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**THE EFFECT OF HEMICELLULOSE ADSORPTION  
ON APPARENT SHEET DENSITY**

By

Christopher M Albert

B.A. University of Maine, 2018

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Chemical Engineering)

The Graduate School

The University of Maine

August 2020

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**THE EFFECT OF HEMICELLULOSE ADSORPTION  
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Thesis Advisor: Dr. Thomas J. Schwartz

An Abstract of the Thesis Presented  
in Partial Fulfillment of the Requirements for the  
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In recent years the demand for packaging paper grades has increased while the demand for printing and writing grades has continue to decline. Packaging grades are increasing in importance and are sold based on a combination of thickness and area rather than basis weight. This issue has driven the industry to produce paper board sheets of low apparent density to save fiber costs. The use of extracted xylan to produce paper with higher strength at a given density has been suggested in the literature; however the direct relationship between hemicellulose addition and apparent sheet density has received little attention in the literature.

Our work includes a literature review of the pulp fiber characteristics that affect apparent sheet density. Bleached pulp was treated with hemicellulose (beechwood xylan) in a 0.5M sodium chloride solution at 120°C for two hours. We observe a small decrease in apparent sheet density and a decrease in tensile strength index as the xylan loading increases. Analysis of the handsheets shows a lower hemicellulose uptake than the literature suggested. This discrepancy prompted an investigation into the mechanism by which hemicellulose, particularly xylan, attaches to cellulose surfaces. If the mechanism is

understood then the adsorption process can be tuned to maximize xylan uptake on pulp fibers, thus maximizing the effect on apparent sheet density.

The literature almost exclusively concludes that hydrogen bonding is the primary mechanism for xylan attachment onto cellulose surfaces, which we verify using a thermodynamics approach. We attempt to calculate an enthalpy of adsorption using the Van 't Hoff relationship and equilibrium constants from adsorption isotherms. Isotherms were collected in a temperature range of 35-95°C in 0.5M sodium chloride solution using Whatman 42 filter paper as a pure cellulose source. Isotherms were also collected using SigmaCell pure cellulose instead of Whatman 42 filter. Additional experiments were conducted with SigmaCell cellulose using deionized water and 1.0M sodium hydroxide for solvents.

The observed isotherms do not appear to be temperature-dependent, suggesting a very weak attraction between hemicellulose and cellulose. However, a decrease in uptake was observed in cases where sodium chloride was omitted from the system and increases in uptake when aqueous sodium hydroxide solution was used as a solvent. The ionic strength provided by the sodium chloride mitigates the negative charge repulsion between the xylan and cellulose. It is likely that the alkaline environment cleaves glucuronic acid substituents from the xylan backbone. This decreases the solubility of the xylan polymer causing it to aggregate, precipitate from solution, and finally adsorb onto cellulose surfaces. As suggested in the literature, hydrogen bonding and Van der Waal's forces are likely the dominant mechanisms for xylan adsorption onto cellulose.

## DEDICATION

*To Mike, Jane, Matthew, and everyone else who has helped me along the way. This is for you.*

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## TABLE OF CONTENTS

DEDICATION .....	ii
ACKNOWLEDGEMENTS .....	iii
LIST OF TABLES .....	vi
LIST OF FIGURES .....	vii
Chapter	
<b>1. THE EFFECT OF HEMICELLULOSE ON THE APPARENT SHEET DENSITY OF PAPER BOARD GRADES .....</b>	<b>1</b>
1.1. Motivation.....	1
1.2. Factors that Control the Apparent Density of Paperboard.....	3
1.3. Methods.....	6
1.3.1. Initial Moisture Experiments.....	6
1.3.2. Adsorption Experiments.....	7
1.4. Results & Discussion.....	8
1.5. Conclusions.....	14
<b>2. ADSORPTION OF XYLAN ONTO CELLULOSE FIBERS.....</b>	<b>15</b>
2.1. Adsorption of Xylan onto Cellulose Fibers: Literature Review .....	15
2.2. Methods.....	18
2.3. Results & Discussion.....	20
2.4. Conclusions.....	25
<b>3. METHODS FOR RETAINING HEMICELLULOSE DURING KRAFT PULPING AND SUGGESTIONS FOR FUTURE WORK.....</b>	<b>27</b>
3.1. Methods for Retaining Hemicellulose During Kraft Pulping: Literature Review.....	27
3.2. Methods.....	29
3.3. Cooking Data.....	31
3.4. Suggestions for Future Work.....	32
3.4.1. Factors that Control the Apparent Density of Paperboard.....	32

3.4.2. Fundamental Adsorption Experiments.....	33
3.4.3. Methods for Retaining Hemicellulos During Kraft Pulping.....	34
<b>4. REFERENCES.....</b>	<b>35</b>
BIOGRAPHY OF THE AUTHOR.....	38



## LIST OF TABLES

Table 1.	Xylan uptake calculated from acid hydrolysis of the handsheets.....	12
Table 2.	Carbohydrate compositions (%on carbohydrates) of pulps used for xylan adsorption.....	13
Table 3.	Control cooking data.....	31
Table 4.	Layered cooks at the following conditions: 85% Hardwood, 15% Softwood, 13.5% effective alkali, and 34% sulfidity.....	32

## LIST OF FIGURES

Figure 1.	Influence on apparent density of pulp solids content (obtained by partial drying of disintegrated pulp).....	9
Figure 2.	Comparison of guar galactomannan (■) and beechwood xylan (◆) and their influence on apparent sheet density.....	10
Figure 3.	Comparison of guar galactomannan (■) and beechwood xylan (◆) and their influence on tensile index .....	11
Figure 4.	Adsorption isotherms of four structurally different xylans adsorbed to bacterial cellulose.....	17
Figure 5.	Xylan uptake as a function of equilibration time, with each point collected in duplicate (■, ◆).....	20
Figure 6.	Isotherms collected at 95°C (●), 70°C (▲), 55°C (◆), 45°C (■), and 35°C (—).using beechwood xylan and Whatman 42 filter paper .....	21
Figure 7.	Isotherms collected with Sigma Cellulose at 35°C and 70°C.....	22
Figure 8.	Isotherms collected with Sigma Cellulose in the absence of Sodium Chloride at 35°C and 70°C.....	23
Figure 9.	Isotherms collected using Whatman 42 filter paper, Sigma Cellulose, and Sigma Cellulose in the absence of sodium chloride.....	24
Figure 10.	Isotherms collected at 35°C and 70°C using 1M sodium hydroxide.....	25

## CHAPTER 1

### THE EFFECT OF HEMICELLULOSE ON THE APPARENT SHEET DENSITY OF PAPER BOARD GRADES

#### 1.1. Motivation

When quantifying the benefits of recycling paper one needs to consider many factors such as the diminished sheet properties that come with recycling fiber and the impact of recycling on the environment. As pulp is recycled some of its properties diminish such as the tensile and burst strength indexes and fiber flexibility [1, 2]. These losses can be regained by refining [3]; however, this is not easily accomplished given the suspected strong hydrogen bonds formed when fibers undergo hornification [4]. Other end-of-life processing strategies should be considered for paper, namely incineration and landfilling. While recycling is always considered more favorable than landfilling from an environmental perspective, in the life cycle assessment (LCA) studies reviewed by Villanueva and Wenzel [5] there are a few circumstances that may lead to incineration being the more environmentally friendly option. Another factor when considering the environmental impact of a process is the global warming potential (GWP). GWP is defined as the amount of energy 1 ton of gas emissions will absorb relative to the amount of energy 1 ton of carbon dioxide will absorb over a given amount of time [6]. On the basis of GWP, there is little difference between incinerating and recycling paper fiber, dependent on many factors including mill efficiencies, energy sources used during production, and paper grade produced. Björklund and Finnveden claim that the GWP is higher for recycling paper board when waste incineration is used to replace the burning of fossil fuels. Björklund and Finnveden state that recycling and incineration are both better than landfilling. The methane

captured from the landfill provides less energy than incineration would, making landfilling undesirable from a GWP and energy perspective [7]. However, a more recent study by Merrild *et al.* claims that paper recycling is always favorable when biomass normally used for paper production is used to produce energy [8]. Given this information, it would make sense to use virgin fiber as efficiently as possible. If less fiber can be used to produce a given sheet of paper, then a mill will observe material and energy savings. These savings can be carried further through the process as well. Papermaking with recycled fibers requires less energy than is required for paper production from virgin sources [8]. Presumably if less fiber is used for the initial sheet (thereby requiring less energy and material) there will be a decrease in the energy required to recycle that sheet of paper. To put it differently, less pulp fibers used in a given paper sheet means less energy used for production of virgin and recycle sheets. Packaging grades are in a unique position to reduce pulp fiber usage. Unlike printing and writing grades that are traditionally sold by basis weight, packaging paper grades are often sold by area. If papermakers can produce a sheet of equal volume but with less fiber (*i.e.*, a less dense sheet) while holding the physical and optical properties constant then they may reduce their material consumption. In 2005 Danielsson and Lindström claimed that material savings of 7.3 million euros could be achieved assuming 3.3% less pulp could be used and pulp costs were 440 euro ton<sup>-1</sup>. There is also an uncalculated additional energy savings from having to beat the fiber less [9]. A significant body of work exists documenting various strategies to increase pulp yield [10], and the effects of hemicellulose on paper strength [9, 11, 12]; however limited attention has been given to factors that influence apparent sheet density. Some methods of reducing sheet density include the modification of pulp fibers and the optimization of paper fillers. Knox *et al.*

show that the addition of attritor-treated, bleached softwood pulp to a paperboard sheet reduces sheet density. They propose it is possible to reduce fiber usage by adding attritor-treated softwood fibers to a paperboard sheet while refining the base softwood furnish to maintain the elastic modulus of the paperboard sheet [13]. Zhang *et al.* show that co-flocculating fines and fly ash-based calcium silicate in a ratio of 0.3 (fines to fly ash-based calcium silicate) can significantly decrease sheet density while increasing the tensile index of a paper sheet [14]. This thesis aims to first review the literature on sheet density and pulp yield improvements to elucidate which fiber properties and pulping conditions can be linked to apparent sheet density. Then, knowing these factors we will investigate the effect of adsorbed hemicellulose on apparent sheet density. Once the effect hemicellulose has on sheet density is understood, we will investigate methods of increasing the hemicellulose content in pulp and their effect on sheet properties.

