Desilication of bamboo for pulp production

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ABSTRACT: Bamboo is one of the world's fastest growing feedstocks. It is a promising nonwood resource that can be used in the pulp and paper industry. Among more than 1200 species of bamboo, the timber varieties can be processed much like trees, allowing current pulp mill logistical systems to be used. Bamboo can be difficult to pulp because of its high silica content, which creates issues for black liquor recovery. This study compares two methods of reducing the silica content of a common species of timber bamboo. Specifically, the dermis layer of Moso bamboo (*Phyllostachys edulis*) was removed through mechanical treatment and then chipped. The same species was also chipped without treatment. The two chipped materials were then alkali-extracted and subjected to kraft pulping experiments. The pulps were bleached with an $OD_0(EP)D_1$ sequence. The material was then refined and formed into handsheets. The results indicate that 80% of the silica could be removed from the bamboo material through a combination of dermal mechanical treatment and caustic chip extraction. Caustic chip extraction removed a significant portion of hemicellulose materials, which in turn lowered cooking yields but had minimal effect on pulp properties.

Application: Mills that use bamboo fiber in a kraft process might be able to use mechanical abrasion to remove the outer tissue or a mild alkaline steeping to reduce high silica levels that cause operational issues in the recovery process.

The subfamily *Bambusoideae* of the family *Poaceae* includes more than 1200 species of bamboo. Bamboo is one of the fastest growing plants in the world, achieving growth rates of 1 m/day during shoot growth [1,2]. Bamboo is woody in nature and can be harvested most of the year, similar to trees. However, as a member of the *Poaceae* family, it is a grass, and like other grasses is capable of high land yields of biomass [3].

The reported productivity of bamboo stands has varied widely, with a range of 2.2 to 15.5 dry metric tons/ha/year of woody material from natural stands, and typically around 8 dry metric tons/ha/year [2,4]. Productivity varies widely because of a number of growth rate factors, including species, climate, soil fertility, and stand management practices. Productivity may have additional potential, with higher yields possible from hybrids and the use of intensive agro-forestry management.

In addition to bamboo's high land productivity, some species have similar fiber properties to many hardwood and softwood species [5], which makes bamboo an interesting nonwood feedstock for paper applications. Because of their natural abundance, bamboo plants are already used extensively in Asia for timber, and for pulp and paper, although most mills are small. Bamboo plants flower infrequently. They primarily reproduce through rhizomal propagation, which creates a shortage of seeds or creates high-cost root-stocks. Recent advances in micropropagation suggest the technical and economic barriers for large-scale propagation have been removed, which opens the way for single species bamboo plantations [6]. The so-called timber species are large enough to be handled in a similar manner as pulpwood for harvesting and chipping [3].

Recent studies have shown that Moso bamboo (*Phyllostachys edulis*), a common timber species, cooks similarly to hardwoods and can be co-cooked with hardwood species with up to 25% inclusion without loss in yield. Co-cooking has been suggested as an easy method to incorporate bamboo into traditional wood furnishes [7]. However, even with co-cooking the high silica content in bamboo can accumulate during the kraft recovery process, causing issues such as scale on evaporators, glass formation in the lime kiln, and increased dead load in the liquor cycle. Substantial research and demonstration work has been done to address this, with most of the published work focused on desilication of the black liquor [8-11]. We approached the problem differently, with the idea to remove silica as early as possible before pulping by investigating both a dermal abrasion and an alkali-leaching treatment. If silica can be reduced to a low enough content, the bamboo could be conventionally cooked, or with minimal lime mud purging in the recovery system.

MATERIAL AND METHODS

Provitro Biosciences, LLC, provided mature Moso bamboo stalks from plants grown in Anderson County, SC, USA. The green culms, which are the woody stalks of bamboo, were shipped, mechanically treated, and chipped within 1 week of harvest. Half of the culms were treated by manually scraping with a two-handed drawknife to remove thin slivers of the dermal layer between nodes. Although most of the dermal layer was removed, the culm weight loss was only approximately 5%. Although moisture content varies throughout the culm, we did not want to oven dry the material before pulping. Therefore, the exact losses were not determined.

The abraded and standard culms were chipped with a disc chipper. The chips were screened with accepts set at 2 mm and 8 mm holes and were cold stored (4°C) at approximately 40% moisture content before use. The chips were air-dried to approximately 25% moisture and frozen until used. Chemicals used for the pulping and bleaching reactions were purchased from VWR International (Radnor, PA, USA) and used as received.

