Biphasic 1-butanol/water delignification of miscanthus *for manufacturing papermaking pulp*

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ABSTRACT: *Miscanthus* has emerged as a promising nonwoody fiber source for papermaking and fiber molding as the world has sought alternatives to wood-based products. A diverse range of chemistries have been explored at the laboratory scale to turn nonwoody biomass into fibers; however, few have been successful at pilot or commercial scales.

An emerging organosolv delignification chemistry that has demonstrated previous technical success is butanol/water, having been shown to produce papers with similar properties to other, more conventional chemistries, but offering the benefit of a built-in sugar and lignin coproduct separation. While a range of fiber lengths were achieved (0.45–0.95 mm), addition of sodium hydroxide (NaOH) to the butanol/water delignification chemistry resulted in fiber lengths comparable to commercially available hardwood pulps (0.7–1.0 mm). Lignin concentration was reduced from 19.1 wt% in the raw *miscanthus* to under 3.5 wt% for most trials. The lowest lignin concentration (2.5 wt%) was achieved at 180°C for 180 min with 50:50 butanol:water and 2 wt% acetic acid. Yet, the high severity of this condition (and similar ones) resulted in a significant truncation of fiber length, which is detrimental for papermaking applications. The highest quality pulp for papermaking was generated at 180°C for 180 min with 50:50 butanol:water and 10 wt% NaOH. This pulp had one of the longest fiber lengths, the highest brightness, and the highest hemicellulose concentration. Thus, butanol/water delignification, especially with NaOH addition, resulted in the successful production of cellulose-rich pulps that have potential in commercial papermaking and fiber molding applications.

Application: This study provides a fundamental investigation of how butanol/water delignification conditions, especially additives, influence the resulting fiber and pulp properties. This information can be used as a benchmark to help assess the potential of butanol/water delignification against more common pulping chemistries.

Miscanthus, a type of nonwoody biomass, has been the subject of intense interest as an alternative fiber source for the papermaking and fiber molding industries. *Miscanthus* is a perennial rhizome grass encompassing several species, including *Miscanthus sinensis*, *Miscanthus sacchariflorus*, and *Miscanthus giganteus* (referred to as "*miscanthus*" in this paper), a hybrid of *M. sinensis* and *M. sacchariflorus* that is commonly studied for papermaking and biomass energy applications [1,2]. *Miscanthus* has many desirable properties as an alternative fiber source, including its hardiness, high biomass production per hectare, and ability to grow back when harvested properly [1-3]. It also has a proven track record in the paper and fiber molding industries, with several commercial miscanthus pulp products currently available [4,5].

Common delignification chemistries investigated for *miscanthus* processing (pretreatment or pulping) include ethanol [6-17], soda [8,9,15,18-23], and autohydrolysis [6,15,21,24,25]. These efforts have resulted in the successful valorization into pulps for papermaking and sugars for fermentation while also gaining some understanding of the coproduct lignin structures [6-25]. In addition to significant laboratory-scale research, *miscanthus* is currently being used commercially as a fiber source for paper and fiber molded products [4,5].

The 1-butanol/water delignification can be classified as a biphasic organosolv delignification process; i.e., the solvent system is two phase at room temperature, but a single phase at the elevated temperatures used during delignification [26-28]. This built-in phase separation once the reactor is cooled is one of the most significant advantages compared to conventional single-phase delignification systems due to its potential to reduce solvent recovery costs and simplify separation of coproducts [26-28]. While this paper is primarily focused on butanol/water systems, the biphasic delignification phenomenon has already been reported in similar organosolv biphasic systems, such as 1-pentanol/water and methyl isobutyl ketone (MIBK)/water [29,30].

First reported in 1936 by Aronovsky and Gortner, delignification using butanol/water chemistries has shown promise for processing both woody and nonwoody bio-

mass sources into a variety of products, including pulps for papermaking and sugars for fermentation [26-28,31-40]. The platform work of Aronovsky and Gortner established two key aspects of butanol/water delignification: (1) Pulps created from butanol/water and soda delignification of aspen chips had similar properties, indicating the potential of butanol/water chemistries for papermaking applications [28]; and (2) the unique phase separation behavior of butanol/water delignification systems upon cooling of the reactor results in preferential partitioning of the sugars and lignins liberated during delignification into the aqueous and organic phases, respectively [28]. The significance of the phase separation behavior cannot be understated, as a built-in separation has the potential to substantially improve the process economics of biphasic organosolv biorefineries compared to the traditional, most-studied ethanol/water organosolv biorefinery or the kraft pulping process [26-28,31-40].

Due to the phase separation behavior, which has the potential to simplify solvent recovery, butanol/water chemistries are especially amenable for processing of nonwoody biomass. In the paper industry, it is well known that the low density of nonwoods, as compared to woods, limits the economically feasible harvest area around a mill due to increased transportation costs per ton of feedstock. As a consequence, biorefineries for nonwoody biomass valorization would be smaller in scale, spaced more closely, and receive feedstock from a smaller area than current kraft pulp mills. From conversations with industry experts, it is clear that smaller-scale biorefineries based on current commercial delignification chemistries would not be economically feasible due to the enormous costs associated with chemical recovery (i.e., recovery boilers). The phase separation of butanol/water chemistries has the potential to address this critical issue and unlock the potential to develop smaller standalone biorefineries that are economically feasible.