## **1.2. Factors that Control the Apparent Density of Paperboard**

Dinwoodie discusses physical fiber characteristics that affect sheet density. Sheet density is related to three factors: the fiber length, diameter, and cell wall thickness. Dinwoodie claims that at a constant fiber length an increase in fiber diameter will reduce fiber rigidity and result in more fiber collapse, *i.e.*, a denser sheet of paper. An increase in the length of fiber at a constant diameter will increase the number of fiber crossings and is expected to decrease sheet density [15]. Dinwoodie in his review of the literature also reports that there is a positive correlation between sheet density and the ratio of lumen size to total fiber diameter, that is as fiber wall thickness decreases fiber flexibility increases, resulting in fiber conformability and a

denser sheet of paper [16]. As the fiber diameter grows in relation to the lumen size the density of the paper sheet should decrease. The difference between the lumen size and overall fiber diameter is the cell wall thickness, and one can expect that as cell wall thickens sheet density decreases. We know this to be true. Gorres sees this in the measured sheet densities of different species of wood. Sheets made of Douglas Fir have the lowest sheet density of any sheets produced from the 10 chemical pulps measured in the study. This finding is unsurprising because Douglas Fir fibers are long, coarse, inflexible, and have a thick cell wall [17]. The important question then becomes how does hemicellulose influence fiber morphology and thereby contribute to sheet density? Köhnke *et al.* investigated the preventative effect of hemicellulose on hornification and showed that hemicellulose adsorbed onto bleached softwood pulp improves the rewetted fiber flexibility when compared to the control. BET surface area measurements were made for treated and untreated pulps before and after drying. It was found that the pulps treated with xylan before drying retained a significant amount of their original surface area. This suggests that the adsorbed xylan prevents fiber wall collapse during drying. An increase in fiber saturation point of never-dried and rewetted fibers treated with hemicellulose also suggests an increase in fiber swelling [18]. Joutsimo and Asikainen note that fibers swell in the direction of the fiber lumen, increasing fiber wall thickness [19]. Increasing the cell wall thickness should decrease fiber flexibility and decrease sheet density. By filling the pores in the interrupted lamellae with hemicellulose [20], the fibers should be more resistant to collapse, which would lead to higher stiffness and lower apparent densities. Recent work from Tavast *et al.* [21] and Ban *et al.*, [11] support this hypothesis. Each show that sheets with increased amounts of hemicellulose are stronger for a given sheet

density at constant basis weight. Put differently, a sheet with added hemicellulose is less dense than an equivalently strong sheet containing no added hemicellulose. Therefore, by increasing the hemicellulose content of pulp one should be able to produce sheets of a lower basis weight without any substantial loss in strength. Danielsson and Lindström demonstrate this effect by replacing the black liquor in a softwood cook with xylan-rich black liquor (from a hardwood cook) after 3 hours of reaction time. The resulting pulp had an increased tensile stiffness index at a given sheet density and had an improved beating response, *i.e.*, it takes less beating energy to get to a given tensile strength index. Molin and Teder pulp spruce chips 10 different ways to demonstrate the effect of hemicellulose content on paper properties. Similar to the previously mentioned literature, pulp with a higher hemicellulose content is shown to have a higher tensile strength index at a given sheet density [22]. This is of particular interest because when xylan is added a less dense sheet can be produced if less beating is used [9]. We hypothesize that the relationship between hemicellulose content and apparent density is similar to that associated with hornification and apparent density. For chemical pulps, the fiber wall collapses and the pores in the surface of the fiber are closed during drying. It is often proposed that the inside surfaces of the fiber pores and walls hydrogen bond to each other during drying. Upon rewetting, the fibers become stiffer despite the fact that they are collapsed due to the irreversibility of the pore closures and fiber wall collapse [18]. Zhang *et al.* show that unbleached pine kraft pulp fibers lose flexibility after drying and rewetting [2] and Howard *et al.* have shown that sheets made from beaten, unbleached kraft pulp decrease in density and fiber saturation point the more the fiber is recycled [1].

To demonstrate that stiff fibers lead to a sheet of low density, we induced hornification in a virgin pulp by drying the pulp to various solids content. This should lead to sheets of various densities, based on the recycle paper literature discussed above. We next evaluated the influence of hemicellulose sheet density. The literature shows that increasing the xylan content on softwood pulp fibers should lead to an increase in the sheet strength at a given sheet density. The increase in sheet strength due to xylan addition could allow for a decrease in basis weight while maintaining the strength of the original sheet. The increase in sheet strength has not been observed for hardwood fibers [9,11]. Because the favorable sheet properties are observed when hardwood hemicellulose is applied to softwood fibers it stands to reason that there may be a benefit to cooking or pretreating mixes of hardwood and softwood chips together. That is, it may be possible to cook the chips and transfer excess xylan from the hardwood onto the softwood inside one digester. Thus, it is necessary to investigate the impact of adsorbed hemicellulose has on sheet properties for a consistent blend of softwood and hardwood fibers.

### **1.3. Methods**

**1.3.1. Initial Moisture experiments.** Pulp, consisting of 85% hardwood and 15% softwood fibers, was obtained from Sappi's Somerset mill. Batches of 24g dry fiber were dried to solids content of 12.4%, 15.4%, 33.4%, 48.1% 65.6%, 78.1%, and 100.0%. The pulp dried to solids content of 65.6% and 78.1% were dried in 5 ODg (oven dried grams) batches to the desired solids content using a hot plate to prevent pulp burning. The rest of the pulp batches were broken up into bead sized pieces and dried to the desired solids content in an oven set at



100°C. These partially dried batches were independently re-pulped, and formed into handsheets following Tappi standard T-205.

**1.3.2. Adsorption Experiments.** Following the procedure outlined by Köhnke [12], 24 ODg of pulp was placed in a 1 L autoclave-safe jar and water was added such that the fiber concentration was 50g L<sup>-1</sup>. The xylan (beechwood xylan >95.0%, Megazyme, Inc.) and sodium chloride (sodium chloride (Crystalline/Certified ACS ≥99.0%, Fisher Scientific) solution was prepared by bringing approximately 500g of water to 95°C, the xylan was added and the solution was allowed to stir at 95°C for 15 minutes. After 15 minutes the heat was turned off and enough sodium chloride was added to produce a 1.0M solution. Initial xylan loadings of 80, 160, and 320 mg ODg<sup>-1</sup> were used. The xylan and sodium chloride solution were then added to the pulp slurry and shaken to produce a final pulp concentration of 25 ODg L<sup>-1</sup> and sodium chloride concentration of 0.5M. An autoclave was used as a heat source for the pulp, which was treated at 120°C for two hours. The pH of the final pulp slurry was measured before and after treatment and was between 3 and 4.. After cooling down enough to be handled the pulp suspension was filtered with Whatman 42 filter paper. A sample of the filtrate was taken and frozen until hydrolysis could be done. The pulp was washed until the conductivity of the suspension was less than 5µS/cm. Handsheets were made using Tappi T205 sp-02. Sulfuric acid was added to the filtrate to yield a concentration of 4wt%. The solution was hydrolyzed for one hour at 121°C. Fucose was used as an internal standard and added to the samples to achieve a concentration of 0.5g L<sup>-1</sup>. The samples were filtered through a 0.45µm syringe filter ((Syringe Filters with Polypropylene Housing, 25mm, Nylon, 0.45µm, Nonsterile, VWR) before being

analyzed by High-Performance Anion-Exchange Chromatography (HPAEC) using a CarboPac PA1 column.

Sheet density for both sets of experiments was calculated using the sheet basis weight and caliper after the sheets had been conditioned in a Tappi Room.

#### **1.4. Results & Discussion**

Figure 1 shows that as the solids content of the pulp increases the apparent density decreases. This is to be expected as Zhang *et al.* show that unrefined pulp fibers lose flexibility when dried. Sheets made from recycled fiber are also shown to be less dense than those made with virgin fiber [2]. Notably, the sheet density starts to decrease substantially at a solids content of approximately 48.1%. Maloney *et al.* propose that hornification for air dried unbeaten pulp starts at a solids content of 45.5% [4]. As more hornification happens the sheet density decreases. This suggests that as the amount of stiff fibers increase sheet density decreases.