Samples were pulped with the kraft pulping process using a 2 L liquor rotating digester following previously optimized conditions of 18% effective alkali (EA), 25% sulfidity, 1100 H-factor, 5 L/W ratio, and 165°C pulping temperature [12]. The moisture and ash content of the biomass and pulp samples were determined according to ASTM Test Methods E 1756-08 "Standard test method for determination of total solids in biomass" and E 1755-01 "Standard test method for ash in biomass," respectively. Mineral ash analyses were performed on the resulting ash samples following ASTM D3682 "Standard test method for major and minor elements in combustion residues from coal utilization processes."

Kappa numbers were measured using TAPPI Standard Test Method T-236 cm-85 "Kappa number of pulp." The cellulose chain lengths were approximated by measuring cupriethylenediamine (CED) viscosity using TAPPI T-230 om-99 "Viscosity of pulp (capillary viscometer method)," and using these values in Eq. (1) to calculate a carbohydrate degree of polymerization (DP) [13].

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

where X is the measured viscosity in cP.

Silicon content of black liquor samples were measured following the ultraviolet/visible (UV/Vis) spectrum procedure of Wang et al. [14]. In this procedure, a UV measurement is made at 340 nm by taking advantage of the reaction of silicon (Si) with ammonium molybdate forming an Si-Mo heterophonic acid under acidic conditions. Corrections from acid-soluble lignin were made following the procedure outlined by Wang et al., through a second measurement at 480 nm.

Bleaching was performed using a Quantum Mark IV reactor (Quantum Technologies; Twinsburg, OH, USA) for oxygen and chlorine dioxide stages and bag bleaching in a water bath for alkaline extraction stages. Samples were well-washed with distilled water, with no carryover. Elemental chlorine free chlorine dioxide was prepared through sulfuric acid acidification of sodium chlorite and collection of the chlorine dioxide gas into chilled water after passing through a sodium chlorite solution trap. After bleaching, the pulp was refined in a PFI mill following TAPPI T-248 "Laboratory beating of pulp (PFI mill method)," and handsheets were prepared using TAPPI T-205 "Forming handsheets for physical tests of pulp." Freeness, basis weight, and tensile index were measured using TAPPI T-220 "Physical testing of pulp handsheets," T-411 "Thickness (caliper) of paper, paperboard, and combined board," and T-414 "Internal tearing resistance of paper (Elmendorf-type method)," respectively.

Biomass and pulp samples were subjected to a two-step acid hydrolysis procedure described in a National Renewable Energy Laboratory (NREL) report [15] to characterize the carbohydrates (hydrolyzed to individual monomers) and lignin (acid-insoluble by gravimetric and acid-soluble by UV-Vis). Acid hydrolyzed supernatant from this procedure was neutralized, centrifuged at 4000 rpm for 5 min, and filtered through a nylon filter to remove any further suspended material. The cleaned samples were then characterized for saccharides using a Dionex ICS-3000 high performance liquid chromatography system (Dionex Corporation; Sunnyvale, CA, USA) equipped with an integrated amperometric detector and Carbopac PA20 guard and analytical columns operating at 20°C [16,17]. Eluent was provided at a rate of 0.6 mL/min, according to the following gradient: 0-20 min, 100% water; 20-30 min, 25% water; and 75% 0.1 mol/L sodium hydroxide (NaOH); 30-35 min, 100% water. An NaOH solution of 0.5 mol/L was used as post-

	Ara, wt%	Gal, wt%	Glu, wt%	Xyl, wt%	Man, wt%	KL, wt%	ASL, wt%	Ash, wt%	Total, wt%
Bamboo	1.2	0.32	46.1	16.6	0.61	23.8	3.15	2.11	93.89
Scraped bamboo	1.51	0.45	47.5	15.6	0.79	25.2	3.06	1.08	95.19
Dermal layer of bamboo	0.99	0.25	39.4	11.5	0.48	18.8	2.11	20.5	94.03
Ara = arabinan; Gal = galactan; Glu = glucan; Xyl = xylan; Man = mannose; KL = Klason lignin; ASL = acid-soluble lignin.									

I. Biomass characterization.

column eluent. References were purchased from Fischer Scientific (Pittsburgh, PA, USA) and subjected to a one-step acid hydrolysis following the suggested NREL procedure [15].