One key factor that is not fully understood for butanol/water delignification is the impact of additives, which have well-known significant impacts on the composition and properties of pulps produced from organosolv delignification. As with any process, the optimal conditions for biomass delignification are heavily dependent on the desired product(s). As pH decreases, cellulose and hemicellulose chains undergo increased degradation reactions, resulting in shorter chains and increased production of byproducts such as furfural and 5-hydroxymethylfurfural (HMF) [41]. Cellulose chain degradation, in particular, is highly undesirable for papermaking and fiber molding applications, as the shortened chain lengths cause the resulting papers to have poorer strength properties, increased fines contents, and decreased yields [42]. However, if being used as a precursor for fermentation, hydrolysis of the polysaccharide chains into oligosaccharides and monosaccharides is desirable, as it reduces the amount of additional processing needed to fully convert the polysaccharides into monomeric sugars. Other major factors explored in this effort include temperature and delignification duration.

This work will discuss the impact of delignification reaction conditions on the composition and properties of *miscanthus* pulps generated across a range of chemistries to advance the emergence of butanol/water delignification in the biorefining field with a focus on papermaking. Pulp composition, as well as yield, average fiber length, freeness, and strength properties, can be correlated to changes in pH modification additives and delignification time. Ultimately, the potential of butanol/water chemistries to generate pulps for papermaking and fiber molding applications is assessed to address gaps in the current literature and contribute to the development of this emerging biorefinery chemistry.

MATERIALS AND METHODS

Materials

Miscanthus (*Miscanthus giganteus*) was generously provided by Genera Inc. (Vonore, TN, USA). The 1-butanol (99.9 wt%), glacial acetic acid (99.7 wt%), sodium hydroxide (98 wt%), furfural (99 wt%), ethanol (190 proof), toluene (99.3 wt%), D-(+)-glucose (99.5 wt%), D-(+)-xylose (99.0 wt%), D-(+)-galactose (99 wt%), D-(+)-mannose (99 wt%), and L-(+)-arabinose (99 wt%) were obtained from Sigma Aldrich (St. Louis, MO, USA) and used as received. Sulfuric acid (72 wt%) and calcium carbonate (99.0 wt%) were obtained from Fisher Scientific (Thermo Fisher Scientific; Waltham, MA, USA) and used as received.

Methods

Delignification trials were conducted in an SKZ1021 laboratory rotary digester (SKZ Indusrial; Jinan, China) equipped with a four-tube insert, allowing for up to four different delignification chemistries to be tested simultaneously. To ensure enough pulp was produced for analysis, two tubes were used for each experimental condition in this study. Each tube was filled with 125 g oven-dry (OD) *miscanthus*, and then the chosen delignification chemistry was added at a liquid-to-solid ratio of 6:1 mL/g OD A range of conditions (**Table I**) were explored to assess their impact on the properties and processability of the resulting pulps, lignins, and sugar streams.

The acetic acid, none, and sodium hydroxide (NaOH) additive conditions were chosen due to their common use for pH control in organosolv delignification, with the objective of understanding their impact on pulp composition, yield, and properties. Furfural was chosen as an additive due to its potential presence in butanol recycle streams, so its impact on delignification must be assessed to understand if additional purification of the recycled butanol is required prior to reuse as a delignification reagent [43].

Following an initial temperature ramp, delignification trials were performed for 90, 135, or 180 min at a tempera-

Condition	Value
Time at temperature, min	90, 135, 180
Additive, wt% relative to OD *miscanthus*	2 wt%, 5 wt%, and10 wt% sodium hydroxide; none; 2 wt% acetic acid; 10 wt% furfural*
* For the trials with furfural, the total alcohol-to-water ratio was kept at 50:50, but a portion of the butanol was replaced with furfural to achieve a butanol-to-water-to-furfural ratio of 40:50:10.	

I. Delignification conditions (OD: oven-dry).

ture of 180°C. Initially, lower temperatures (150°C and 165°C) were also considered, but pulps generated during preliminary trials at those lower temperatures did not result in sufficient delignification/biomass degradation, and results will not be reported here. After completion of the delignification time, the digester was cooled and the pulps were separated from the liquors using a cheesecloth. The pulps generated using the same conditions were then combined into a single sample. Extensive characterization of the two-phase spent pulping liquors will be presented in a future work that will include composition analysis of each phase, characterization of the lignins precipitated from the organic phases, and application of a novel butanol recovery technology (vapor stripping-vapor permeation) developed in previous works [44,45] to the aqueous phases.

The unwashed pulp was then diluted to a total volume of 2 L using deionized water and disintegrated for 10,000 revolutions in a standard TAPPI disintegrator. The water added for disintegration was removed via vacuum filtration, completing the first washing. A second washing was then performed by resuspending the pulp in deionized water, followed by vacuum filtration to remove the wash water. A total wash water volume of 3 L was used across the two washing steps, and all wash water recovered during the two vacuum filtrations was saved for analysis. Prior to any additional pulp processing, samples of each pulp (~15 g OD) were removed, freeze-dried, and stored in a desiccator for composition analysis.

