

Addition of corn stover arabinoxylan into hardwood during pulping for improved physical properties

ANURAG MANDALIKA AND TROY M. RUNGE

ABSTRACT: Agricultural residues, such as corn stover, are being considered for biofuels and bioproducts. They represent inexpensive, pentosan-rich feedstock that are available in abundance. These materials are typically pre-treated to make them more amenable to biological processes such as fermentation. One such treatment involves extraction using alkali to remove the hemicellulose, leaving the cellulose more accessible for chemical or enzymatic hydrolysis. Extracted xylan hemicellulose may be considered for use in pulp and paper, or for providing a potential value stream from cellulosic ethanol biorefineries. To be useful, the extracted xylan should be concentrated and adsorbed into the pulp using existing equipment or a minimal number of new unit operations. In this work, we explored the concept of size-exclusion membrane-filtration to concentrate xylan that was extracted from corn stover in mild alkaline conditions. We examined hollow-fiber and tangential-flow filtration types and achieved a nearly two-fold increase in the xylan concentration using the former with a 50 kDa molecular weight cut-off (MWCO) membrane. Cassette-type tangential-flow filtration resulted in slightly greater xylan concentration with the use of a 10 kDa MWCO membrane. Hemicellulose extracts were then used as an additive during kraft pulping of hybrid poplar to show that the xylan could be adsorbed onto pulp fibers and retained even after washing. Pulp tensile strength improved after xylan addition following refining. An average of 33% of the xylan added in this method was retained, with xylan loading between 5 wt% and 20 wt%, compared with the control pulp sample that did not have added xylan. These results suggest potential for further exploration of biorefinery extracts use as additive feedstock for pulping. The study, being an evaluation of the proof-of-concept, aims to push research and optimization in this area that will lend well to scale-up and commercialization.

Application: This work benefits mills in demonstrating that adjunct hemicelluloses may be incorporated into their pulp products, and if obtained from a low-cost source, could provide an increase in sellable pulp mass. This work also underlines the importance of hemicellulose content on pulp properties.

Most bioprocessing operations involving the use of plant material are based on the use of cellulose. These include pulping, the production of cellulosic ethanol and other high-value cellulosic products and solvents. Access to the valuable cellulosic material, is however, impeded largely by the presence of the lignin, and to a smaller extent, the hemicellulose fractions. Physical associations between the carbohydrate and lignin fractions, and extensive hydrogen-bonding networks, render the feedstock recalcitrant. Removal of hemicellulose and lignin generally improves access to cellulose for chemicals and, more so, for enzymatic conversions. Several researchers have documented improvement in enzymatic cellulose digestibility resulting from removal of lignin and hemicelluloses, and the techniques for affecting this [1,2].

Delignification and solubilization of the hemicellulose sugars are also the basis for chemical pulping, of which the alkaline kraft process is the most prominent. It frees up the cellulose fibers from the rest of the plant material so they can be laid into paper. The approach is similar in modern-day biorefineries where the extraction and separation of cellulose is

imperative for the production of cellulose-derived chemicals and fuels. By the same token, researchers have explored the utility and advantages of extracting the hemicelluloses before pulping and bioprocessing, and finding value-added conversion processes to produce bioproducts from hemicellulose sugars, such as furfural [3,4], furfuryl alcohol [5], γ -valerolactone [6], etc. This is seen as a promising way of adding value to existing cellulose-dependent bioprocessing operations, and to add value to the currently underused hemicellulose fraction of biomass.

In the development of modern biorefineries centered on the use of cellulose for products such as cellulosic ethanol, considerable value is lost by failing to realize the utility of hemicellulose-derived carbohydrates. The hemicellulose that can be recovered from agricultural residues represents a valuable source of inexpensive carbohydrates, the potential of which must be adequately realized.

The primary deterrent to the use of the hemicellulose carbohydrates, arabinoxylans from grasses in this instance, is a problem of efficient separations. Realizing value from hemicelluloses has been impeded by traditional bioprocessing op-

erations, which accumulate these carbohydrates in the reaction mixture, with a focus on increasing access to the cellulose fraction of lignocellulosic biomass. Improving hemicellulose recovery and valorization is key to furthering the concept of the biomass-based integrated biorefinery, where the majority of lignocellulosic constituents are used toward the production of value-added products. Efficient separation strategies in the preliminary stages of the bioprocessing operations are, therefore, key to preserving the chemical and biological fidelity of the substrate that can enable its conversion into these chemicals and fuels. It is with this objective that we explored membrane filtration as a means to extract, purify, and concentrate corn stover-derived arabinoxylan. A potential application of this product to the integrated pulp biorefinery is then explored as an additive to improve the strength properties of hybrid poplar pulp.

LITERATURE REVIEW

Alkaline extraction of hemicelluloses from Gramineae

Extraction and removal of hemicellulose sugars from plant feedstock using alkali is accomplished by the peeling reaction mechanism, where reducing end sugars are slowly “peeled off,” leading to the generation of oligomeric hemicelluloses. This is in sharp contrast to the mechanism in acid where the sugars are cleaved randomly, leading to shorter-chained oligomers and monomers. Xylans, being the primary hemicellulosic oligosaccharide, have conventionally been extracted in high yield in alkaline conditions. Even though the concentration of the alkali used affects the amount of xylans extracted, there are theoretical limits to the amount that can be extracted, due in part to the interactions of the hemicelluloses with the lignin and cellulose fractions in biomass.

Lignins present in species of the *Gramineae* are structurally different and more heterogeneous than hardwood and softwood lignins. Straw lignins present higher alkaline solubility, rendering this treatment as a way to increase their digestibility [7]. Along with removal of hemicelluloses, alkaline treatment also delignifies the biomass and yields a feedstock that is richer in cellulose (by proportion). The hemicellulose carbohydrates that are liberated in the process are also chemically and structurally different than those obtained from softwoods and hardwoods. The primary hemicellulose oligomers in cereal crops and grasses are arabinoxylans, whereas galactoglucomannans and glucuronoxylans are characteristic of softwood and hardwood hemicelluloses, respectively [8].