RESULTS AND DISCUSSION

Biomass characterization

Samples from the scraped and unmodified bamboo chips were analyzed for saccharides, lignin, and ash to characterize the material. Inspecting the results shown in **Table I**, the measured components were near 100% of the original biomass, suggesting other non-measured materials, such as extractives, were only present in trace amounts. The scraped bamboo had significantly less ash, suggesting that much of this material resides in the dermal tissue.

The ash was further studied through elemental analysis with the results shown in **Tables II and III**. The ash content

Weight % of Ash	Bamboo Chips	Scraped Bamboo Chips	Dermal Layer of Bamboo Slivers
SiO_2	24.4	23.1	27.8
Al_2O_3	0.66	1.25	0.44
TiO_2	<0.01	<0.01	<0.01
Fe_2O_3	0.45	0.86	0.56
CaO	8.9	10.8	16.3
MgO	5.33	9.19	6.13
Na_2O	0.25	0.15	0.56
K_2O	34.5	40.4	22.3
SO_3	10.1	5.56	7.81
P_2O_5	2.64	1.15	1.76
Cl	2.2	1.16	1.51
Ash content % dry basis biomass	2.11	1.08	20.5

SiO_2 = silicon dioxide; Al_2O_3 = aluminum oxide; TiO_2 = titanium dioxide; Fe_2O_3 = ferric oxide; CaO = calcium oxide; MgO = magnesium oxide; Na_2O = sodium oxide; K_2O = potassium oxide; SO_3 = sulfur trioxide; P_2O_5 = phosphorus pentoxide; Cl = chlorine.

II. Elemental ash analysis (ash mass basis).

Element/Compound	Weight % of Biomass		
	Bamboo Chips	Scraped Bamboo Chips	Dermal Layer of Bamboo Slivers
SiO_2	0.515	0.250	5.707
Al_2O_3	0.014	0.014	0.090
TiO_2	<0.01	<0.01	<0.01
Fe_2O_3	0.009	0.009	0.115
CaO	0.188	0.117	3.350
MgO	0.112	0.099	1.257
Na_2O	0.005	0.002	0.115
K_2O	0.728	0.436	4.565
SO_3	0.213	0.060	1.601
P_2O_5	0.056	0.012	0.361
Cl	0.046	0.013	0.310
Ash content % dry basis biomass	2.11	1.08	20.5

SiO_2 = silicon dioxide; Al_2O_3 = aluminum oxide; TiO_2 = titanium dioxide; Fe_2O_3 = ferric oxide; CaO = calcium oxide; MgO = magnesium oxide; Na_2O = sodium oxide; K_2O = potassium oxide; SO_3 = sulfur trioxide; P_2O_5 = phosphorus pentoxide; Cl = chlorine.

III. Elemental ash analysis (biomass mass basis).

	Ara, wt%	Gal, wt%	Glu, wt%	Xyl, wt%	Man, wt%	KL, wt%	ASL, wt%	Ash, wt%	Total, wt%
Bamboo control	1.51	0.45	47.5	15.6	0.79	25.2	3.06	1.08	95.19
0.5% NaOH	1.10	0.41	47.5	14.1	0.79	25.8	3.40	0.77	93.87
1.0% NaOH	0.97	0.34	49.5	12.3	0.48	27.5	3.31	0.51	94.91
1.5% NaOH	0.87	0.25	50.1	12.9	0.48	27.2	2.69	0.45	94.94
2.0% NaOH	0.75	0.23	50.5	12.5	0.48	27.1	2.55	0.48	94.59

Ara = arabinan; Gal = galactan; Glu = glucan; Xyl = xylan; Man = mannose; KL = Klason lignin; ASL = acid-soluble lignin; NaOH = sodium hydroxide.