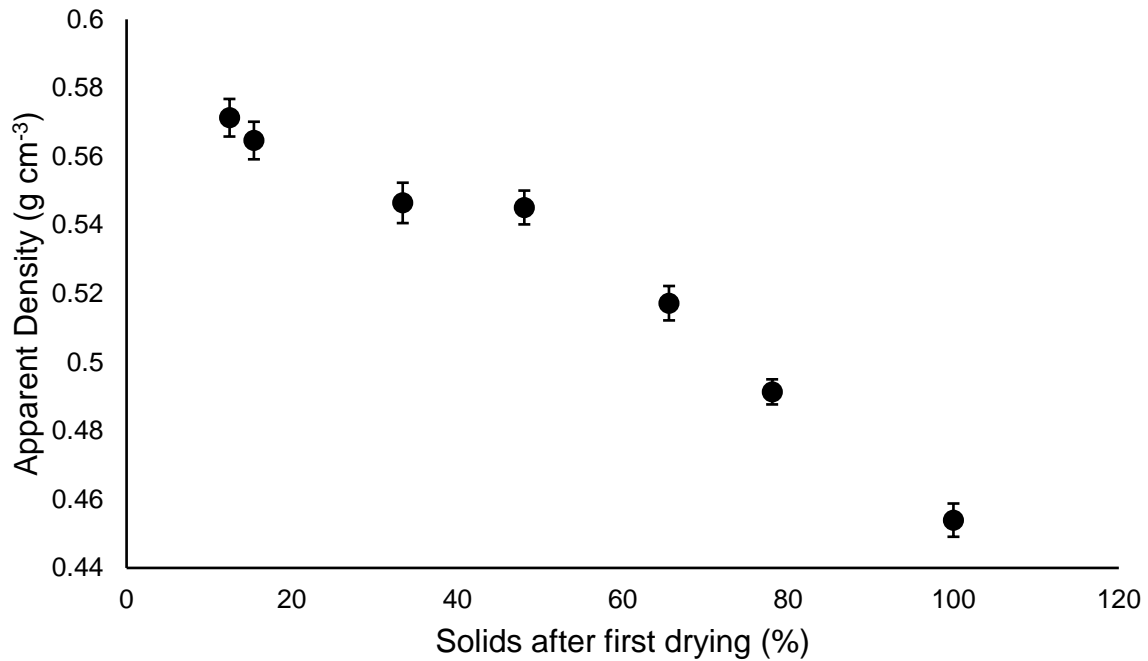


Figure 1: Influence on apparent density of pulp solids content (obtained by partial drying of disintegrated pulp). Error bars correspond to 95% confidence intervals obtained from at least 10 measurements.

As shown in Figure 2, there is a small decrease in the apparent density of the sheet when treating the pulp with beechwood xylan or guar galactomannan. While this trend appears significant, it is not immediately clear how impactful such a small decrease in density will be.

The data presented in Figure 3 indicates that the tensile index (as a metric for sheet strength) varies non-monotonically with respect to increasing hemicellulose loading, suggesting a complex effect.

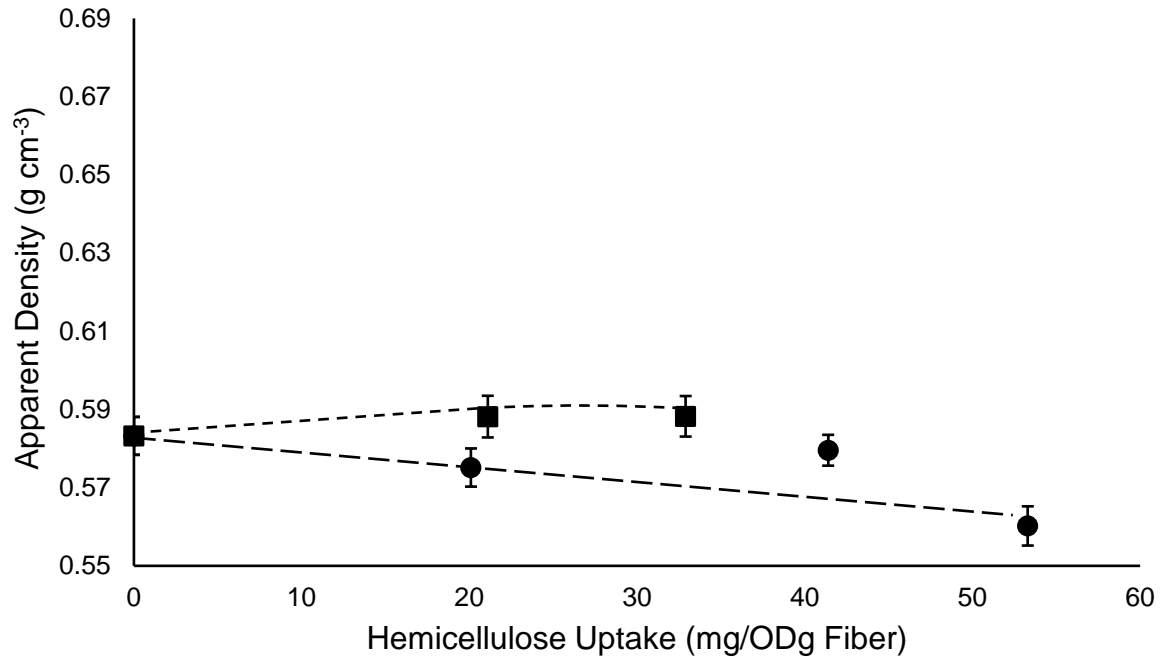


Figure 2. Comparison of guar galactomannan (■) and beechwood xylan (◆) and their influence on apparent sheet density. Error bars correspond to 95% confidence intervals obtained from at least 10 measurements.

Based on the literature for xylan adsorption (*vide supra*), the moderate effects observed here are unsurprising given that the pulp used is mostly hardwood [11]. One possibility for the minimal observed effect is the structure of beechwood xylan. To identify whether xylan structure has a meaningful influence on density, we used guar galactomannan as a source of hemicellulose and followed the same procedure as above. As shown in Figures 2 and 3, there is no substantial difference between the influence of guar galactomannan and that of beechwood xylan. There were also minimal differences in the tensile index when comparing beechwood xylan and guar galactomannan (guar galactomannan medium viscosity >98%, Megazyme Inc.)

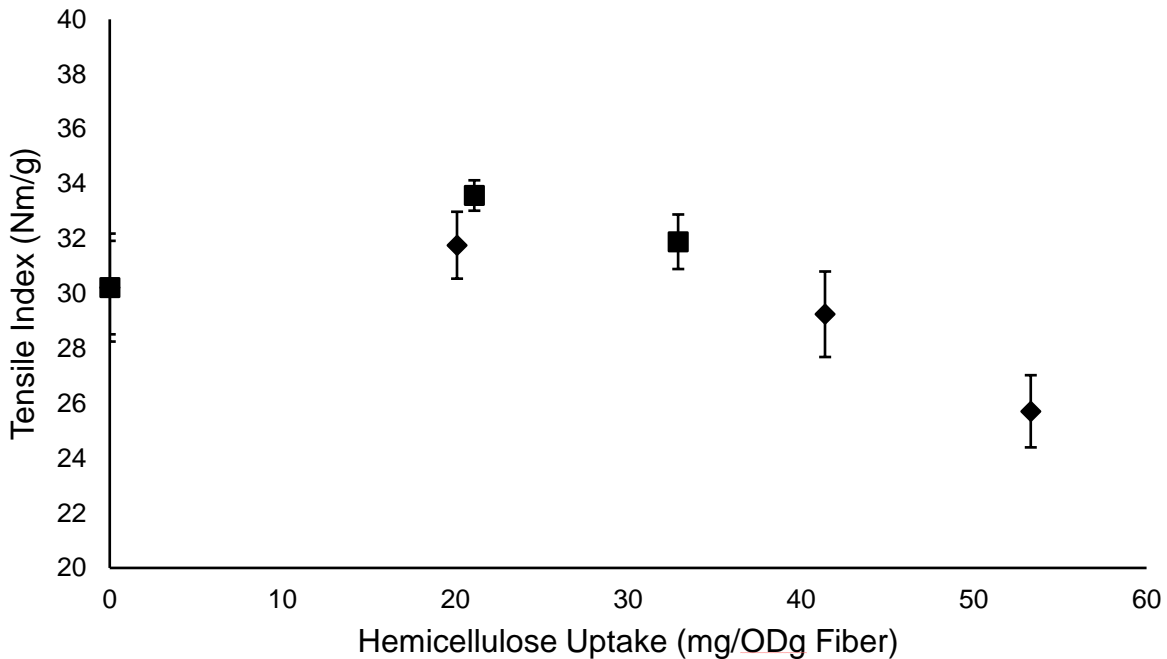


Figure 3. Comparison of guar galactomannan (■) and beechwood xylan (◆) and their influence on tensile index. Error bars correspond to 95% confidence intervals from 10 independent measurements.