Additionally, a fraction of the hemicellulose sugars is more easily removed from the plant lignocellulosic matrix than the remainder, which are tightly embedded and cross-linked to the lignin present in plants. Studies on hardwoods have shown that glucomannans are the first type of hemicellulose sugars to rapidly degrade via the peeling mechanism, followed by the xylans, which are extracted in the oligomeric form [9]. When considering the optimum conditions for hemicellulose extraction, it is imperative to design for the removal of the

more labile sugar moieties and render the extraction more efficient to reduce process conditions and cellulose degradation to cater to digestibility considerations.

Sun et al. [10] reported improved xylan extraction in alkaline-methanol solvent aided by ultrasound treatment. The same group has also studied lignin solubilization in alkaline-methanol solvent aided by ultrasound treatment and extracted up to 78.5% of the original lignin contained in wheat straw [11]. Oliveira et al. [12] have reported delignification of up to 80% of the original lignin in sugarcane bagasse in an alkaline ethanol solvent system, subsequently extracting 55% of the hemicellulose. These studies take into account improved dissolution of the lignin in the organic solvents, thereby liberating the hemicellulose.

The present study does not focus on optimization of the alkaline extraction process because that aspect has been extensively investigated. Instead, we decided to outline a separation and concentration strategy to valorize hemicellulose from agricultural residues and have used mild alkaline extraction to evaluate the concept.

The principal hemicellulose type in corn stover is arabinoxylan, which essentially consists of a xylan backbone with arabinose substituents. A series of experiments were constructed to extract arabinoxylans from corn stover over a range of alkaline conditions by varying the temperature and the time of extraction. Mild extraction conditions were chosen to reflect scale-up and implementation into biorefineries from a green chemistry perspective.

Membrane filtration pertaining to bioprocessing

In contrast with conventional depth filtration, most membrane filters operate primarily on the superficial scale, accomplishing filtration on the surface and sub-surface [13]. The field of membrane filtration is classified primarily based on the particle size of the materials being separated. For the separation of macromolecules such as monosaccharides and polysaccharides, ultrafiltration is needed, operating in the range of 0.001 to 1 μm .

Ultrafiltration has previously been considered as a way to concentrate biopolymers, such as polysaccharides, over other techniques such as centrifugation and precipitation, primarily because ultrafiltration can be carried out at room temperature, and has greater scalability. From the perspective of generating concentrated hemicellulose extracts, membrane filtration affords a convenient way to separate hemicellulosic oligomers based on molecular weight, while preventing their degradation or chemical modification, because the unit operation can be undertaken at ambient conditions. The latter aspect also makes the technique attractive for implementation in larger-scale settings, because process conditions are not likely to be a limiting factor.

Jorda et al. [14] have studied the effect of filtering arabinoxylan and rhamnogalacturonan solutions. They found that a hollow fiber membrane with a molecular weight cut-off (MWCO) of 6 kDa provided the best results for arabinoxylan

purification. To improve pulp properties via addition of hemicellulosic oligomers to the kraft pulping mix of hybrid poplar, the oligomeric sugars were concentrated using membrane filtration as a less intensive and ambient temperature technique. This also provided the advantage of screening the sugar fractions based on their MWCO values.

Schlesinger et al. [15] used ultrafiltration and nanofiltration to separate and retain near-quantitative hemicellulose oligomers at sizes over 1000 g/mol. When it comes to preserving and retaining hemicelluloses, research efforts have shown progress using membrane separation techniques to separate galactoglucomannan oligomers from pulping liquors [16]. Wang et al. [17] have tried to retain hemicelluloses in a different fashion, by agglomerating the various interfering lignin macromolecular entities and then destabilizing them to separate these from hemicellulose-derived oligosaccharides. Similarly, Krawczyk and Jonsson [18] have studied microfiltration of thermomechanical pulp liquor, achieving a galactoglucomannan yield of ~50% using microfilters of various pore sizes.

Wallmo et al. [19] used a combination of precipitation and membrane filtration to study the role that kraft black liquor hemicelluloses play in the separation of lignin. Their findings, which show a considerable reduction in filtration resistance of the liquor when the hemicellulose content was reduced, clearly allude to an interference effect enacted by the carbohydrates. This finding raises interesting consequences for separations operations that need to account for the hemicellulose and the lignin fractions.

Li et al. [20] explored extraction of hemicelluloses from a kraft dissolving pulp preparation of three different hardwood chips in an acidic pre-hydrolysis stage before pulping. Inevitably, the authors noted conversion of the hemicellulose sugars into their respective hydrolysis monomers, and their subsequent degradation into small amounts of furfural. Although such a technique can be used for hemicellulose removal to convert into xylose-derived value-added products, it also strips off yield, which is already a matter of concern in the conventional kraft pulping operation. Interestingly, the presence of hemicelluloses that leads to their precipitation onto the cellulose fibers during kraft pulping is seen as an operational hindrance that leads to quality issues.

During alkaline kraft pulping, the glycosidic bond linking the uronic acid groups (4-O-methyl glucuronic acids) to the xylan backbone attached to it are preferentially cleaved. Release of the uronic acids results in a decrease of the solubility of the xylan, causing it to precipitate out of solution and subsequently adsorb onto the surface of the cellulose fibers [21]. Evidence for this re-precipitation of xylan oligomers onto cellulose (from bacterial, cotton, and dissolving pulp sources) was observed using atomic force microscopy and light scattering measurements [22]. Moreover, there is evidence that some of the hemicellulose oligomers in the alkaline cooking liquor act as sacrificial candidates to the peeling reaction, thereby preserving cellulose from small amounts of degradation. Extracting the hemicellulose before the alkaline pulping

process can reduce pulp yield by way of cellulose degradation.

To reduce the possibility of degrading cellulose by extracting the hardwood hemicellulose before pulping, we made use of the observation that extracted xylan can re-precipitate onto cellulose fibers during pulping by adding corn stover hemicellulose to increase bonding between pulp fibers. This strategy allows for the preservation of pulp yield, while providing a new application to an overlooked and underused resource. The fact that there is easily recoverable hemicellulose present in lignocellulosic feedstocks is exploited by the use of mild conditions that do not lead to full recovery, but enable better implementation into a cellulosic ethanol pretreatment regime, opening up the pathway to integration with a pulp biorefinery.