To prepare the pulps for handsheet production, three 24-g OD samples were removed from each pulp for PFI milling according to TAPPI Standard Test Method T 248 "Laboratory beating of pulp (PFI mill method)": Pulp samples were diluted to 10% consistency with deionized water and PFI milled for 500, 1000, or 1500 revolutions. The milled pulps were diluted to 2 L with deionized water and disintegrated for 10,000 revolutions. The pulp samples were then vacuum filtered to remove water and stored in a refrigerator prior to characterization. The fiber length and fines content of each pulp were determined using an OpTest Fiber Quality Analyzer - 360 (FQA). Pulp and handsheet properties were determined according to the following TAPPI Standard Test Methods:

- Pulp freeness (Canadian standard freeness): TAPPI T 227 "Freeness of pulp (Canadian standard method)."
- Handsheet preparation from each pulp: TAPPI T 205 "Forming handsheets for physical tests of pulp."
- Brightness: TAPPI T 452 "Brightness of pulp, paper, and paperboard.
- Tensile: TAPPI T 494 "Tensile properties of paper and paperboard."
- Tear: TAPPI T 414 "Internal tearing resistance of paper".

The compositions of the pulps and the unprocessed *miscanthus* were determined according to the procedures outlined by the National Laboratory of the Rockies, formerly the National Renewable Energy Laboratory (NREL), in their comprehensive biomass composition analysis procedures:

- Sample preparation: NREL/TP-510-42620 [46].
- Ash: NREL/TP-510-42622 [47].
- Klason and acid soluble lignin: NREL/TP-510-42618 [48].
- Sugars: NREL/TP-510-42618 [48].
- Extractives content: NREL/TP-510-42619 [49] with a modified solvent sequence consisting of: (1) 2:1 toluene:ethanol (v/v) for 8 h, followed by (2) 190 proof ethanol for 4 h.

RESULTS AND DISCUSSION

Pulp composition and yield

Composition and yield are key metrics that provide insights into the delignification process, and at the industrial scale, determine potential applications and if additional processing is needed. Lower lignin content generally corresponds to whiter pulps that are typically more desirable for bleached grades, but there is generally a tradeoff between lignin content and pulp yield; as harsher processing is used to increase lignin removal, additional damage to cellulose and hemicellulose chains occur, resulting in a reduction in pulp yield [50]. Furthermore, the added processing required to generate pulps with lower lignin concentrations results in increased operating costs.

To understand the impact of delignification conditions, the raw material composition must first be determined. The composition of the unprocessed *miscanthus* used for this research is shown in **Table II**. Compared to other unprocessed *miscanthus* compositions reported in the literature, the *miscanthus* used is relatively high in cellulose and low

Component	Composition, wt% OD
Cellulose	66.0 ± 4.0
Hemicellulose	8.2 ± 1.8
Klason lignin	19.1 ± 1.2
Acid soluble lignin	2.3 ± 0.3
Ash	1.1 ± 0.1
Extractives	2.1 ± 2.0

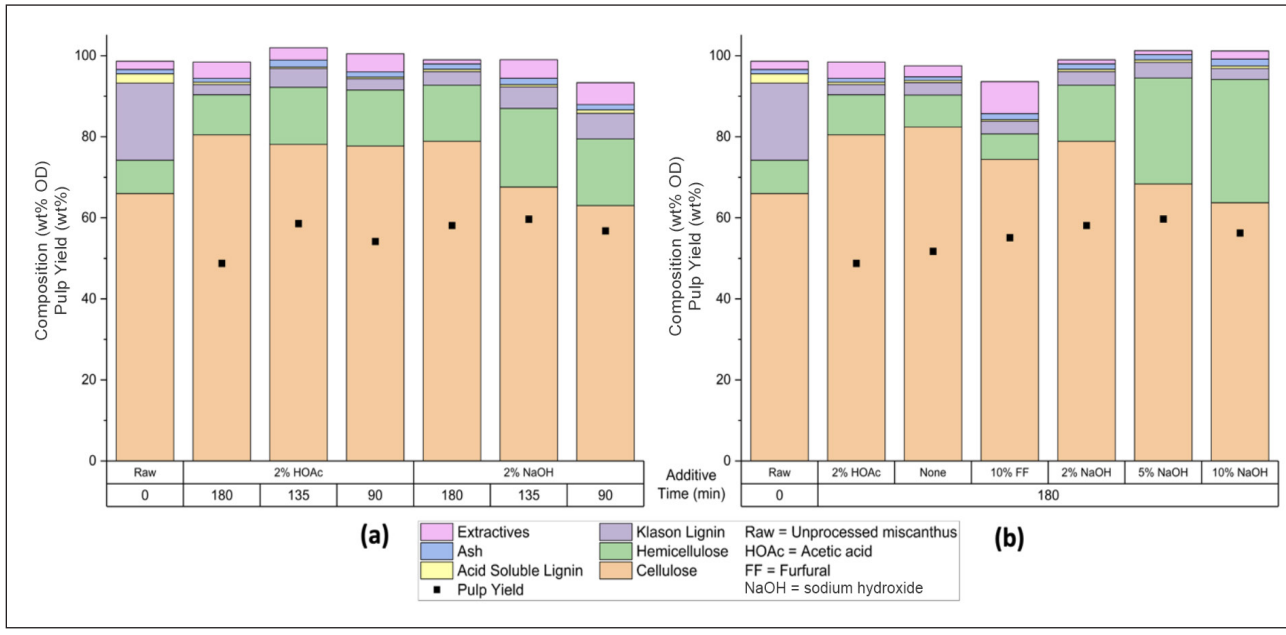
II. Unprocessed miscanthus composition (OD: oven-dry).

in hemicellulose, with a normal lignin composition [3]. Pulp compositions and yields are shown in **Fig. 1**.