Another potential reason for the moderate effects observed in Figures 2 and 3 is the low uptake of xylan on the Co-Pulp fibers. Consequently, the filtrate from each experiment was hydrolyzed and analyzed using HPAEC. The amount of adsorbed xylan was calculated by the difference between the mass of xylan charged and the mass of xylan remaining in the filtrate following adsorption. Control sheets and sheets loaded with 320mg/g dry fiber were also hydrolyzed and analyzed by HPAEC. The amount of adsorbed xylan was determined by difference between the control and treated sheets. Table 1 shows the amount of adsorbed xylan compared to Köhnke's small scale adsorption experiments [12]. The amount of adsorbed xylan calculated from the sheet hydrolysis is likely more accurate because the amount of xylan in the sheet is being measured. After the pulp was treated it was washed several times it is possible that some

adsorbed xylan was lost during these washing steps. The measurement of the filtrate may be an overestimation. There is a large difference between the amount of xylan adsorbed in the experiments with Co-pulp and Köhnke’s experiments. Notably, adsorbing less xylan is consistent with the minimal effect observed in Figures 2 and 3.

Table 1: Xylan uptake calculated from acid hydrolysis of the handsheets.

<i>Hemicellulose Charged (mg/g OD Fiber)</i>	<i>Adsorbed Xylan From Sheet Hydrolysis<sup>a</sup> (mg/g OD fiber)</i>	<i>Adsorbed Guar From Sheet Hydrolysis<sup>a</sup> (mg/g OD fiber)</i>	<i>Adsorbed Xylan From Literature (small scale experiments)<sup>12</sup></i>
80	20.1	21.1	40
160	41.4	32.9	60
320	53.3	N/A <sup>b</sup>	100

a. Adsorbed xylan calculated using the difference between charged xylan and xylan remaining in the filtrate is not shown due to the inaccuracy of measurement.

The difference in carbohydrate composition of each of the pulps could explain the difference in uptake. Table 2 below shows the carbohydrate composition for the TCF bleached softwood as well as an estimate of the carbohydrate composition for pulp used in our experiments. The hardwood pulp has a larger percentage of xylan than the softwood, which is possibly a cause of the low amount of adsorbed xylan observed in our experiments. The xylan on the hardwood fibers may inhibit more xylan from adsorbing onto the fiber surface. Köhnke used TCF bleached softwood for his experiments while Co-pulp is a mixture of softwood and hardwood pulps. The pulp received from the mill is also bleached using elemental chlorine free (ECF) methods. We do not believe at this time that the difference in bleaching method is the cause of the contrast in adsorption yields as the literature shows that tree species has a greater effect on carbohydrate composition than bleaching method [23].

Table 2: Carbohydrate compositions (% on carbohydrates) of pulps used for xylan adsorption.

TCF bleached softwood pulp,<sup>12</sup> ClO<sub>2</sub> bleached hardwood pulp<sup>23</sup>, and the Pulp used in this work.

	<i>TCF Bleached Softwood<sup>12</sup></i>	<i>ClO<sub>2</sub> Bleached Hardwood<sup>23</sup></i>	<i>Pulp Used in This Work<sup>a</sup></i>
<i>Arabinan (Arabinose)</i>	0.8	0.4-0.5	0.5
<i>Galactan (Galactose)</i>	0.2	0	0
<i>Glucan (Glucose)</i>	84.7	72.8-77.8	74.6-78.8
<i>Xylan (Xylose)</i>	8.3	19.9-25.1	18.2-22.6
<i>Mannan (Mannose)</i>	6.0	1.6-1.9	2.3-2.5

a. Estimated as the weighted average of hardwood (85%) and softwood (15%) pulps.

However further investigation of the literature shows that xylan uptake for unbleached softwood and hardwood pulps are similar [11]. This would suggest that the initial xylan in the pulp is not the root cause of the hindered adsorption. The literature has shown that pH has an effect on adsorption which will be discussed at length in the next chapter of this thesis. It is likely that the low pH of our experiments (between 3 and 4) adversely affected the adsorption (*vide infra*). Similar work involving the treatment of unbleached softwood pulp shows with galactomannan shows that almost complete adsorption is observed at low addition levels (1-4% on pulp). At higher addition levels, greater than 6%, the uptake starts to plateau [24]. While we are primarily concerned with xylan uptake, the plateau observed during galactomannan adsorption suggests there is a maximum uptake of hemicellulose that can be achieved regardless of hemicellulose charge. That is, we will approach a region where hemicellulose uptake will remain constant despite changes in initial hemicellulose charge.

## 1.5. Conclusions

Inducing different levels of hornification in bleached Kraft pulp does decrease the apparent sheet density. This is in agreement with the literature as drying pulp fibers has been shown to reduce fiber flexibility and sheet density [1,2]. As the extent of hornification increases the number of stiffer fibers increases, reducing sheet density. This happens at a solids content of 48.1% which is comparable to the proposal of Maloney *et al.* that hornification starts at 45.5% solids for pulp dried at room temperature [4]. Using the procedure outline by Köhnke resulted in approximately half the amount of xylan uptake expected from the literature [12]. This likely is the cause of the minimal effect observed on sheet density. The cause of the decreased uptake is most likely the low pH of the adsorption experiments and not the initial carbohydrate composition of the pulp as previously thought. The literature shows only slight changes in sheet strength at a constant density for hardwood pulps treated with hardwood hemicelluloses at an adsorption yield of 9.23% [11]. We hypothesize that increasing the adsorption yield will increase the effect on sheet strength at a constant sheet density.



## CHAPTER 2

### ADSORPTION OF XYLAN ONTO CELLULOSE FIBERS

#### 2.1. Adsorption of Xylan onto Cellulose Fibers: Literature Review

To fully explain the results of the above experiments, it is necessary to understand the mechanism by which xylan attaches to cellulose fibers. The literature proposes that hydrogen bonding is the mechanism for adsorption in the wet state [25]. Activation energies for xylan adsorption onto cellulose of  $4.4 \text{ kcal mol}^{-1}$  [26] and  $2.01 \text{ kcal mol}^{-1}$  are reported [9]. These are consistent with the activation energy requirement for adsorption by hydrogen bonding, 3 to 5  $\text{kcal mol}^{-1}$  [26]. Paananen et al suggest that hydrogen bonding may not be the mechanism by which xylan attaches itself to cellulose. They claim that if hydrogen bonding is the mechanism then the hydrogen bonding between xylan and cellulose should be stronger than either of the polymer's hydrogen bonding to water in an aqueous solution. They claim that if the bond is that strong then the xylan should lie flat on the cellulose surface. The weak adhesion and swollen layers of xylan on the cellulose surface suggest that hydrogen bonding is not the primary mechanism of adsorption. The mechanism is suggested to be twofold; a combination of van der Waals' forces and an entropy increase due to solvent release upon polymer adsorption [27]. Linder et al have shown that this is not the case in an alkaline environment, rather xylan aggregates adsorb onto the cellulose surface [28]. Paananen *et al.* also claim that due to the low solubility of xylan at a pH of 10 a weak attraction such as van der Waals' forces would be enough to drive adsorption [27].

CP/MAS  $^{13}\text{C}$  NMR spectroscopy experiments conducted on kraft birch pulp support the idea that xylan is weakly bound to the cellulose surface as multilayers or aggregates. CP/MAS  $^{13}\text{C}$  NMR spectra of fully hydrated xylan displayed the C-4 signal at a resonance of 74.3 ppm. For

dry xylan the C-4 carbon is shown to resonate rather broadly at approximately 82ppm. A broad resonance is an indication of a non-crystalline structure. Birch Kraft pulp was examined in the hydrated state and a decrease in the signal associated with xylan located at accessible fibril surfaces (81.7 ppm) after treating pulp with xylanase. The difference between the C-4 signal for the xylan in the birch pulp (81.7 ppm) and the C-4 signal in the lone hydrated xylan (74.3 ppm) suggests that the xylan structure is different depending on the environment it is in. The shift in resonance coupled with the easy removal of xylan with xylanase (demonstrated with a decrease in intensity at 81.7 ppm) suggests that xylan exists as multilayers or aggregates on the fiber surface [29].

Kabel *et al.* conducted several adsorption experiments using various types of xylan and bacterial cellulose. The xylan types included wheat arabinoxylan, linear oat spelt xylan, acetylated xylan, and deacetylated xylan from eucalyptus. Their findings show that less substituted xylan adsorbs more favorably on a bacterial cellulose surface when compared to a more substituted xylan. The eucalyptus xylan without *O*-acetyl groups still contains a 20 4-*O*-methylglucuronic acid groups per 100 xylosyl residues which is considered high [30]. However, previous work has shown that eucalyptus xylan was nearly completely degraded by endoxylanase I, which suggests a low number of substituents on the xylan backbone [31]. It has also been found that certain oligomeric fractions of eucalyptus xylan are substituted with two 4-*O*-methylglucuronic acid residues. Similar fractions were found to contain an additional hexose unit thought to be galactose [32]. This information leads to the thought that the majority of the xylan backbone is left unsubstituted and available for adsorption onto a cellulose surface. This is in agreement with other literature claiming that less substituted xylan is better suited for

adsorption onto cellulose surfaces. There are several reasons for this including steric repulsions, xylan hydration, and an increase in xylan-xylan interactions. [33]

The plot below shows that isotherms that Kabel *et al.* collected [30].