METHODS AND MATERIALS

Feedstock and chemicals

Dried and baled corn stover (*Zea mays*) composed primarily of stalk and very little cob, was sourced from the Arlington Agricultural Research Station (University of Wisconsin-Madison; Arlington, WI, USA) for performing the corn stover hemicellulose extraction experiments. Hybrid poplar (*Populus maximowiczii x nigra*) was harvested from northern Wisconsin after 10 years of age, and hand-debarked, chipped, and screened (2–8 mm) before air-drying to a moisture content of ~5%. Sodium hydroxide pellets (>97% purity) were sourced from DOT Scientific (Burton, MI, USA). Commercial grade arabinoxylan from corn cobs was procured from Shanghai Yuanye Bio-Technology Co. (Shanghai, China). The received material was analyzed independently and found to be 85.8% arabinoxylan, which was factored into experiments. Avicel PH-101 was procured from Fluka Analytical (Cork, Ireland) and was used to account for a correction factor during the measurement of carbohydrates on the corn stover and pulp samples.

Alkaline extraction

Small-scale extractions were performed in duplicate using 10 g samples of dried, baled, and ground (1.8–2 mm) corn stover in sodium hydroxide (NaOH) solution in 500 mL media bottles at a liquor-to-wood (L/W) ratio of 20:1. The sparse nature of the material necessitated the use of the high L/W ratio. Temperature control and stirring of the sample was accomplished using a shaker incubator set at the conditions being employed. For screening analysis, temperature conditions were selected at 20°C, 40°C, and 60°C. The sodium hydroxide concentration was set at 1 wt%, 2 wt%, and 3 wt%. The extraction times were varied between 1 h, 3 h, and 5 h.

Larger-scale extractions were carried out using 500 g of corn stover (ground and screened to 1.8–2 mm particle size) at conditions derived from the small-scale results in a large 20 gal pail mounted under a stirrer motor. The temperature was controlled by using a feedback-loop immersion heater maintained at 60°C for 5 h at an alkali concentration of 2 wt%. After extraction, the solid and liquid portions were separated. The latter was filtered to separate the undissolved solids in a Buchner funnel and concentrated using membrane filtration.

Membrane filtration

Corn stover extract derived from the large-scale extraction was fractionated into the permeate and retentate portions using a membrane filtration apparatus (Demofilter, Koch Membrane Systems; Wilmington, MA, USA) to separate the oligomeric hemicellulose sugars and concentrate them in the latter fraction. A hollow fiber membrane (Romicon HF UF cartridge, Koch Membrane Systems) with a pore size of 50 kDa was used to accomplish the filtration.

Tangential flow filtration was accomplished by using a Vivaflow 200 setup (Sartorius; Bohemia, NY, USA) with a 10 kDa MWCO cassette filter made of polyether sulfone membrane. Less than 1 L of the alkaline extract was filtered for 60 min; the retentate fraction measured about 100 mL. Tangential flow filtration with the 10 kDa MWCO cassette was also used to concentrate 6955 g of the corn stover alkaline hemicellulose extract to produce ~2056 g of the retentate for use in the large batch kraft cook. This gave rise to an effective concentration of 3.38-fold. Because of the large volume involved, this step was performed in multiple batches.

Kraft pulping

Preliminary experiments testing the addition of pure compound xylan to hybrid poplar kraft cooks were tested at a constant H-factor of 1200–1300 and an L/W ratio of 5:1. The effective alkali was 16 and the target sulfidity was set at 20. The cooks were carried out at the 30 g scale in pressurized reactors heated in a temperature-controlled oil bath, with frequent rotation. Xylan loadings were tested at the 5%, 10%, 20%, and 50% levels in duplicate by adding arabinoxylan from corn cobs. No xylan was added to the control cook. After pulping, the pulp was separated from the black liquor by decantation, washed with copious amounts of water to reduce the pH, and air-dried.

The large batch cook was conducted using 280 g (dry mass) hybrid poplar chips, with 2163.4 g of neutralized and concentrated corn stover hemicellulose extract that contained ~56 g xylan by mass, giving rise to a L/W ratio of 6.44:1. The cook was performed in a 20 L circulating flow reactor with a T_{max} of 165°C, an H-factor of 1200, a L/W ratio of 5:1, an effective alkali of 16, and sulfidity of 20.

Chemical analysis

Kappa numbers of pulps produced were determined using the micro-kappa method (TAPPI UM 246 “Micro kappa number”) in duplicate. Carbohydrate analyses for the corn stover feedstock, hybrid poplar pulps, and the extracted liquors were performed using ion-exchange chromatography using a Dionex ICS-3000 system (Thermo Fisher Scientific; Waltham, MA, USA) on a CarboPac PA-20 column (Thermo Fisher Scientific) equipped with a pulsed amperometric detector over a disposable gold electrode. This is according to a modified version of a previously described method [23] incorporating a correction factor based on Avicel conversion to calculate the final carbohydrate concentrations.

RESULTS

Carbohydrate content of corn stover

Extractive-free (acetone) samples of the corn stover were characterized for the carbohydrate content using high-performance liquid chromatography to account for the five prominent sugars, giving a total carbohydrate content of 62.8%. **Figure 1** shows the distribution, and these values were used to calculate xylan yields in subsequent sections.

Extracted liquor characterization

The percent solids (g/100 g) in the original extracted material and the membrane-separated fractions were determined by freeze-drying and weighing the dry material. This quantity allowed us to account for the separation of (primarily) the hemicellulosic sugars as a result of the membrane separation. The original extracted, unfiltered material contained ~8.27% solids (dissolved and undissolved). The undissolved materials were separated using a size 4 qualitative filter to yield a solids content of ~5.48%. The membrane separation resulted in a retentate solids content of ~7.51%. The permeate contained ~3.43% dissolved solids. Estimating the solids content makes it possible to quantify the oligomers as percent solids (rather than individual sugar oligomers), which can be useful for studying the effects of adding concentrated hemicellulose solutions to improve pulp properties.