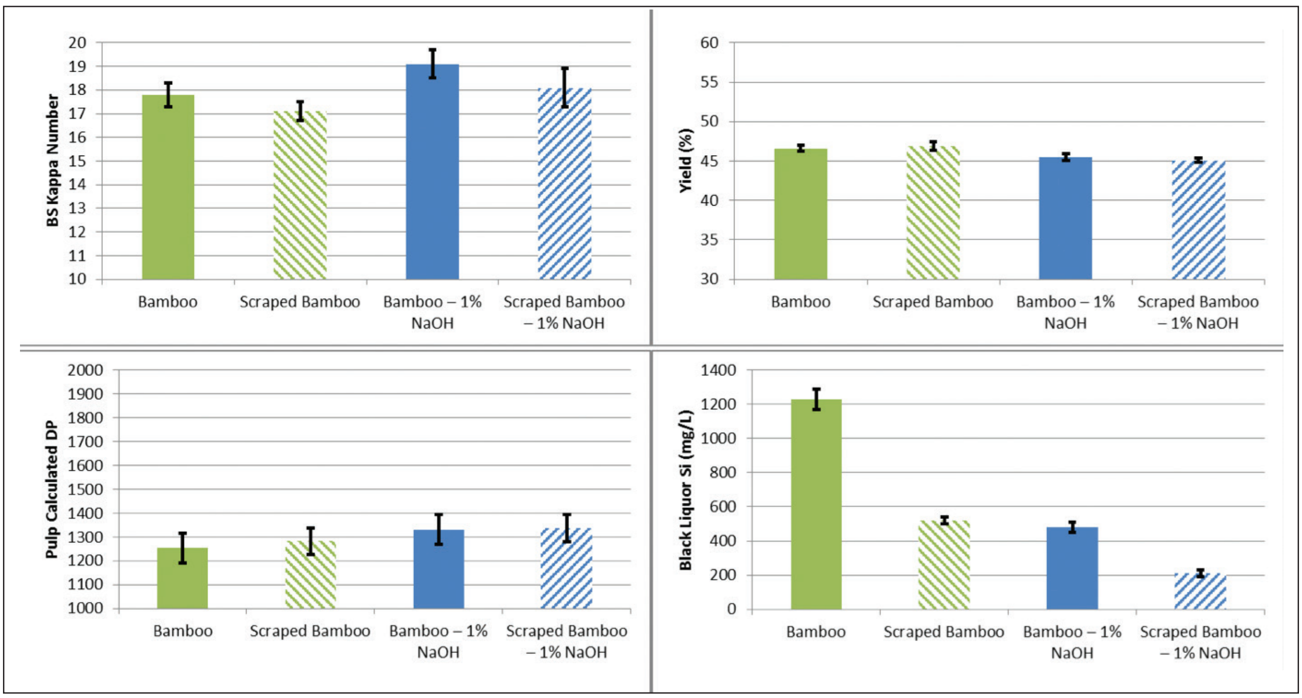
IV. Alkali desilication screening experiments.

was primarily silica, calcium, and potassium. The higher ash content in bamboo species, as compared to wood, can adversely affect the pulp process, especially in the black liquor recovery process. The results show that the weight percent of silica in the ash of the bamboo chips, scraped chips and dermal layer is similar at around 25%. However, the high ash content of the dermal layer reduced the silicon dioxide in the scraped bamboo chips by more than 50% as compared to the original culms.

Caustic chip extraction experiments

Approximately 50 g (oven dry) of bamboo chips were placed with 1 L of deionized water in 1 L autoclave bottles. A set amount of NaOH was added to each bottle, which was sealed and heated to 100°C for 1 h. After allowing the chips to cool, the material was washed with deionized water until pH neutrality was achieved. Screening experiments were conducted to find an appropriate level of NaOH to be alkaline enough to dissolve silica without extensive degradation of the hemicellulose material. Pre-extraction of hemicellulose has been shown to hurt yield and fiber properties during kraft pulping [18-20]. The extracted pulp was measured for carbohydrate, lignin, and ash to determine an appropriate NaOH charge to lower the ash content. The results of the experiments (**Table IV**) indicate that a 1% NaOH charge (based on oven dry biomass weight) is adequate to reduce the ash content significantly, but with significant hemicellulose loss.

Following the conditions derived from the screening experiment, a larger amount of chips (1000 g) from the scraped bamboo chips were placed into a 20 L digester for one experiment, and a similar amount of unscraped bamboo chips were placed into a 20 L digester for a separate experiment. For each, the reactor was filled with tap water



1. Pulping results with 95% confidence intervals.

Stage	Conditions
O	Sparged reactor with O_2 for 5 min, pressurized with O_2 to 80 psig, 10% consistency, 2.5% NaOH, 60 min, varying temperatures
D_0	0.20 Kappa factor, 3.5% csc, 50°C, 45 min, pH adjustment to achieve final pH between 2.0 and 2.5 with 10% H_2SO_4
(EP)	0.5% H_2O_2, 10% csc, 70°C, 60 min, 2.5% NaOH, terminal pH ~ 11.0
D_1	1% ClO_2, 10% consistency, 80°C, 120 min, pH adjustment to achieve final pH between 4.5 and 5.5 with 10% H_2SO_4
O_2 = oxygen; NaOH = sodium hydroxide; H_2SO_4 = sulfuric acid; H_2O_2= hydrogen peroxide; ClO_2 = chlorine dioxide.	