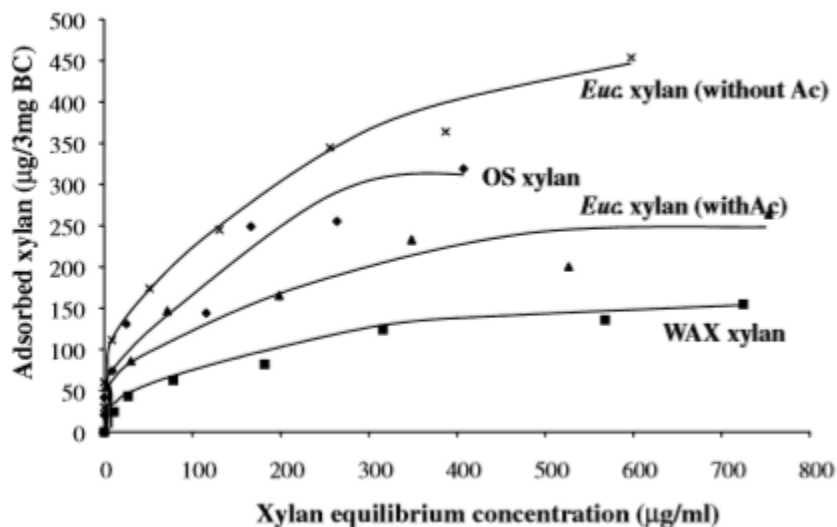


Figure 4: Adsorption isotherms of four structurally different xylans adsorbed to bacterial cellulose [30].

Temperature has been shown to increase the amount of xylan adsorption under alkaline conditions [26,34]. This is somewhat unexpected because typical adsorption processes display a decrease in uptake when temperature is increased [35]. This may be explained by the reduction of substituents on the xylan backbone under these conditions. Autoclaving at high temperature and pH (170°C and 10 respectively) has been shown to reduce the number of glucuronic acid groups on xylan. The absence of glucuronic acid groups decreases the solubility of xylan in solution and promotes the aggregation of xylan. The large and less soluble xylan aggregates then adsorb onto the cellulose surface [28].

Ribe *et al.* have demonstrated the effects of pH and ionic strength quite well. A low pH in the alkaline domain is said to decrease the negative charge repulsion between the cellulose and the number of uronic acid substituents on the xylan, promoting adsorption. A high ionic strength is said to also mitigate the negative charge repulsion. They show this in their experiments at 127°C and 167°C. Most of the uptake occurs in an aqueous solution of 0.001M sodium hydroxide and 2.0M ionic strength. This being the lowest loading of sodium hydroxide and the highest ionic strength (provided by sodium carbonate) [34]. Danielsson and Lindström also show that lower pH in the alkaline range increases xylan adsorption onto cellulose fibers with xylan uptake being higher in 0.2M hydroxide solution compared to a 0.6M hydroxide solution [9].

In our experiments we will take a more fundamental approach where isotherms are collected and the uptake is plotted against the equilibrium concentration. Equilibrium constants are calculated from these isotherms and plotted against temperature and the Van 't Hoff relationship (equation 1) is used to calculate and enthalpy of adsorption. The enthalpy of adsorption can then be compared to literature values to determine the type of bonding.

$$\ln(K) = -\frac{\Delta H}{RT} \quad (1)$$

## 2.2. Methods

These isotherms will be generated using the method outlined by Köhnke [12] but instead of pulp, Whatman 42 (GE Healthcare Whatman Quantitative Filter Paper: Grade 42 Circles, Fisher

Scientific) filter paper and Sigma Cellulose will be used as pure sources of cellulose. In a typical experiment, 0.225g of dry cellulose was loaded into a 10mL glass batch reactor (Thermo Scientific Reacti-Vial Small Glass Reaction Vials, Fisher Scientific) with approximately 9mL of 0.5M sodium chloride. Experiments without sodium chloride were loaded with approximately 9mL of deionized water and those with sodium hydroxide were loaded with approximately 9mL of 1.0M sodium hydroxide solution. The sodium hydroxide solution was made using a 250mL volumetric flask and sodium hydroxide pellets. Xylan charges of 40-1250mg/g dry cellulose will be investigated as well as a temperature range of 35-95°C. The batch reactors were allowed to stir at room temperature to ensure they were well mixed before being brought to temperature in an oil bath (Silicone oil, Fisher Scientific). Experiments were run at 40mg/g dry cellulose and 70°C to determine the time necessary to reach equilibrium. Equilibrium was reached after 10 hours. In practice experiments at 70°C and 95°C were allowed to equilibrate overnight. Experiments less than 70°C were assumed to reach equilibrium within 48 hours. Sodium chloride will also be omitted from some experiments with Sigma Cellulose to evaluate its effect on adsorption. Xylan adsorption was calculated by the difference between the charged and remaining xylan in the liquid phase of the reactor. A portion of the liquid phase in the reactor was extracted via syringe and filtered using a 0.45µm syringe filter. Sulfuric acid was charged to the filtrate such that the final concentration was 4wt% and solution was hydrolyzed at 121°C for two hours. Samples containing sodium hydroxide were brought to a pH of 5-6 with 10M acetic acid before the addition of sulfuric acid. The acetic acid (Acetic Acid, Glacial (Certified ACS), Fisher Scientific) was made down with a 100mL volumetric flask. The hydrolysates were filtered through a 0.2µm syringe filter (Syringe Filters with Polypropylene Housing, 13mm, PTFE,

0.2 $\mu$ m, Nonsterile, VWR) before being analyzed analyzed by HPLC using an Aminex HPX-87H column.

### 2.3. Results & Discussion

Figure 5 below shows the results of the equilibrium experiments at 70°C. For the rest of the experiments at 70°C and higher it was assumed after 10 hours the samples were at equilibrium.

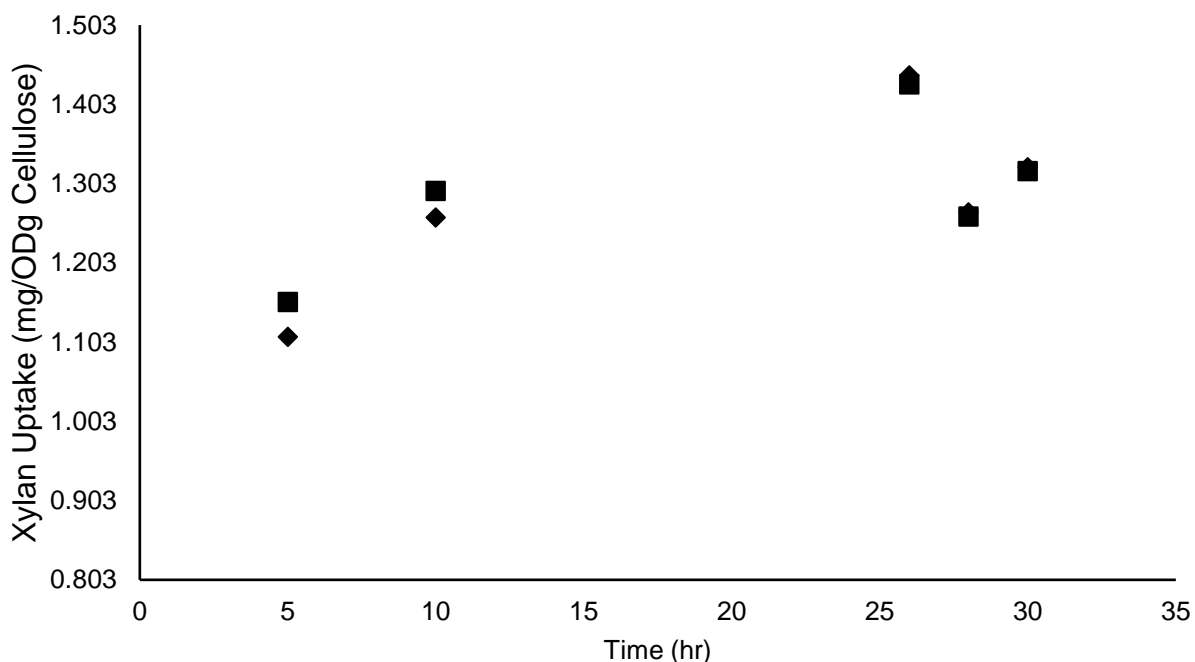


Figure 5: Xylan uptake as a function of equilibration time, with each point collected in duplicate (■, ◆). After 10 hours the uptake of xylan is constant, therefore, it is assumed that samples after 10 hours are equilibrated.

Isotherms at various temperatures were collected and are shown below in Figure 6. It is worth mentioning that only one experiment was conducted above 95°C (120°C) and no significant changes in coverage were observed so it is not shown here. Given that there was no significant

difference in surface coverage between 70°C and 95°C and that consistent sampling at 120°C was difficult it was decided to investigate lower temperatures. More time was allowed for these samples to reach equilibrium. Experiments conducted at lower temperatures also showed no significant changes in xylan uptake. This suggests that there is a low enthalpy of adsorption or that the filter paper may have some physical obstruction that prevents us from seeing a true equilibrium between xylan and cellulose.