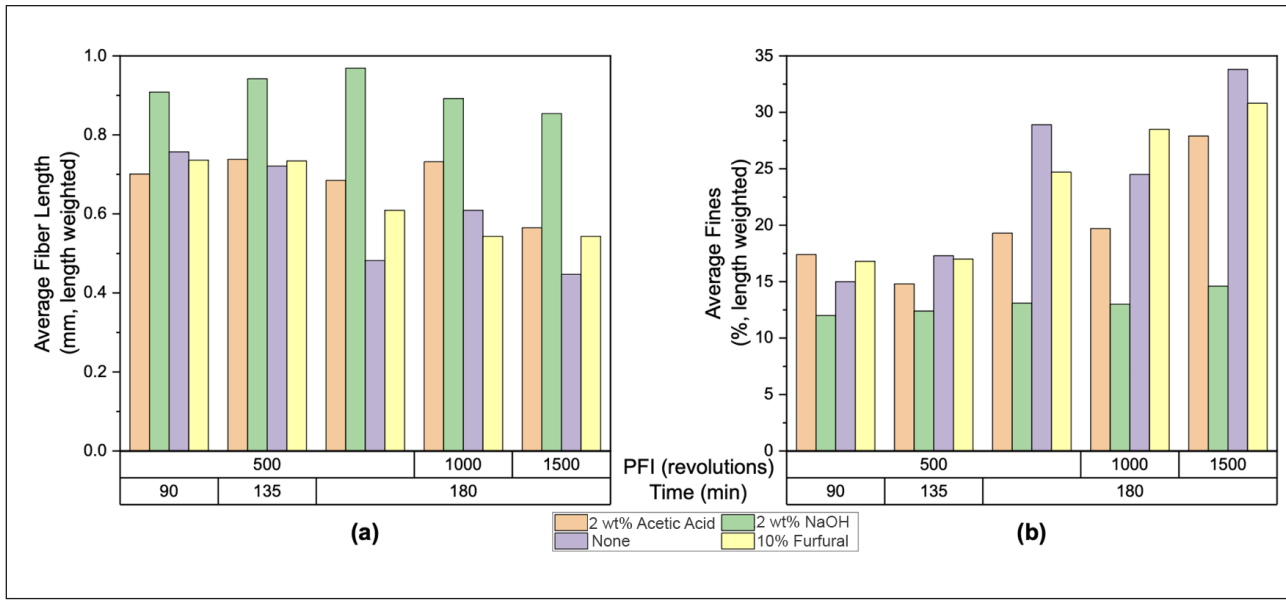
In general, all processing conditions were successful at significantly reducing the Klason lignin content from 19.1 wt% in the biomass to a range of 2.5 wt%–6.3 wt% in the pulps, a value comparable to most bleached grades. Delignification duration had a significant impact on pulp composition, with longer delignification times correlating to less lignin in the pulps. The lowest (2.5 wt%) and highest (6.3 wt%) lignin contents were achieved at 180 min and 90 min trials, respectively. The decrease in lignin content when delignification duration increased can be attributed to the additional time allotted for delignification reactions. Cellulose content was found to have the opposite trend, where increases in reaction time resulted in enrichment in cellulose content, attributed to the increased removal of other biomass components (lignin and hemicellulose).

Additives also had a significant impact on the compositions and yields of the butanol/water delignification. As anticipated, the harshest condition, 180 min with 2 wt% acetic acid added, resulted in the pulp with the lowest lignin concentration (2.5 wt%) and highest cellulose abundance (81.2 wt%). This is because addition of acetic acid decreases pH, resulting in increased hydrolysis of lignin and hemicellulose and the subsequent solubilization of the reaction products. As a result, a more cellulose enriched pulp is produced. However, the significant removal of biomass components for the 180 min/2 wt% acetic acid trial resulted in one of the lowest pulp yields (48.8%) of all tested conditions.

Hemicellulose content was highest in trials with NaOH addition and increased as NaOH concentration increased from 2 wt% to 10 wt%. The pH moderation provided by NaOH addition protects the cellulose and hemicellulose chains from acid hydrolysis degradation, resulting in the highest hemicellulose concentration of 30.4 wt% in the 180 min/10 wt% NaOH trial. The comparatively low cellulose content of that pulp (63.7 wt%) is due to the large amount of retained hemicellulose rather than degradation of the cellulose chains. Hemicellulose retention is desirable for many papermaking applications, as increased hemicellulose content is associated with improved tear properties and better drainage on the paper machine [51]. The polysaccharide protection effect imparted by NaOH addition resulted in some of the highest pulp yields (56+%), even at the longest reaction times. Thus, the low lignin and high polysaccharide content combined with a good yield make the 180 min/10 wt% NaOH trial the best of the conditions tested for papermaking when only composition and yield are considered.



1. Selected pulp compositions and yields demonstrating (a) the impact of time and (b) the impact of additive.



2. Impact of delignification conditions on (a) average fiber length and (b) fines percentage.

Fiber properties

Two of the most important fiber properties for papermaking are average fiber length and fines percentage. Shorter average fiber lengths negatively impact the strength properties of the resulting paper and if short enough, make a pulp unsuitable for papermaking due to decreased water drainage and resultant reduced production rates and/or steam energy penalties [42]. Higher fines percentages are also undesirable, as fines result from excessive damage to the polysaccharide chains that corresponds to decreased yields and shorter fiber lengths. **Figure 2** shows the impact of delignification conditions on (a) average fiber length and (b) fines percentage.