V. Bleaching conditions.

Pulp	Kappa #	Screened Yield, %	O_2 kappa	Final Brightness
Bamboo	17.8±0.5	46.6±0.4	8.9±0.3	88.9±0.5
Scraped bamboo	17.1±0.4	46.9±0.5	8.3±0.3	89.1±0.8
Bamboo – 1% NaOH	19.1±0.6	45.5±0.4	9.2±0.4	88.1±0.6
Scraped bamboo – 1% NaOH	18.1±0.8	45.1±0.3	10.3±0.4	88.7±0.7
O_2 = oxygen; NaOH = sodium hydroxide.				

VI. Pulp bleaching response with 95% confidence intervals.

and a 1% NaOH charge (based on oven dry biomass weight). The chips were then heated to 100ºC for 1 h and washed to neutral pH with deionized water. The resulting chips were then split into three equal fractions and used to produce three separate kraft cooks using a 2 L steel container in a rotating steam jacketed digester, with the three cooks done simultaneously. The resulting pulps were screened, black liquor was collected, and the screened pulp was washed. The pulps were weighed for yield (based on the incoming biomass into the digester) and samples were tested for kappa and degree of polymerization (DP) by CED viscosity. **Figure 1** shows the results of the testing and for kraft cooks of chips that were not subjected to a caustic extraction. The data suggest that pulp yields were slightly lower for the alkali-leached chips. Because the yields were based on mass into the digester, the lower yields were thought to result from hemicellulose and ash removal during the alkali pretreatment. All of the tested pulps had similar kappa and calculated carbohydrate DP values.

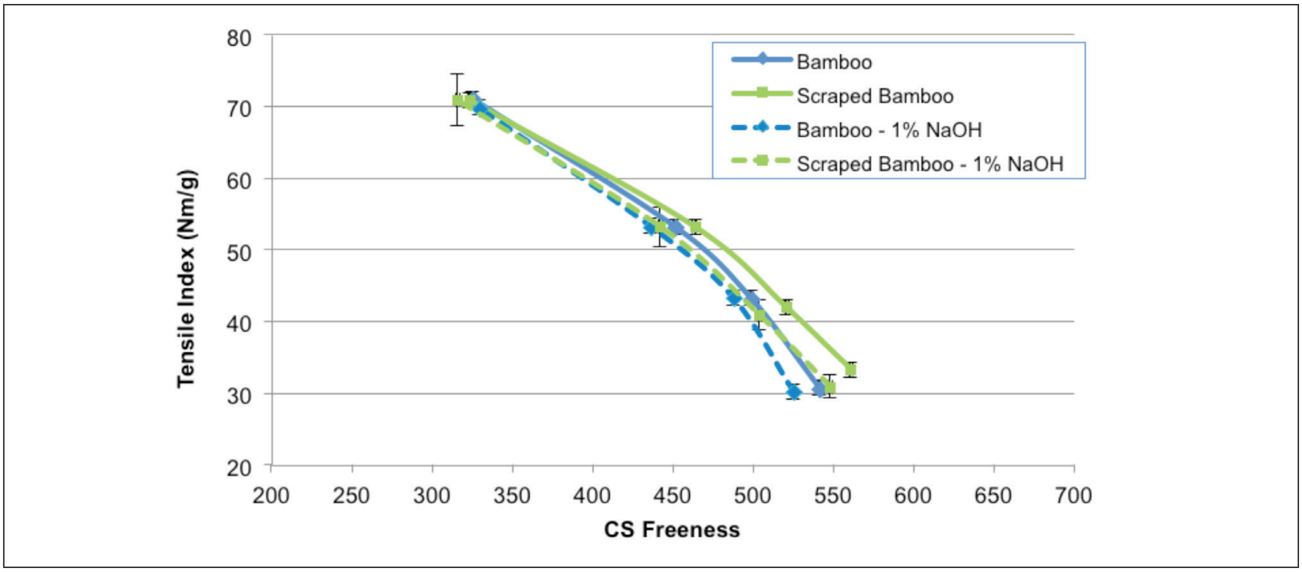
Black liquor from the end of the cooks were collected and analyzed for silica content using UV/Vis. The results (Fig. 1) indicate a significant elimination of silica, as expected from both the scraping and caustic treatment. Each treatment was effective at reducing the silica content of the bamboo black liquor by more than 50%. By combining the two treatments (scraping and 1% NaOH), the black liquor atomic silicon content was decreased more than 80% in the bamboo control sample, suggesting that this combined approach could be an effective technique for silica removal, if also demonstrated through economic feasibility studies.