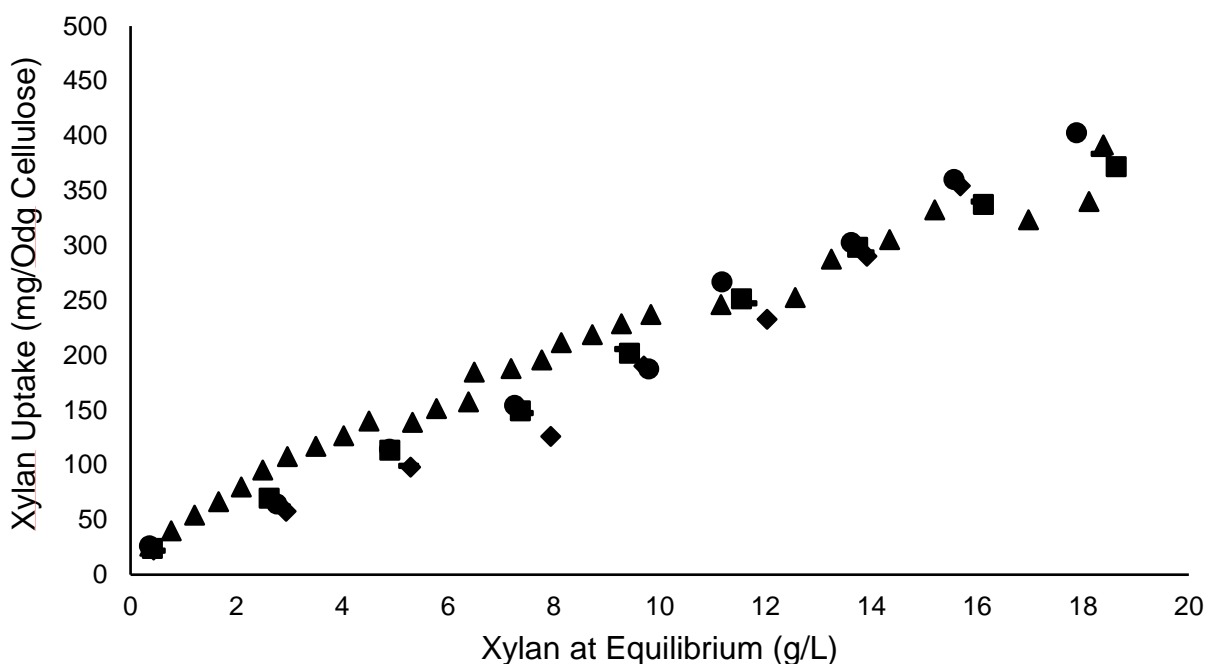


Figure 6: Isotherms collected at 95°C (●), 70°C (▲), 55°C (◆), 45°C (■), and 35°C (●). using beechwood xylan and Whatman 42 filter paper. There is no observable temperature dependence. This suggests a very small enthalpy of adsorption.

To see if the type of cellulose used influenced the xylan adsorption we switched to Sigma Cellulose from Sigma Aldrich. Isotherms at 70°C and 35°C are shown below in Figure 7. Again,

we see that there is no significant difference in uptake between experiments conducted at 35°C and 70°C.

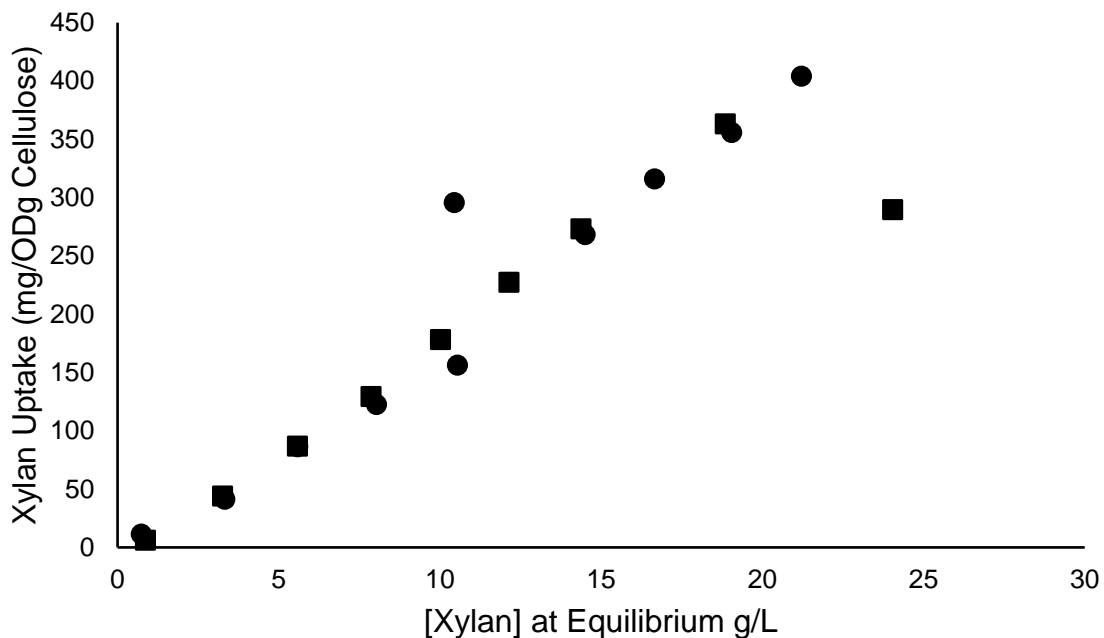


Figure 7: Isotherms collected with Sigma Cellulose at 35°C (●) and 70°C (■). There is no observable temperature dependence.

Upon observing no temperature dependence in the isotherms generated with Sigma Cellulose, we then became concerned as to the role sodium chloride played in the reaction. We decided to remove sodium chloride and collect more isotherms. In Figure 8 below the isotherm at 70°C generated with Sigma Cellulose in the absence of sodium chloride shows no significant decrease in xylan uptake when compared to the experiment conducted at 35°C.



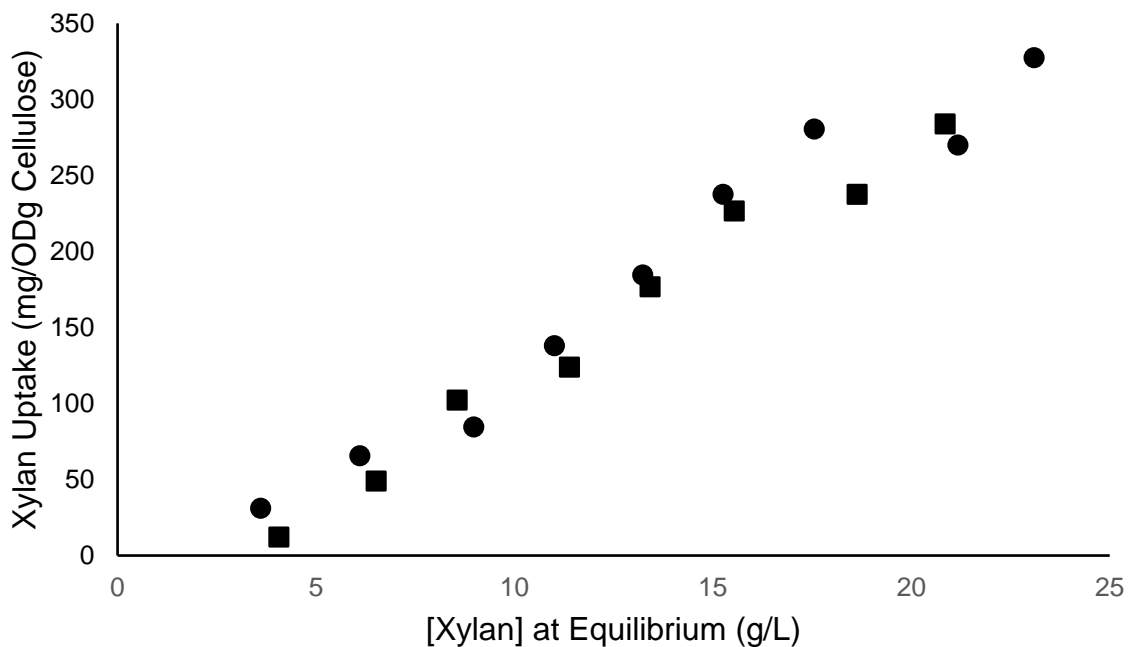


Figure 8: Isotherms collected with Sigma Cellulose in the absence of Sodium Chloride at 35°C (●) and 70°C (■). These experiments also do not display any temperature dependence.

Figure 9 below shows all of the isotherms collected on one plot. All experiments conducted with sodium chloride (including Whatman 42 filter paper and Sigma Cellulose) show similar uptake and a lack of temperature dependence. When sodium chloride is removed a small decrease in overall uptake is observed. According to the literature this is to be expected as xylan adsorption is favored at higher ionic strengths [34,36].

The small differences in uptake between temperatures suggests a small enthalpy of adsorption which would be consistent with hydrogen bonding. This is to be expected as Mora *et al.* showed that xylan that had been adsorbed onto pure cellulose can be removed using hydrogen bond disrupting agents such as urea, sodium hydroxide, and dimethyl sulfoxide [25].