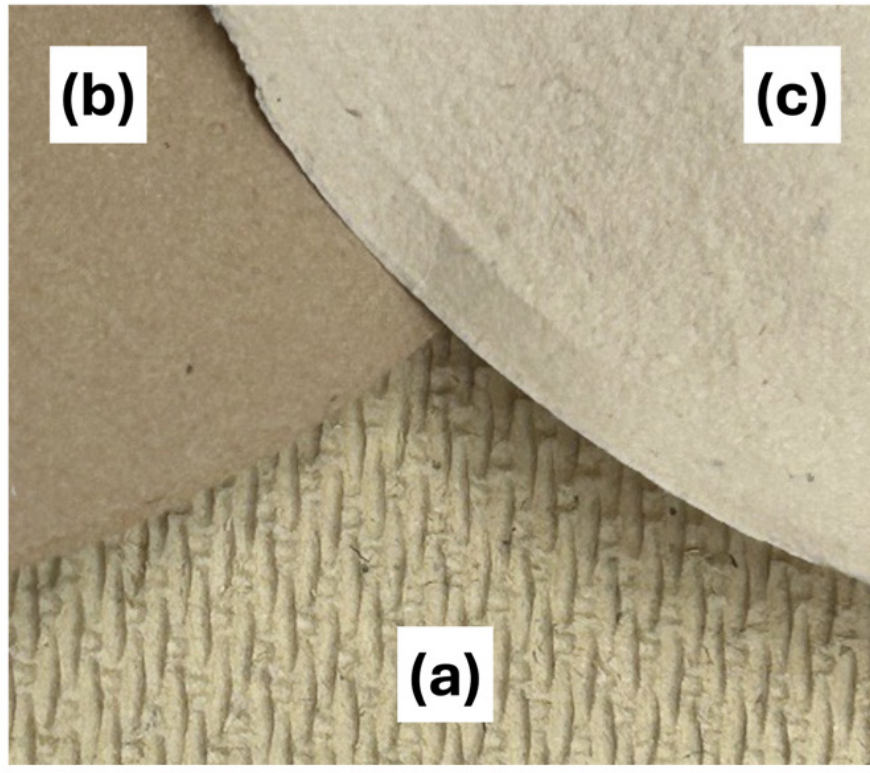
A wide range of average fiber lengths was observed, ranging from 0.45 mm (too short for papermaking) to 0.95 mm (comparable to hardwood fibers). The most significant factor impacting fiber length was additive. The addition of 2 wt% NaOH resulted in the longest fiber length for each temperature and PFI revolution combination tested, with 2 wt% NaOH for 180 min and 500 PFI revolutions producing pulps with the longest fiber lengths. This can be attributed to a reduction in polysaccharide chain acid hydrolysis due to maintaining a moderately higher pH during the delignification process to yield meta-saccharinic acid end capped moieties, thus reducing end chain scission reactions ("peeling"). However, as pH decreases, glycosidic hydrolysis to monosaccharide units becomes increasingly prevalent, ultimately resulting in the generation of shorter polysaccharide chains, and thus, decreased fiber length [52]. A fiber length reduction due to acid hydrolysis is present even in systems without additives due to the presence of acetyl groups on hemicellulose chains that decrease the pH during delignification [52]. While NaOH addition is beneficial for maintaining longer fiber lengths, addition of excessive NaOH would also be expected to result in a reduction in fiber length due to chain scission (hydrolysis), where blocks of oligosaccharides are cleaved from the polysaccharide chains [53].

Delignification time had negligible impact on fiber length over the time frame of 90 to 135 min; however, a significant decrease in fiber length was observed for all trials except for those with added NaOH over 180 min. Longer times allow for more polysaccharide degradation reactions to occur, as well as a larger reduction in pH that further promotes polysaccharide degradation, resulting in shorter fibers. However, as previously noted, pH moderation due to NaOH addition protects the fibers from degradation, and this effect appeared to be increasingly prevalent as delignification severity increased (i.e., longer times).

Fines percentage trends were consistent with fiber length trends. At all conditions, NaOH addition and increased delignification time resulted in the lowest and highest fines percentages, respectively. As with fiber length, NaOH addition protects the polysaccharide chains from degradation, resulting in fewer small sugar fragments and thus lower fines percentage. Conversely, longer delignification times result in increased polysaccharide degradation and thus a higher fines percentage.

Pulp properties

One of the most significant visible differences between pulps was a stark contrast in the brownness/lightness of the handsheets. An example of this can be seen in **Fig. 3**, which compares a commercially available *miscanthus* pulp produced using a soda process with two pulps produced using butanol/water delignification with different amounts



3. Comparison of (a) a commercially available miscanthus pulp and handsheets produced from trials with (b) 2 wt% NaOH and (c) 10 wt% NaOH.