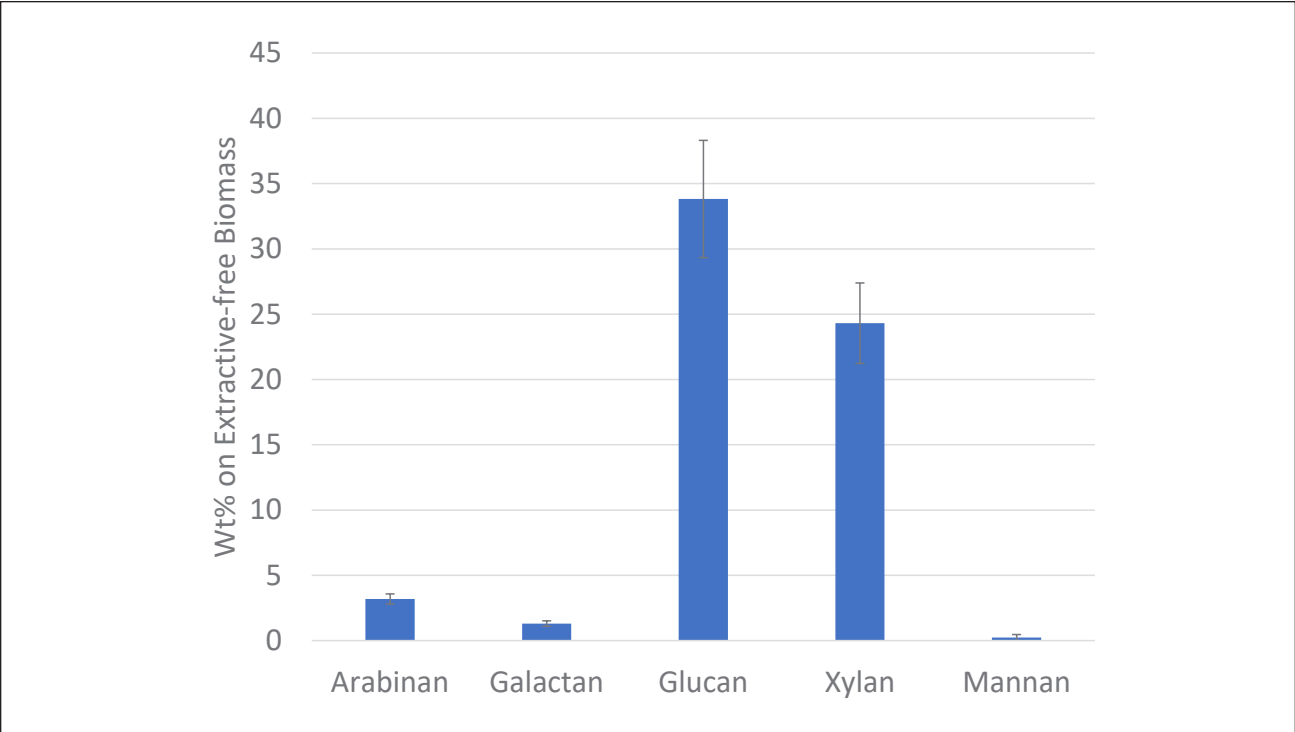
Small-scale extraction

Small-scale runs were conducted to identify optimal conditions to extract arabinoxylans. **Figure 2** shows the carbohydrate concentrations obtained from these experiments. As anticipated, xylan was preferentially extracted into the alkaline liquor at these mild conditions, whereas much of the cellulose was preserved in the stover solids. Run 8 with extraction conditions of 2 wt% NaOH for 5 h at 60°C yielded the highest xylan concentration at 8.76 g/L. Assuming complete recovery of the liquor, this xylan concentration corresponded with an extraction amount of 17.4 wt% on a dry solids basis, and 71.5 wt% based on the xylan amount present in the original feedstock; glucan extraction was minimal. The mannan concentration for the small-scale extraction runs were very dilute (this data has not been included in the figure). However, after concentration using membrane filtration, these were able to be detected (**Figs. 3 and 4**).

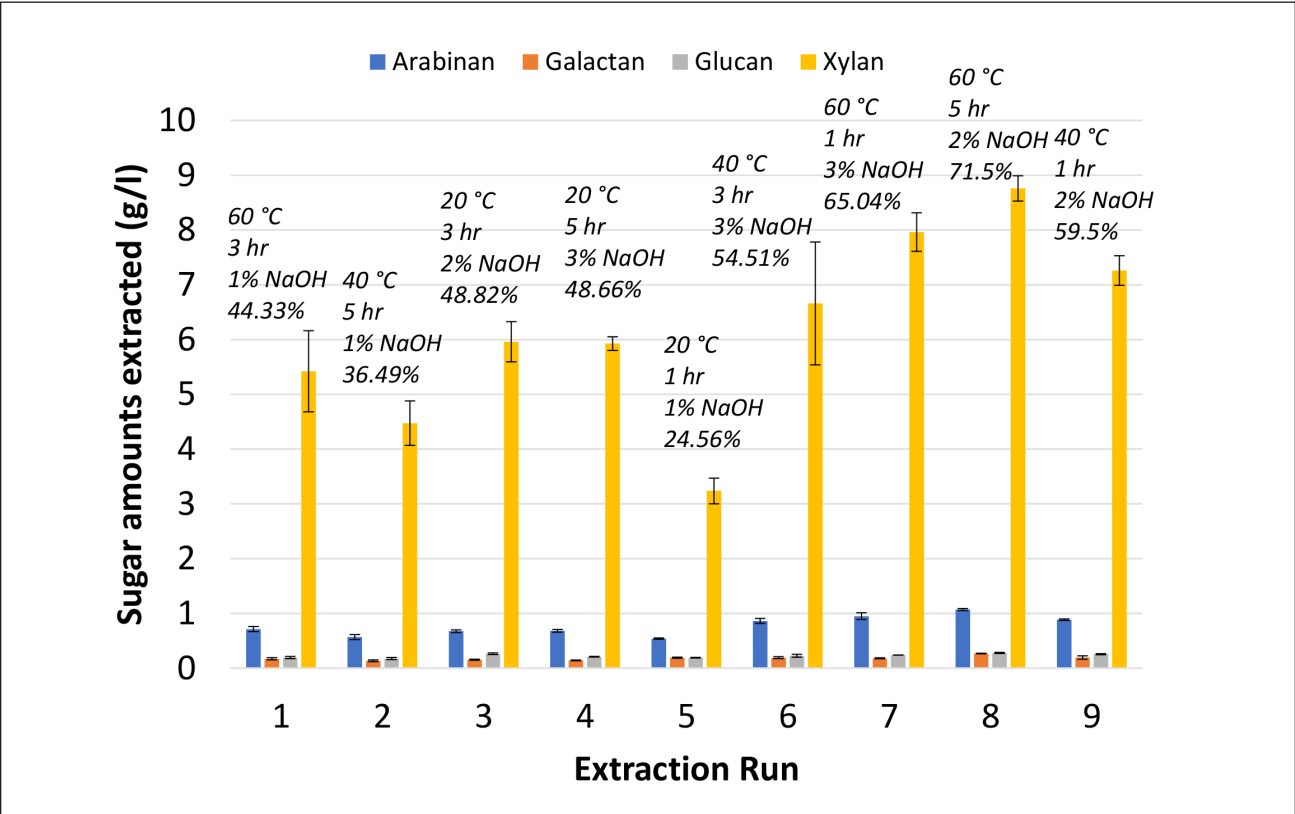
Large-scale extraction

Based on results from the small-scale extraction, the conditions that resulted in the greatest amount of arabinoxylans extracted were scaled up to extract 500 g of corn stover (in 2 wt% NaOH at 60°C for 5 h). Membrane ultrafiltration using hollow-fiber and tangential filters concentrated the xylan amount present in alkaline corn extract, accompanied by a reduction in total volume.