Bleaching experiments

The pulps were subjected to an $OD_0(EP)D_1$ bleach sequence, following the conditions shown in **Table V**, which represents a typical sequence used for hardwood pulp [21] and was used previously with Moso bamboo kraft pulps [12]. Samples were taken and used to measure the resulting kappa around the oxygen delignification stage and the final brightness values of the pulps (**Table VI**). In general, all the pulps bleached easily, with no statistical differences observed in bleachability between the four kraft pulps.

Handsheet properties

The bleached pulps were refined with a PFI refiner to four different levels. The pulps' drainage was measured using CSF. Afterward, the refined pulps were made into TAPPI standard handsheets to measure the pulps' strength properties. Because Moso bamboo pulp has been previously shown to have properties between softwoods and hardwoods, lower refining levels of 100, 500, 1000, and 2000 PFI revolutions were chosen, similar to a previous study [12]. The results demonstrate that all four treated bamboo types have similar tensile indices (**Fig. 2**), suggesting that the mechanical and alkali treatment did not have a detrimental effect on fiber bonding.



2. Physical properties of handsheets from the 2 L cooks with 95% confidence intervals.

CONCLUSIONS AND NEXT STEPS

Kraft pulping of bamboo chips can create a nonwood pulp with yields and brightness similar to those of wood pulps. However, higher silica content of this lignocellulosic material creates black liquor recovery issues, forcing lime mud purging to remove silica from the system. In this study, we demonstrated a novel method of reducing silica levels in bamboo pulp through mechanical treatments to remove much of the dermis layer, where the bulk of the ash and silica resides. This treatment was comparable to an alkali desilication method, where each method is able to reduce the silica content of the black liquor by more than 50%. When the two treatments were used in series, more than 80% silica elimination was possible. Following previously developed conditions, the chips were pulped and bleached. The resulting material showed lower yields for the alkali-extracted chips, but similar delignification and bleachability characteristics. The lower yield was believed to result from lower hemicellulose content, because a portion was hydrolyzed during the caustic chip extraction. Handsheets created from the pulps did not show significant difference in tensile index properties, suggesting that the treatments will not create pulp quality issues.

This paper represents the first steps in investigating the idea of epidermal tissue removal as a means to lower bamboo silica levels. To further this idea, additional research will be needed, including studies using additional species beyond Moso bamboo, larger scale experiments, and the use of mechanized operations for abrading and removing the dermal tissue. Additionally, an economic analysis will need to be performed using production expertise to identify the amount of silica elimination required, the most feasible methods, and the process costs. **TJ**

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ABOUT THE AUTHORS

This research is a continuation of work we are doing on timber bamboo as a viable nonwood pulp source. In the past, we have shown results of pulping and bleaching of the Moso bamboo, along with its ability to be co-cooked with hardwoods. Feedback from TAPPI conferences indicated that the silica levels need to be addressed before commercialization, which we attempted to do with this work.

The most difficult aspect of the research was to find a method to "de-bark" bamboo. From past work we had a theory that much of the silica was in the outer layer, but there was no equipment we could find to process the small amount of bamboo material. We ended up using a drawknife to manually abrade the surfaces, which of course is not industrially practical, but provided the results we needed.

The most interesting aspect of the research was when we accidentally found a reduction in silica by removing the epidermal layer. We were chipping bamboo, and because of the condition of the equipment, we had a large amount of the outer layer to screen out as slivers. The resulting pulp was significantly lower in ash, which led to this study.

Mills that are already processing bamboo or are looking to process bamboo in a kraft process could consider these desilication methods as an alternative to lime mud purging or other methods to remove silica from the black liquor.

Our next step would be to take this laboratory scale work and investigate equipment and processes for larger scale trials.

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