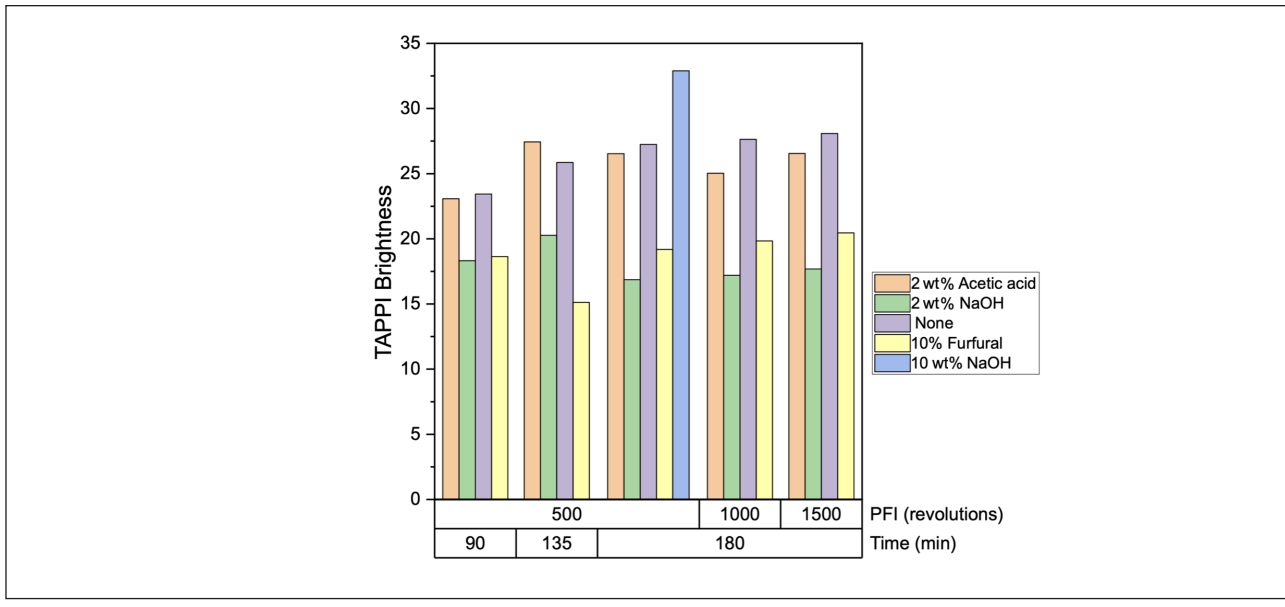
of added NaOH.

The 10 wt% NaOH handsheet is significantly lighter than the 2 wt% NaOH handsheet, demonstrating the beneficial impact of added NaOH for papermaking using butanol/water chemistries. Brightness is the most common method to describe how white a sheet of paper appears according to how it scatters light (either TAPPI or ISO) and is heavily impacted by lignin content. Brightness measures the reflectance of a blue light (457 nm for TAPPI T 452), with higher values corresponding to lighter pulps and lower lignin content. Brightness is often a key determinant when considering the appropriate application for a pulp with high-brightness white printing papers in the 90+ range. However, to achieve brightness values that high, pulping alone does not generally provide sufficient delignification, and as a result, additional delignification and/or bleaching is typically required. The pulps produced and discussed in this publication did not undergo any bleaching steps, which is evident in their lower brightness values. While investigation into bleaching is necessary to determine the ultimate potential of butanol/water pulps, the brightness values of the unbleached butanol/water pulps can be found in **Fig. 4**.

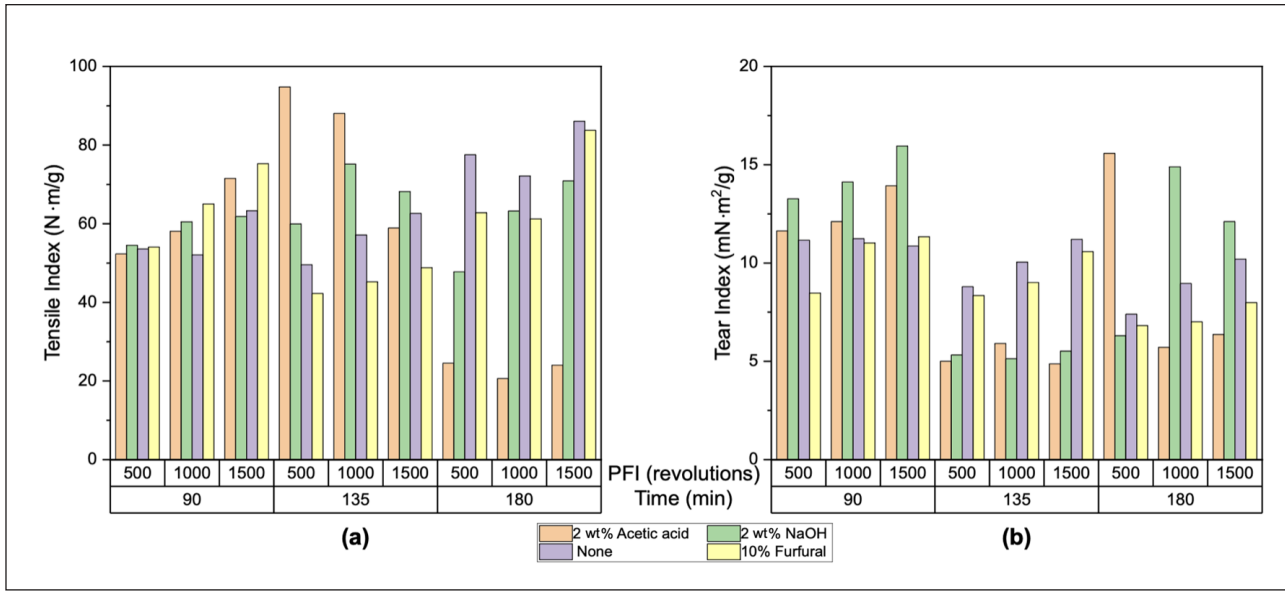
The pulp with the highest brightness (32.9), shown in Fig. 3c, was generated using 50:50 butanol:water for 180 min with the addition of 10 wt% NaOH. While 10 wt% NaOH addition resulted in the best brightness, none of the pulps from trials with 2 wt% NaOH addition had high brightness when compared against other additives at similar conditions. This is likely due to the lignin content of the pulps; i.e., at each comparable condition, 2 wt% NaOH addition produced a pulp with the highest lignin content, resulting in the brownest paper. This emphasizes the importance of higher NaOH concentrations to increase delignification and produce brighter pulps while maintaining the fiber damage mitigation provided by pH moderation. Furfural was found to have a negative impact on brightness, indicating a potential issue if too much furfural is present in butanol recycle streams.