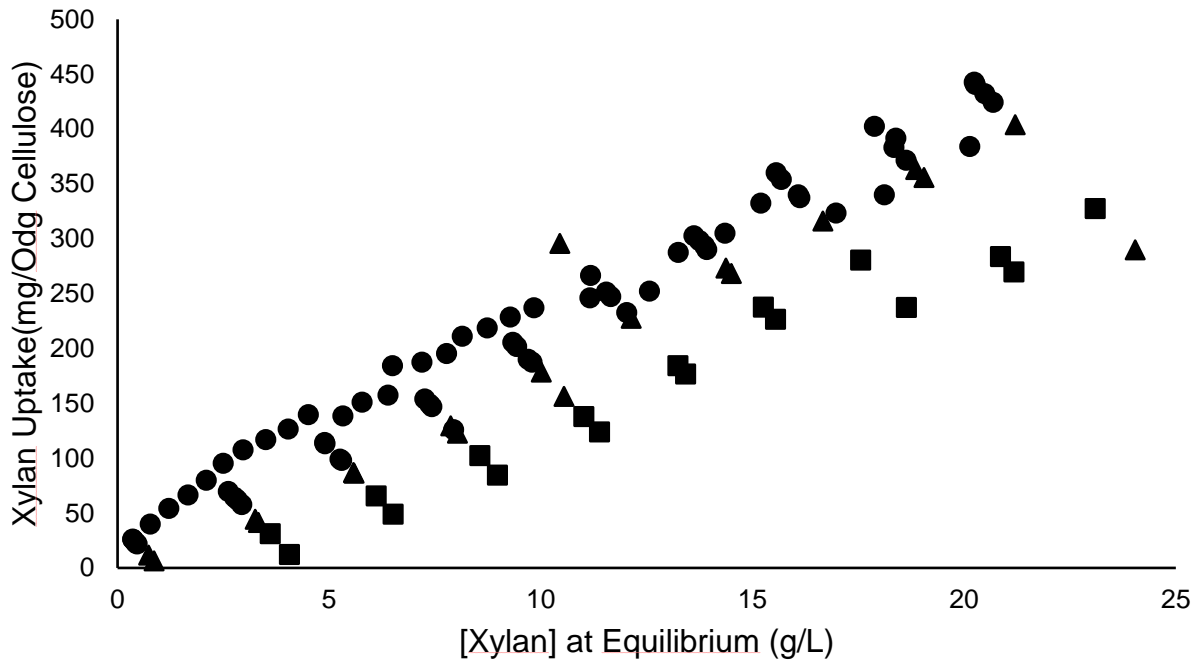


Figure 9: Isotherms collected using Whatman 42 filter paper (●), Sigma Cellulose(▲), and Sigma Cellulose in the absence of sodium chloride (■). While the experiments run without sodium chloride appear to have less uptake than the other experiments all sets of experiments display a lack of temperature dependence.

Figure 10 below shows the isotherms collected using 1M Sodium Hydroxide. While there is a great deal of scatter in the data there is a greater uptake at lower equilibrium xylan concentrations at 70°C. These isotherms also exhibit significantly higher uptake than the experiments run in water. This is to be expected as the literature mentioned above suggests that xylan adsorption is favored at higher pH values and temperatures. It is likely that at these higher temperature (70°C) and pH more acid groups are being cleaved off of the xylan backbone resulting in a less soluble, more aggregated xylan that will readily adsorb onto the

cellulose surface. In order to confirm this more experiments at higher temperatures need to be conducted.

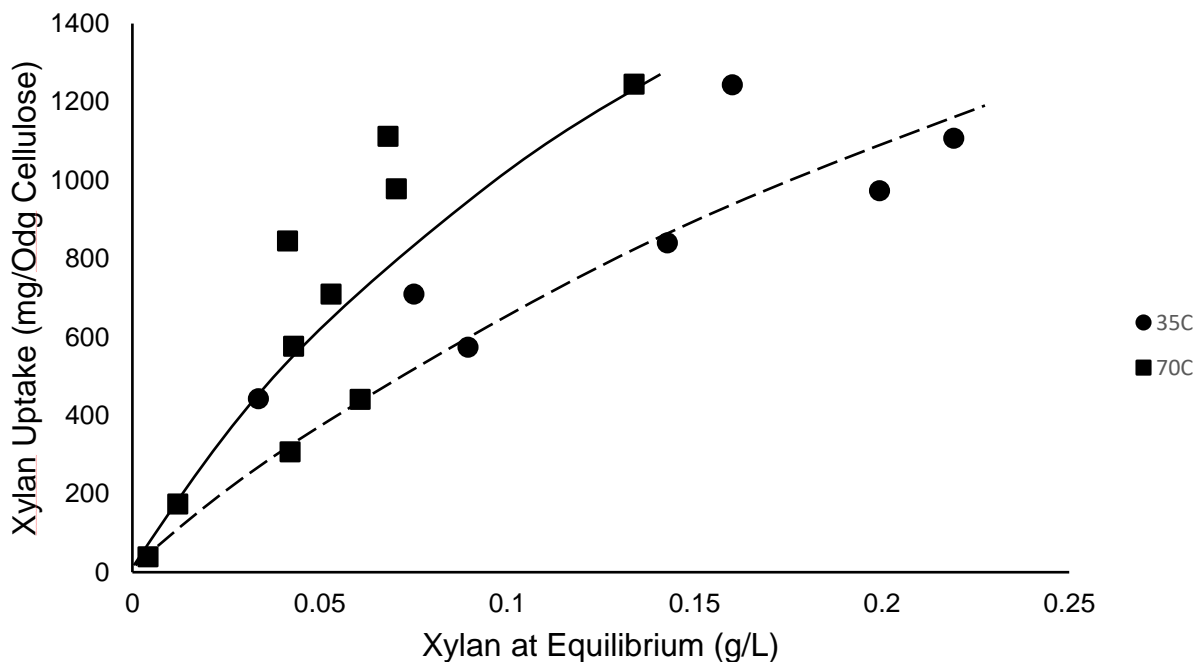


Figure 10: Isotherms collected at 35°C (●) and 70°C (■) using 1M sodium hydroxide. The scatter in the data makes it difficult to draw conclusions but it appears that more uptake occurs at 70°C which is expected [31].

#### 2.4. Conclusions

The first three sets of experiments (Whatman 42 filter paper, Sigma Cellulose, and Sigma Cellulose without sodium chloride) display a lack of temperature dependence. When sodium chloride was removed from the system the xylan uptake decreased slightly. This is in agreement with the literature as more xylan uptake occurs at higher ionic strengths. When sodium hydroxide was introduced the xylan uptake increased when compared to the first experiments. Again, this agrees with the literature as xylan adsorption is favored in an alkaline environment.

It appears that more xylan uptake occurred at 70°C when compared to 35°C. Given the literature we hypothesize that more glucuronic acid is removed from the xylan backbone at the higher temperature resulting in a less soluble, more aggregated xylan which more readily adsorbs onto the cellulose surface. To confirm this more experiments, need to be conducted to first, reduce the amount of scatter in the data, and second, to confirm that relationship between xylan uptake and temperature by running experiments at higher temperatures.

## CHAPTER 3

### METHODS FOR RETAINING HEMICELLULOSE DURING KRAFT PULPING AND SUGGESTIONS FOR FUTURE WORK

#### 3.1. Methods for Retaining Hemicellulose During Kraft Pulping: Literature Review

Given that hemicellulose in pulp may influence its density and that hemicellulose retention increases pulp yield it becomes necessary to investigate how best to retain hemicellulose during Kraft pulping. In principle there are two ways to go about increasing the hemicellulose content of wood pulp. First, one can adjust cooking parameters to retain more hemicellulose during a Kraft cook. Second, one can pretreat the wood before cooking, extracting the hemicellulose from the wood, and then adsorb it back onto the pulp fibers after cooking.

Genco *et al.* mention several guidelines that can be used to retain hemicellulose during Kraft cooking [10]. Decreasing the temperature at the beginning and end of a cook will mitigate the carbohydrate losses observed at high initial temperatures. Low levels of ionic strength minimize lignin condensation and carbohydrate reactions. A high concentration of bisulfide ions combats carbohydrate peeling and a consistent alkali concentration throughout a cook can minimize carbohydrate dissolution. More hemicellulose can also be retained by thinning the chips when cooking to a constant kappa number, however, this only works to a certain point as significant wood weight can be lost due to an increase in fines during chipping if the desired chip thickness is too thin. When cooking to a constant H-factor more hemicellulose is retained by increasing chip thickness, but this also leads to an increase in kappa number and is not desirable [10].

As previously mentioned Ban *et al.* demonstrates the pulp property benefits of green liquor extraction and hardwood hemicellulose adsorption for softwood pulp. This result is only part of the picture, because the wood has undergone extraction the actual pulping is less severe. Less cooking chemicals are needed (Effective alkali decrease from 15 to 12 for hardwood and 15.5 to 13.5 for softwood) to reach the same kappa number which will result in material cost savings. A 3.0% green liquor charge on wood was used with a liquor to wood ratio of 4.0. The extraction took place in a M and K digester at 160°C for 110 minutes and the ramp time was 50 minutes [11]. This resulted in approximately 10% of the wood weight being extracted with 35.75% of that being reported as xylose [37]. The adsorption took place at 95°C for 60 minutes at a pulp consistency of 2.5%, extracts to pulp ratio of 4.0, and a pH of 5.5. The adsorption yield for hardwood and softwood pulp were 9.23% and 10.17% respectively. The kappa numbers of the final pulp increase from 17.11 to 22.24 for hardwood and 27.80 to 39.83 for softwood [11].