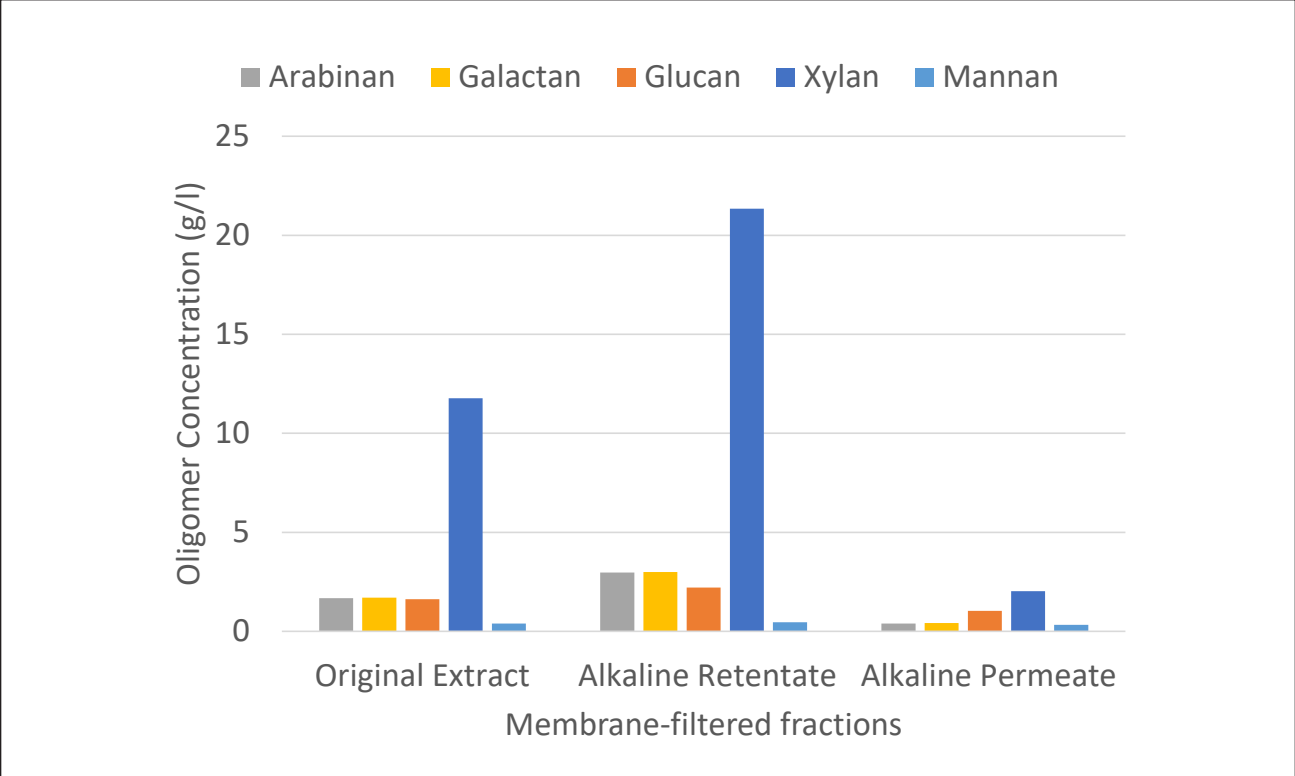
Based on the carbohydrate analysis performed (Fig. 3), ~11.7 g/L of xylan was extracted into the alkaline liquor extract when we replicated the conditions found during the



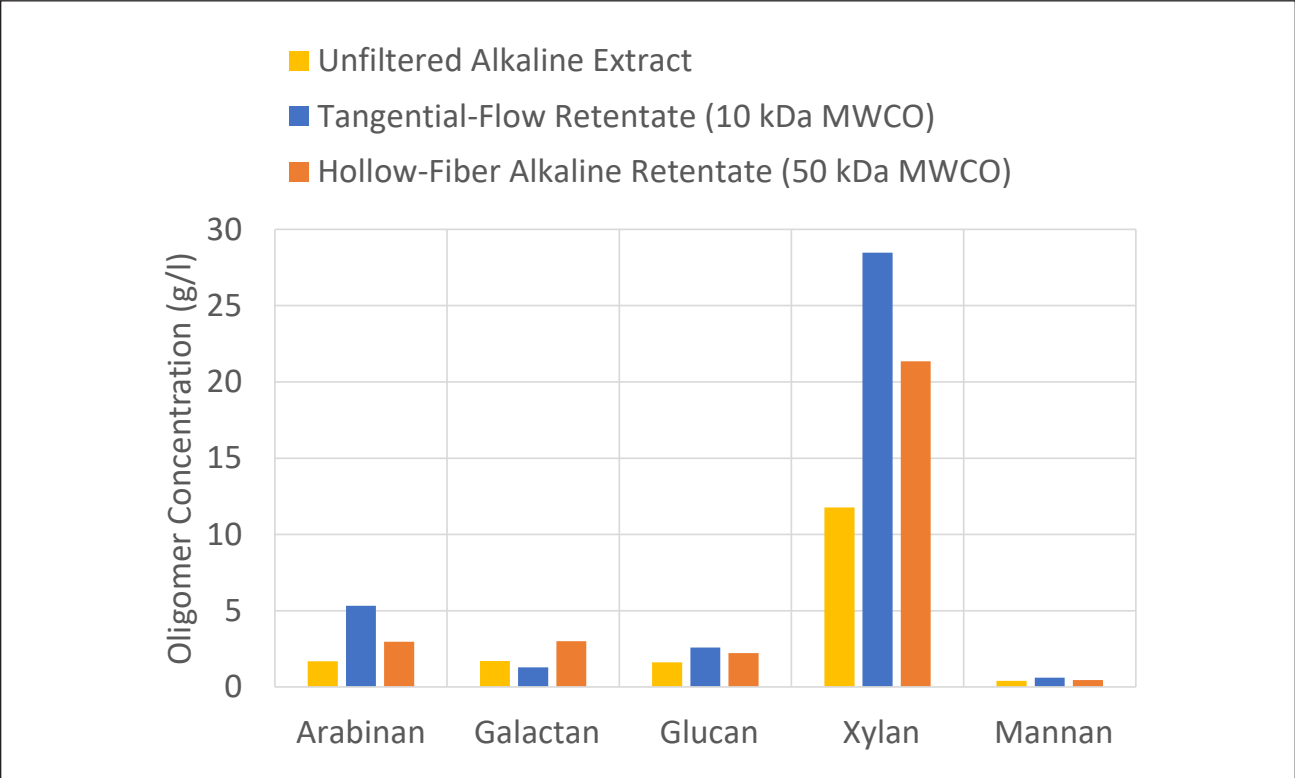
1. Carbohydrate content of the corn stover feedstock, as determined by high-performance liquid chromatography; error bars are shown as standard error for duplicate measurements.



