduction of reactive hemicellulose material that inhibits cellulose degradation.

Results showed that LHW extraction of hemicelluloses did not lower the cooking yield, but lowered the overall yield of the pulp by approximately 8%-10% when the extraction and cooking processes were both considered. These hot water extracted biomass pulps were found to have a much lower proportion of hemicelluloses than did the extracted materials, even after pulping, which can lower the strength potential because the fibers would be expected to have lower swelling.

The LHW and nonextracted soda-AQ pulps could be bleached to greater than 85% ISO brightness using a $O_2D(EP)D$ sequence, with slightly higher final brightness achieved for LHW extracted pulps. The LHW extracted pulps had lower kappa numbers coming into the bleach sequence, but similar Klason lignin, presumably because of lower carbohydrate degradation products. These degradation products can consume oxidative bleach chemicals and are thought to be the cause of the slightly higher bleachability. CED viscosity losses during oxygen delignification were found to be greater in the LHW extracted pulps, possibly because of the lower hemicellulose content, which might have a stabilizing effect on alkali induced cellulose damage. The CED viscosities were not severe, and no morphology differences were seen in the pulps, but it is apparent from the cooking and oxygen delignification stages that hemicellulose content influences cellulose degradation. **TJ**

ACKNOWLEDGEMENTS

This material is based on work support by the National Institute of Food and Agriculture, U.S. Department of Agriculture, under ID number WIS01521. The authors are also grateful to the Wisconsin Bioenergy Initiative at the University of Wisconsin for financial support of this work. Additionally, the authors thank JunYong Zhu and Carl Houtman of the U.S. Department of Agriculture Forest Products Lab for their assistance with this research.

LITERATURE CITED

1. Bajpai, P., in *Biotechnology for Pulp and Paper Processing*, Springer, New York, 2012, pp. 375-402.
2. Pu, Y., Treasure, T., Gonzalez, R., et al., *Bioresources* 6(4): 4856(2011).
3. Ingram, T., Rogalinski, T., Bockemuhl, V., et al., *J. Supercrit. Fluids* 48(3): 238(2009).
4. Amidon, T.E. and Liu, S., *Biotechnol. Adv.* 27(5): 542(2009).
5. Liu, S.J., Mishra, G., Amidon, T.E., et al., *J. Biobased Mater. Bioenergy* 3(4): 363(2009).
6. Duarte, G.V., Ramarao, B.V., Amidon, T.E., et al., *Ind. Eng. Chem. Res.* 50(17): 9949(2011).
7. Lu, H.F., Hu, R.F., Ward, A., et al., *Biomass Bioenergy* 39: 5(2012).
8. Yoon, S.-H., Cullinan, H.T., and Krishnagopalan, G.A., *Ind. Eng. Chem. Res.* 49(13): 5969(2010).
9. Mandalika, A. and Runge, T., *Green Chem.* 14: 3175(2012).
10. Xing, R., Qi, W., and Huber, G.W., *Energy Environ. Sci.* 4(6): 2193(2011).

ABOUT THE AUTHORS

Runge

Zhang

Our research group has been looking at the role of hemicelluloses in pulp properties, as well as investigating products that can be made from these polysaccharides. With new research on valorization of the hemicelluloses, we were interested to find out whether their extraction would improve the bleachability, similar to a xylanase treatment in a bleach plant.

It was difficult to find conditions that were harsh enough to extract a significant amount of hemicelluloses, but gentle enough to not significantly degrade the cellulose. Fortunately, saccharide analysis has become increasingly better and easier to perform, allowing experiments to more easily detect small changes in carbohydrates.

We are always surprised at how easily a portion of hemicelluloses is removed from biomass. In our case, using a simple liquid hot water extraction was sufficient. What is always interesting is even though a large portion can be easily extracted, fully bleached pulp still retains a high portion of hemicelluloses.

Mills considering creating products through extraction and valorization of hemicelluloses can use this research to identify potential costs and benefits. Unfortunately, in the case of extracting hemicelluloses before pulping, more research is still required to find the optimum processes to maximize the economics for mills.

Runge is assistant professor in the Department of Biological System Engineering, University of Wisconsin-Madison, USA, and Zhang is assistant professor at the State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China. Email Runge at trunge@wisc.edu.

11. Tunc, M.S. and van Heiningen, A.R.P., *Ind. Eng. Chem. Res.* 47(18): 7031(2008).
12. Runge, T., Wipperfurth, P., and Zhang, C., *Biofuels* 4(1): 73(2013).
13. Runge, T., Zhang, C., and Wipperfurth, P., "Forest biorefinery for fuel and fiber," *Proceedings of the 4th International Symposium on Emerging Technologies for Pulp and Papermaking*, South China University of Technology, Guangzhou, China, 2010.
14. Zhang, C. and Runge, T., *Ind. Eng. Chem. Res.* 51(1): 133(2011).
15. Mazumder, B.B., Ohtani, Y., Cheng, Z., et al. *J. Wood Sci.* 46(5): 364(2000).
16. Sluiter, A., Hames, B., Ruiz, R., et al., "Determination of structural carbohydrates and lignin in biomass: laboratory analytical procedure," National Renewable Energy Laboratory, Golden, CO, USA, 2008.
17. Shill, K., Padmanabhan, S., Xin, Q., et al., *Biotechnol. Bioeng.* 108(3): 511(2011).
18. Davis, M.W., *J. Wood Chem. Technol.* 18(2): 235(1998).
19. Wipperfurth, P.J., "Optimizing the energy potential of lignocellulosic biomass," M.S. thesis, University of Wisconsin-Madison, Madison, WI, USA, 2011.
20. Colodette, J.L., Longue Jr., D., Pedrazzi, C., et al., *Ind. Eng. Chem. Res.* 50(4): 1847(2011).
21. Chakar, F.S., Allison, L., Ragauskas, A.J., et al., *TAPPI J.* 83(11): 62(2000).
22. Yang, R., Lucia, L., Ragauskas, A.J., et al., *J. Wood Chem. Technol.* 23(1): 13(2003).