While the fiber consistency, extracts to fiber ratio, and temperature were optimized to give the maximum adsorption yield there may still be some optimization to be had, particularly with pH. As mentioned above xylan adsorption favors a lower pH in the alkaline range, this experiment could benefit from a pH increase to 8-10. The pH increase should increase the adsorption yield and mitigate the kappa number rise due to the adsorption. The kappa number rise may seem relatively small but may still result in an increased bleaching load which is undesirable. Alkali added to the adsorption step should increase the adsorption yield due to a decrease in xylan solubility and mitigate the kappa number increase.

Further optimization of the extraction process may also be possible. Presumably 3% green liquor on wood was chosen because the extraction yield and subsequent pulp yield were

acceptable. This appears to be the case when considering the Near Neutral Process development by van Heiningen *et al.* Using water with 0.55% anthraquinone achieves the highest extraction of anhydro sugars, 26.7 g/L, with xylan accounting for 22.0 g/L. Hot water extraction also leads to problems with sticky lignin and an unacceptably low pulp yield of 38.8%, however, this pulp yield does not include a re-adsorption step that could increase the total yield on wood to an acceptable value, especially if the resulting pulp is of higher quality [38].

We stated earlier that there may be a benefit to cooking or pretreating hardwood and softwood together, hypothesizing that the adsorption of hardwood hemicelluloses onto softwood fibers would occur during cooking. There is some documented benefit to cooking hardwood and softwood at the same time. Gulsoy and Tufek show that adding hardwood to a softwood cook increases total and screened yields of the cook. Other benefits include a shorter cook time or a lower kappa number for a given cook time and an improved beatability [39]. Given these potential benefits will investigate the effects of cooking softwood and hardwood chips mixed together. To quantify the difference in cooking between hardwood and softwood we will layer the chips in the digester by species.

### **3.2. Methods**

For the control cooks 1000g of oven dried chips comprised of 85% hardwood and 15% softwood were mixed before being packed with a plastic rod into a recirculating batch digester (M/K Systems, Inc.). Sodium hydroxide (Sodium Hydroxide (Pellets/Certified ACS) 97.7%, Fisher Scientific) and sodium sulfide (Sodium Sulfide Hydrate, 60-64%, Extra Pure, Scales, Acros Organics) were mixed in a bucket containing enough water to achieve a liquor to wood ratio of

4. The effective alkali was 13.5% and the sulfidity was 34%. The ramp to 165°C and cook time were approximately 55 minutes and 110 minutes respectively. The exact H-factor was calculated using time and temperature data collected during the cook.

It was also of interest to quantify the differences in cooking between the hardwood and softwood. Cooks were conducted with a chip furnish of 85% hardwood and 15% softwood. Chips were screened and allowed to air dry for one week before cooking. The chip moisture was measured before each cook. Two layered cooks were conducted in the m and K digester with the same cooking conditions mentioned above. The softwood fraction was wrapped in cheese cloth to separate it from the hardwood. For the first cook the softwood was placed in the middle of the digester with equal amounts (by mass) of hardwood were placed above and below it. The softwood was placed above the hardwood for the second cook. This was done in case a significant amount of channeling occurred during cooking.



### 3.3. Cooking Data

Table 3 below shows that with an H-factor of 1230 hours a screen yield of approximately 51% can be expected with a Kappa number of 19 for a blend of hardwood and softwood chips, 85wt% and 15wt% respectively.

Table 3: Control cooking data.

<i>Run</i>	<i>Date</i>	<i>H-Factor</i>	<i>Total Yield</i>	<i>REA (g/L Na<sub>2</sub>O)</i>	<i>Screened Yield</i>	<i>Kappa Number</i>
1	2/4/20	1231	52.3%	1.88	50.3%	19.5
2	2/11/20	1227	53.2%	1.36	51.6%	18.1

As can be seen in Table 4 below the softwood is significantly less cooked than the hardwood with Kappa numbers in the mid 50's compared to the Kappa number of the hardwood hovering around 14. The lower screened yield for the softwood also indicates an undercooked product. The difference in kappa number and screened yield is somewhat expected as softwood contains more lignin than hardwood [40]. Ultimately this data shows that there is optimization to be done when cooking hardwood and softwood together.

Table 4: Layered cooks at the following conditions: 85% Hardwood, 15% Softwood, 13.5% effective alkali, and 34% sulfidity.

<i>Run</i>	<i>H-Factor</i>	<i>Total Wood Yield</i>	<i>HWD Total Yield</i>	<i>SWD Total Yield</i>	<i>REA (g/L Na<sub>2</sub>O)</i>	<i>Screened Yield HWD</i>	<i>Screened Yield SWD</i>	<i>Weighted AVG Screened Yield</i>	<i>HWD Kappa Number</i>	<i>SWD Kappa Number</i>
1	1238	52.4%	52.1%	54.0%	1.43	50.5%	44.8%	50.5%	13.7	55.8
2	1221	52.2%	51.9%	54.0%	1.36	51.1%	45.0%	50.8%	13.6	52.3

### 3.4. Suggestions for Future Work

**3.4.1. Factors that Control the Apparent Density of Paperboard.** The literature [34] and our fundamental adsorption experiments (Figure 10) show that xylan uptake is increased in an alkaline environment, the previous experiments should be redone at a pH between 8 and 10 to facilitate higher xylan uptake by the pulp. Presumably an increase in xylan uptake will have a more pronounced effect on apparent sheet density. Then the process can be optimized for maximum xylan uptake by adjusting the temperature, pH and ionic strength to achieve a maximum effect on apparent sheet density. The tensile strength index of the paper should be considered. Our previous experiments (Figure 2, b) show that an increase in xylan uptake will negatively impact the sheet tensile strength index. There will likely be a compromise between an acceptable decrease in sheet density and an acceptable decrease in tensile strength index. Investigations into fiber morphology would also be insightful. Measurements of fiber flexibility and cell wall thickness of treated and untreated fiber would provide the framework for useful

correlations between hemicellulose uptake, cell wall thickness, fiber flexibility, and their influence on sheet density.

**3.4.2. Fundamental Adsorption Experiments.** The experiments using 1M sodium hydroxide need to be repeated. First the scatter in the data needs to be reduced. Provided the scatter in the data can be reduced we should observe that uptake is a function of temperature. The removal of the glucuronic acid substituents increases the uptake of xylan. An increase in temperature will result in an increase in the cleavage of glucuronic acid groups from the xylan backbone, thus increasing the uptake of xylan by cellulose. We can then apply the Van 't Hoff relationship and calculate an enthalpy of adsorption. In this instance the enthalpy of adsorption would include the hydrolysis of glucuronic acid groups. This value gives insight into the interaction between xylan and cellulose in an alkaline environment, particularly during Kraft Pulping.

Taking advantage of CP/MAS  $^{13}\text{C}$  NMR (Cross Polarization/Magnetic Angle Spinning Carbon-13 Nuclear Magnetic Resonance) measurements described by Teleman *et al.* [29] may also give information on the interaction between xylan and cellulose. By observing the chemical shifts of untreated, alkaline treated, and xylan adsorbed onto cellulose surfaces we will be able to comment on the xylan structure on the cellulose surface.  $\text{C}^{13}$  MAS DNP NMR measurements as demonstrated by Viger-Gravel *et al.* would also describe the surface interaction between cellulose and xylan. In their work Viger-Gravel *et al.* are able to determine the position (secondary cell wall and the inner middle lamellae) of lignin in the cell walls of poplar wood [41]. We hypothesize that by using  $\text{C}^{13}$  and deuterium enriched materials we will be able to distinguish between cellulose and xylan and determine the orientation of xylan on the cellulose

surface. CNC (cellulose nanocrystals) may serve as an acceptable cellulosic material for adsorption experiments with CP/MAS  $^{13}\text{C}$  NMR because the specific surface area can be reasonably approximated using NMR techniques [42].

**3.4.3. Methods for Retaining Hemicellulose During Kraft Pulping.** Green liquor extraction and re-adsorption should be conducted following the procedure outlined by Ban *et al.* [11] using a layered style similar to the layered cooks we conducted. Extracting, cooking and re-adsorbing in a layered fashion would allow us to quantify the hemicellulose uptake for each pulp. Ban *et al.* [11] show the benefits of treating softwood fibers with hardwood hemicellulose, understanding the uptake of hardwood hemicellulose by hardwood and softwood fibers that are co-cooked would partially explain the pulp strength increases observed by Gulsoy and Tufek when pine is added to a aspen cook [39]. Once control data has been collected it is necessary to adjust the pH of the adsorption step to between 8 and 10. Increasing the pH during adsorption will increase the amount of hemicellulose uptake, thereby increasing the effect on sheet properties. The literature suggests that problems with bleaching may occur due to the hemicellulose acting as a physical barrier to the bleaching chemicals [43]. Treated pulp will also need to be bleached to investigate the hemicellulose retention across the bleaching process.

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Chris Albert is from Bradford, Maine and graduated from Central High School in East Corinth, Maine, in 2014. Chris attended the University of Maine from 2014 to 2018 where he received a bachelor's degree in Chemical Engineering in May 2018. Chris was a University of Maine Pulp and Paper Foundation Scholarship recipient and completed a coop with Twin Rivers Paper Company in Madawaska, Maine and an internship with Sappi North America in Westbrook, Maine.

In the late summer of 2018 Chris entered the graduate program in Chemical Engineering at the University of Maine. He is employed as a process engineer with ND Paper at the Old Town Mill. Chris is a candidate for the Master of Science degree in Chemical Engineering from the University of Maine in August 2020.