2. Carbohydrate oligosaccharides extracted using mild alkali conditions (error bars showing the standard error for duplicates). The conditions used for the extraction runs, along with the yield of xylan (in percentages) based on the original amount in the corn stover is also reported (NaOH = sodium hydroxide).



3. Carbohydrate content showing the extent of oligomers extracted and separated using hollow-fiber membrane filtration (50 kDa molecular weight cut-off [MWCO]) in the original extract (unfiltered sample) and the membrane separated permeate and retentate fractions.



4. Comparison of the oligomer concentrations obtained by concentrating the corn stover alkaline extract using hollow-fiber and tangential membrane filtration processes, as determined by acidic hydrolysis followed by ion-exchange chromatography. The unfiltered extract is shown alongside for comparison.

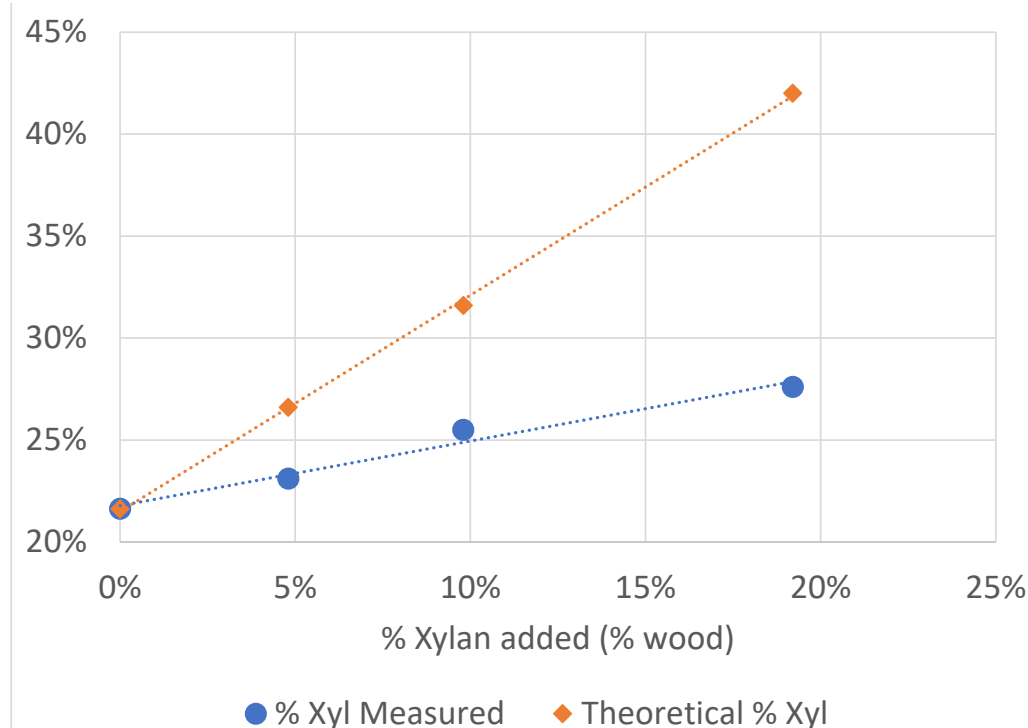
screening study (90.81% of the original xylan). This was greater than the xylan amount obtained in the screening study, and could be attributed to better mixing that was accomplished in the large batch extraction. Similar to the small-scale extraction runs, very small amounts of glucan (though greater than the small-scale) and other carbohydrates were extracted. Monomeric sugars were very low in concentration, and those of xylose and mannose were not detected in any of the fractions generated.

When filtered using the 50 kDa hollow-fiber membrane, the xylan concentration was increased almost two-fold, to 21.3 g/L. Slightly greater xylan and arabinan concentrations (28.5 g/L and 5.3 g/L, respectively) were obtained using the 10 kDa tangential flow membrane filtration apparatus (Fig. 4). For the tangential filtration system, 72.8% of the xylan contained in the feed was retained and concentrated during the filtration unit operation. Smaller oligomers and monomers would not have been retained, and 10.2% were collected in the filtrate. Although the smaller arabinoxylan oligomers and monomeric sugars are lost in the filtration operation, the goal of the study was to concentrate larger oligomers, which will translate well into improved bonding with pulp fibers. The concentration results suggest that a smaller MWCO might be a better size for concentrating the xylan oligomers than the 50 kDa hollow-fiber membrane, where there might be greater yield losses.