Another driver of potential pulp applications is strength properties, such as tensile and tear. Tensile index is the tensile strength of the handsheet normalized for the grammage of the handsheet being tested. Similarly, tear index is the tear strength normalized for grammage. Tensile and tear indices depend on factors including interfiber bonding, fiber length, and the individual strength of the fibers [54]. Tensile and tear data as a function of delignification conditions can be found in **Fig. 5**.

The general increase in tensile index with increased PFI milling can be attributed to greater fibrillation and fiber flexibility, which results in stronger interfiber bonding [55]. The impact of delignification duration and additive on tensile index was variable, which can be attributed to the com-



4. Impact of delignification conditions on pulp brightness.

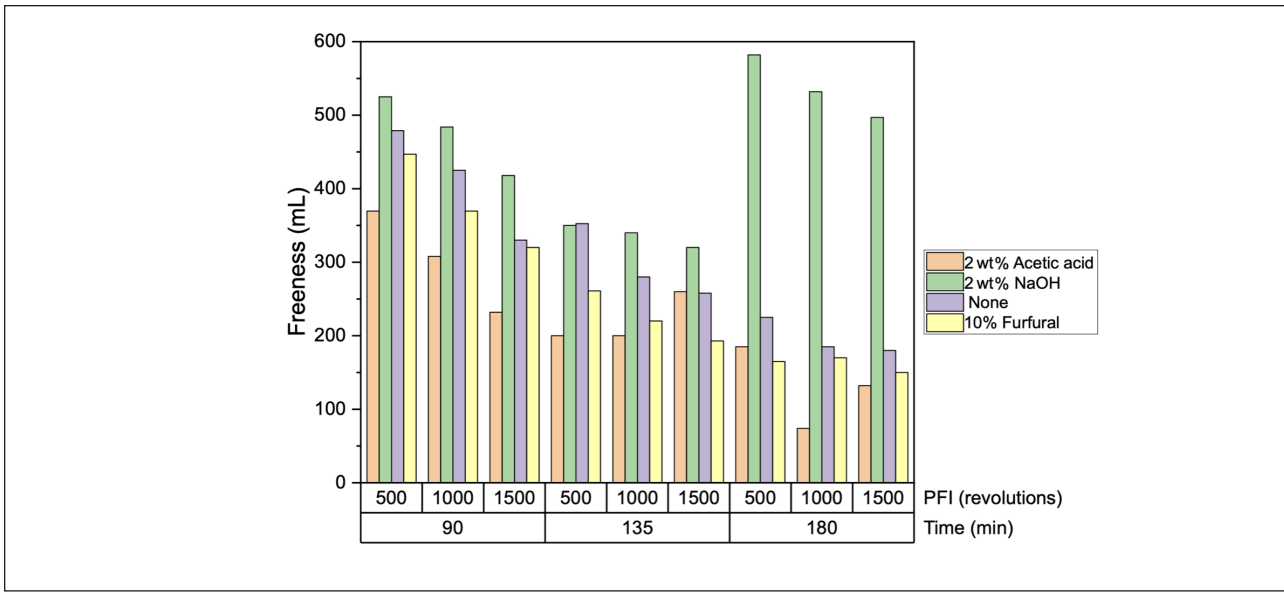


5. Impact of delignification conditions and PFI milling revolutions on (a) tensile index and (b) tear index.

bined effects of composition and the physical properties of the fibers. For example, addition of acetic acid was found to improve tensile strength for a delignification duration of 135 min, but severely decreased the tensile strength at 180 min. While the lowest lignin levels found in the pulps produced with acetic acid addition were beneficial for increasing interfiber bonding and tensile strength, the benefit was outweighed by the reduction in fiber length and removal of hemicellulose as delignification time increased.

The impact of delignification duration on tear index varied depending on additive. For all trials, except for those with NaOH, tear index generally decreased with increasing delignification duration due to the shortening of fibers limiting their combined ability to stop the propagation of tears. For trials with NaOH addition, a tear index minimum was observed at 135 min. The variation in the tear index trend could be a result of the balance between fiber length decrease and lignin removal increase. Depending on the rates, there could be a delignification duration that produces pulps with decreased fiber lengths, but without extensive lignin removal. This could result in handsheets with a comparatively lower tear index than handsheets produced from shorter (longer fiber length outweighs low lignin removal) and longer (extensive lignin removal outweighs shorter fiber length) delignification durations.

Increasing PFI milling revolutions from 500 to 1500 gen-



6. Impact of delignification conditions and PFI milling revolutions on pulp freeness.

erally resulted in an increase in tear index that can be attributed to greater interfiber bonding due to fibrillation. However, it is well known that increases in mechanical action will eventually result in a decrease in tear index due to the excessive reduction in fiber length causing an inability to prevent tear propagation [55]. The highest tear index was generally obtained in trials with 2 wt% NaOH addition, which can be attributed to fiber length preservation and hemicellulose retention provided by a reduction in polysaccharide chain degradation reactions when performing delignification at higher pH.

Freeness, a measurement of the water retention of pulp, is an important indicator for the processability of the pulp on the paper machine. Higher freeness values correspond to less water retention and thus, faster and/or more easy dewatering of the pulp. Pulps with very low freeness will require additional dewatering, which corresponds to slower production rates and/or increased dryer energy input, or, if dewatering performance is poor enough, they can be unsuitable for papermaking. A comparison of freeness values can be found in **Fig. 6**.

Pulps generated from trials with NaOH addition resulted in the highest freeness values at each temperature–PFI milling combination. This can be attributed to the low fines content and long fiber length, which minimize clogging of the freeness drainage vessel and result in larger pores that water can more easily drain through. Interestingly, this is not consistent with the qualitative dewatering performance observed during pulp washing, where pulps produced from trials with added NaOH were the most difficult to dewater. This discrepancy between dewatering performance during washing and freeness test results is quite important when considering an industrial papermaking process and could be due to several factors, such as the influence of fiber swelling and water retention within the fiber at increased pH.

It is well-known that delignification using NaOH results in significant fiber swelling while the pulp is in the alkali environment and as a result, increased water retention. Prior to resuspension for freeness testing, pulps were washed and dewatered using vacuum filtration, which changed the fiber surroundings from highly alkali to neutral. Upon resuspension for freeness testing, the fibers were likely unable to swell as much due to the moderate pH, and as a result, the true dewatering performance of the NaOH pulps was disguised. While the influence of pH on fiber swelling is the most likely cause for the difference between dewatering during washing and freeness testing, the influence of residual butanol or saponification products generated during delignification could also be an important factor.

Trials with added acetic acid generally resulted in the lowest freeness values, which can be attributed to the densely packed, low porosity fiber mat formed from the shortest fiber lengths and highest fines percentages at each condition. While it might be expected that pulps from trials with acetic acid addition would have high freeness values due to the reduced fiber/water interactions imparted by being less negatively charged, this is likely negated during the washing process. Increases in delignification time or decreases in PFI milling revolutions generally resulted in increases in freeness that can also be attributed to the longer fiber lengths and lower fines content as described previously.

CONCLUSIONS

Broadly, butanol/water delignification was successful in conversion of *miscanthus* into pulps for papermaking. The

impact of additive and duration were both found to significantly impact the properties of the resulting pulps. For papermaking applications, NaOH addition was found to be the most beneficial, producing the brightest pulps with significant hemicellulose retention and fiber lengths like that of commercial hardwood pulps. The NaOH addition moderates the pH of the delignification liquor, resulting in high lignin removal while minimizing degradation of the cellulose and hemicellulose chains. However, observations of dewatering performance during pulp washing indicate that the fiber swelling imparted by processing with NaOH negatively impacts drainage, which could result in issues appearing during pulp production, specifically with the washing and dewatering steps.

While this research focused solely on *miscanthus*, butanol/water chemistries have also been shown to be highly effective at delignification of woods such as aspen, pine, willow, and cedar [28,39,40], indicating widespread potential for this delignification chemistry. To continue the advancement of butanol/water delignification technologies, significant future research is needed and, based on passage of several "stage gates," is warranted, especially in the areas of bleaching for higher-value paper applications and delignification conditions appropriate for producing biofuel precursors. Although many challenges remain for the development and realization of butanol/water-based biorefineries, this work demonstrates the enormous potential of butanol/water delignification for furthering the valorization of nonwoody biomass.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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DATA AVAILABILITY

Data will be made available on request.

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ABOUT THE AUTHORS

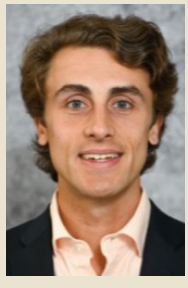
Alternative fiber pulping through organosolv is a very underserved disciplinary area that has incredible promise. The company supporting the work here had a strong interest in its potential for deriving fiber value. Our team works in green chemistry in which we seek out biobased solutions to industrial needs; our current work provides an economic and rapidly replenishable fiber source according to a very sustainable processing approach.

The most difficult part of this study was building the organosolv recovery equipment. We worked extensively with the partnering company who invested both intellectual and financial capital for its realization. Of great help was J.G. Gaynor, who is first author of this study. He has been an exceptionally outstanding Ph.D. candidate who can take a project from a very rudimentary stage of ideation to full-on equipment testing, mathematical modeling, and proof of principle validation.

The most interesting finding from this study was that organosolv can indeed work for an alternative fiber. The fibers were quite attractive from a number of perspectives.

Based on the findings here, mills can begin to assess if vapor stripping–vapor permeation (VSVP) technology for separation of immiscible liquids or even noncondensable gases (NCGs) can be exploited. Our next step is to secure further funding to begin the techno-economic analysis necessary to deliver this technology to the market.

J.G. Gaynor is a Ph.D candidate; Serrano and Clark are undergraduate students in Paper Science and Engineering; and Lucia is professor at North Carolina State University in Raleigh, NC, USA. G. Gaynor is vice president of Research & Development for Fedrigoni in Cohoes, NY, USA. Email Lucia at lalucia@ncsu.edu.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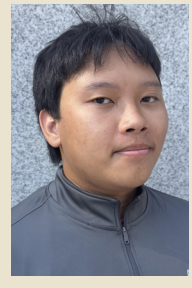
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