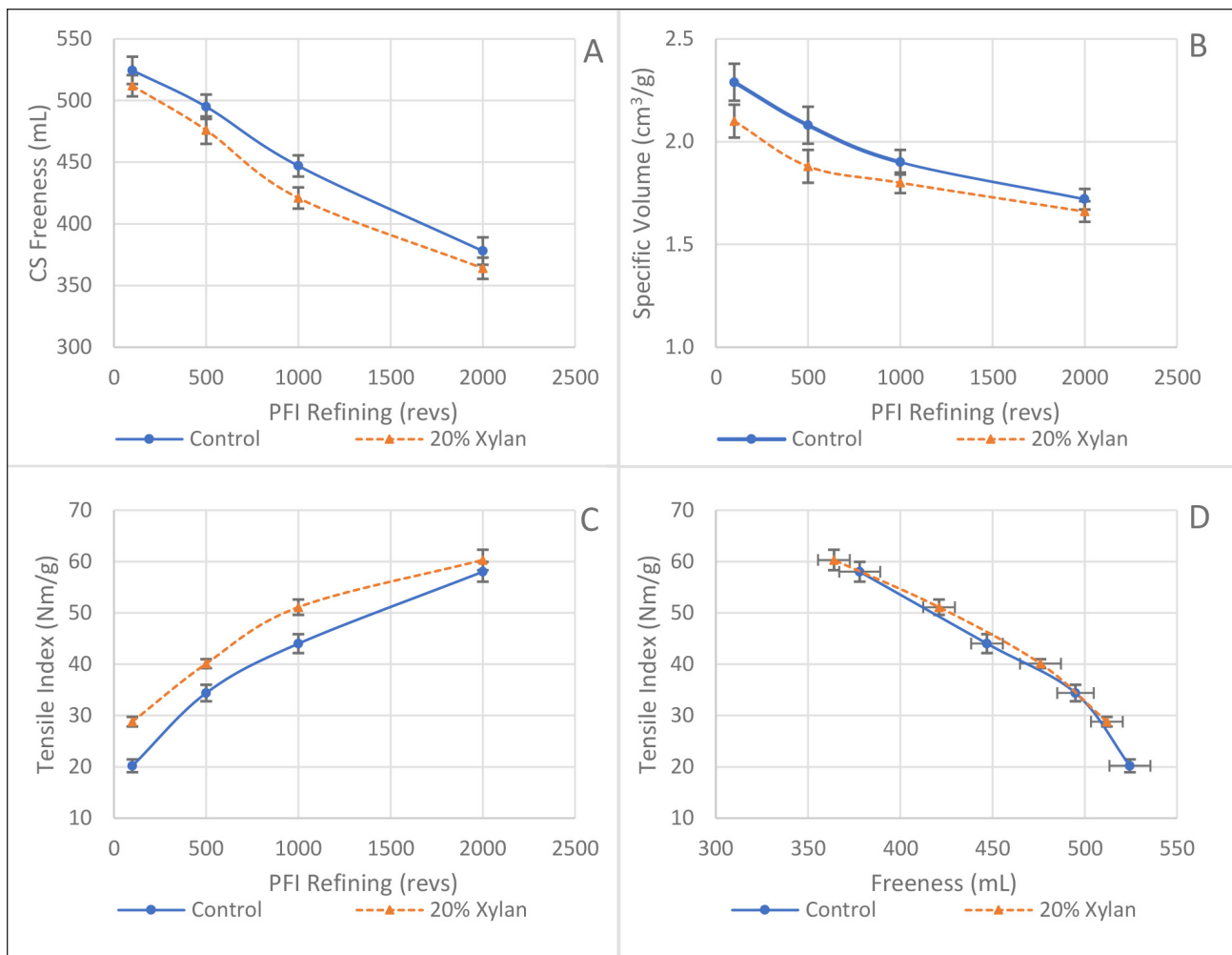
Kraft pulping with xylan addition

Small-scale kraft pulping experiments were performed using conditions mentioned in the experimental section to derive insights into the effect of xylan addition in the kraft cooks. The pulps produced in this study all had kappa numbers ranging from ~21.7 to ~30.4, so that they could all be compared on the basis of similar residual lignin content. Carbohydrate analysis on kraft pulp with xylan addition provided evidence of xylan adsorption on the pulp fibers, as predicted. Of the five wood sugars (arabinose, galactose, glucose, xylose, and mannose) tested for, only glucose and xylose were detected as monomers. The analysis calculated the measured mass percent xylan and the theoretical mass percent xylan, assuming that all the xylan added would be adsorbed (**Fig. 5**). Increased retention was measured for increased xylan loading, as expected. Interestingly, the adsorption linearly increased as a function of arabinoxylans added to the pulp between 5 wt% and 20 wt%, with approximately 1/3 of the xylan added being retained in the final product, regardless of the amount of arabinoxylans added.

Hybrid poplar pulps produced with xylan addition of 0% (control) and 20% charges were refined, measured for Canadian Standard Freeness (CSF), and then used to produce hand-sheets to measure physical properties of tensile index and specific volume. The resulting charts (**Fig. 6**), display a marked strength improvement for the arabinoxylans-modified



5. Kraft pulp carbohydrate analysis showing the amount of xylan adsorbed and how much there theoretically should be if 100% was retained with increasing amounts of xylan loading; control sample represented lack of xylan addition.



6. Handsheet physical properties comparing control to 20% xylan experimental pulps. Error bars denote standard error of handsheet replicates (n=3).

pulp, primarily for low refining levels, with the effect diminishing at 2000 PFI revolutions. Pulp strength increase from higher hemicellulose levels in pulps is well known, though typically the result of retaining the native hemicellulose from the wood, not from addition during pulping. Hemicellulose strength increase has been attributed to increased hydrogen bonding from surface hemicellulose and from an increase in fiber swelling because of the modification.

In conventional papermaking that includes the use of dry-strength additives such as cationic starch or polyacrylamide, the strength increase in the paper product could be attributed to bonding interactions between the strength agent and the pulp fibers. In this situation, as the dry-strength additives are generally added to the papermaking furnish, before forming the paper, the polyelectrolyte additives are retained on the surface. Being of large molecular mass, there is greater probability that these modifiers are retained on the surface through charge interactions, giving rise to greater surface hydrogen bonding [24]. In contrast, when the pulping is performed in conjunction with the hemicellulose modifiers (arabinoxylan,

in this case), the modifiers are hypothesized to be adsorbed into the interior of the fiber, instead of being excluded to just the surface.

The freeness (as measured by CSF in milliliters) decreases with increasing refining, as expected [25]. As this is ideal laboratory refining in a PFI mill, the refining effect increased drainage resistance in pulps. This effect is primarily due to fiber swelling, not an increase in fines. Interestingly, the arabinoxylans-modified pulp sample had a consistently lower freeness throughout the refining range than did the control pulp (Fig. 6A), alluding to increased fiber networks in the latter, and consequently, greater strength. Figures 6B and 6C also support the hypothesis that the arabinoxylans-modified pulps were initially more swollen. The modified pulp has a greater density (inverse of the specific volume) and greater tensile index at the lower levels of refining, but approaches the control at 2000 revolutions, where the effect of refining on swelling overcomes the effect of hemicellulose content on swelling. Swollen fibers are known to provide more strength but lower density after drying because of their im-

proved wet fiber flexibility. Figure 6D shows a correlation between the tensile index and the CSF, displaying both samples on the same strength-freeness curve. As expected, they share an inverse relationship, with increased strength from swelling resulting in decreased freeness. Interestingly, the arabinoxylans-modified pulp appears to be “pre-refined.” Unfortunately, this also suggests the arabinoxylans-modification does not provide greater strength than can be accomplished in pulps through refining.

DISCUSSION

The authors believe that the strategy proposed and evaluated in this paper outlines advantages and limitations to incorporating extracted hemicelluloses into the kraft pulping of poplar wood to incorporate a potentially low-cost material into the pulp and improve pulp strength properties at low refining levels. Such a strategy seeks to address multiple challenges in the current status of the biomass-based industry, add value to concentrated hemicellulose solutions, and demonstrate that they can be incorporated into a high-value pulp product.

Other researchers have studied the alkaline extraction of xylan from graminaceous plants and hemicellulose-rich agricultural residues. Generally, these studies have incorporated harsher extraction conditions, namely alkali concentration, time, and temperature. Chanliaud et al. [26] have reported that 10%–30% of the heteroxylans (arabinan, xylan, galactan, and glucuronic acids) in corn bran could be extracted using mild alkali conditions (1 M NaOH at 25°C for 24 h). Those results are similar to the results obtained in the current study. Greater yields (up to 90%) were also reported by the same authors by using different sources of the hydroxyl anion (KOH) and a temperature of 100°C. Cheng et al. [27] found optimum xylan extraction yields of 90% from depithed corn stover at NaOH concentration of 10% and 75°C, extracted for 2 h. Those authors also reported a slight decrease in the yield and physical strength properties of the soda-anthraquinone pulp as a result of the extraction. Under similar conditions, but over a much greater time, Xiao et al. [28] recovered between ~72% of the original hemicellulose sugars from corn stems, while simultaneously removing more than 7% of the glucan present in the material.

Our experimental results show that significant amounts of easily cleavable and recoverable arabinoxylans can be extracted in mild alkali to avoid degradation of the oligomers, and then concentrated to higher xylan concentration using hollow-fiber membrane filtration. Adding this material as a pulping additive allows approximately 33% of the material to be retained while also increasing pulp strength properties. This approach has the potential to improve the pulp yield and possibly improve profitability if hemicellulose extracts from agricultural resources can be made at low-enough cost. Future research will be required that focuses on concentrating polymeric hemicellulose extracts from agricultural residues and understanding the limitations of retention of the arabinoxylans during kraft pulping.

CONCLUSIONS

This work shows that hemicelluloses from inexpensive feedstock such as agricultural residues (corn stover) can be effectively recovered in mild alkaline conditions, concentrated and purified using membrane filtration, and blended into a kraft pulping cook to improve the strength properties of the pulp produced. This allows for the evaluation of a kraft pulping based biorefinery that integrates use of agricultural residues with novel separation strategies to produce pulp with improved properties. The present study did not address optimization of the various process parameters considered, but serves to illustrate the proof of concept of the implementation of concentrated hemicellulose from waste streams to expand the integrated kraft pulp biorefinery. We used mild alkali extraction that is common in pilot-scale cellulosic ethanol processes to recover easily extracted hemicellulose oligosaccharides and concentrate them to deliver a readily implementable blend to improve the strength properties of hybrid poplar pulp. The extracted residues are now more suited as substrate in a bioprocess that focuses on cellulose use, such as the production of bioethanol, as cellulose accessibility has now been improved. Future work should focus on optimization of the alkaline extraction process through a greater understanding of hemicellulose extractability and a study of the digestibility of the solid residues produced. The membrane filtration unit operations need to be optimized, targeting the parameters that encourage scale-up and commercialization (permeate flux and retentate concentration). **TJ**

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ABOUT THE AUTHORS

We chose this topic to study because, like many others, we have an interest in creating value from biomass hemicellulose, which could be a potential residual stream from cellulosic biorefineries. This led to the question: "Could agricultural residual, such as corn stover hemicelluloses, be incorporated into pulp to improve the economics of both systems, and if so, what would the resulting properties be?"

Previous research by our group has shown that co-cooking woods and nonwoods results in higher hemicellulose pulps. However, this is impractical from a digester loading standpoint. Therefore, we wanted to explore the incorporation of extracted grass hemicelluloses into hardwood pulps.

Determining a practical way of reacting the extracted hemicellulose oligomers with the wood chips for pulping was challenging, because the hemicellulose liquor was very dilute to begin with. Several methods of concentration were explored. Membrane filtration to concentrate the hemicellulose liquor was finally chosen as a promising unit operation for this purpose. Experimenting with different configurations and molecular-weight cutoffs helped us pick the appropriate filtration device for this aspect.

Being new to the field of pulp and paper science, we were fascinated by the number of theoretical conditions that needed to be taken into account when studying the adsorption of hemicelluloses into pulp fibers. An observation that could be practically taken for granted has a very interesting underlying

theory that needed exploration.

It is surprising to note that the added hemicellulose oligomers were incorporated into the pulp with a somewhat consistent ratio, regardless of the amount added. We were expecting higher adsorption at low levels and diminishing adsorption as we added more of the oligomers. This is a facet of the work that needs to be further explored.

This work benefits mills in demonstrating that adjunct hemicelluloses may be incorporated into their pulp products, and if obtained from a low-cost source, could provide an increase in sellable pulp mass. This work also underlines the importance of hemicellulose content on pulp properties.

Our next step will be to study the polysaccharide interactions in more detail, and to try and substantiate the mechanism of the arabinoxylans incorporation into the pulp.



Mandalika



Runge

Mandalika is graduate student and Runge is associate professor, Department of Biological System Engineering, University of Wisconsin-Madison, Madison, WI, USA. Email Runge at trunge@wisc.edu.