

An eco-friendly scheme to eliminate silica problems during bamboo biomass fractionation

Zhaoyang Yuan, Xue Feng Chang, Nuwan Sella Kapu, Rodger Beatson, and D. Mark Martinez

KEYWORDS: Alkaline pre-extraction liquor, Bamboo, Carbon dioxide (CO₂), Hemicellulose, Silica

SUMMARY: In this study, an eco-friendly scheme to resolve the silica associated challenges encountered in processing bamboo for biorefineries was evaluated. Bamboo chips were pretreated with sodium hydroxide (NaOH) at low temperature to completely extract silica and partially extract hemicelluloses for follow up conventional kraft pulping or bioethanol production. Silica and hemicellulose in the alkaline pre-extraction liquor (APEL) were sequentially isolated through carbon dioxide (CO₂) and ethanol precipitation. High purity (> 99.8%) amorphous silica particles were recovered by carbonating the effluent at 60°C to a pH of 8.2 with CO₂. The CO₂ adsorption capacity of the APEL was determined to be 7.15 g CO₂ per liter. After recovering more than 96% of available silica in the APEL, hemicellulose in the CO₂-treated liquor was subsequently separated. This study demonstrated the feasibility of pre-extraction and recovery of silica and hemicellulose to alleviate the silica challenges, thereby allowing to expand bamboo as a feedstock for industrial processes.

ADDRESSES OF THE AUTHORS: Zhaoyang Yuan (yuanzy87@mail.ubc.ca), Nuwan Sella Kapu (nuwan.kapu@ubc.ca) and D. Mark Martinez (mark.martinez@ubc.ca): Department of Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, BC V6T 1Z4, Canada

Xue Feng Chang (Harry_Chang@bcit.ca) and Rodger Beatson (Rodger_Beatson@bcit.ca): Chemical and Environmental Technology, British Columbia Institute of Technology, 3700 Willingdon Ave, Vancouver, BC V5G 3H2, Canada

Corresponding author: Zhaoyang Yuan

Growing concerns about the energy security and climate change have spurred considerable efforts to produce second generation biofuels (e.g. bioethanol and biodiesel) and third generation biofuels (e.g. hydrogen) from lignocellulosic biomasses (Gupta & Verma, 2015; Trajano & Wyman, 2013). Moreover, dissolving pulp and nanocrystalline cellulose (NCC), specialty starting materials from lignocellulosic biomass, are of increasing importance in manufacturing various products such as textiles, paints, drug delivery agents and liquid crystal displays (Kapu & Trajano, 2014). Among the biomasses, bamboo, a perennial woody grass, has received substantial attention due to its chemical composition (similar to wood), fast-growth to become harvest-ready in 3-5 years, and high abundance in many Asian countries (Scurlock et al., 2000). However, compared to woods, most of bamboo species contain a much higher level of silica (0.5-4% w/w) (Ding et al., 2008; Torelli & Čufar, 1995), which greatly challenges the industrial utilization of bamboo (Le et al., 2015). For example, in the

production of cellulosic bioethanol from bamboo (or other silica-rich raw materials), the silica stays in the residual lignin hindering thermal motion and preventing thermal processing of lignin into value-added bio-products such as emulsion stabilizers and dispersing agents (Kadla et al., 2002) and (Pye, 2008). In conventional kraft pulping or dissolving pulp production, silica causes serious problems in the recovery cycle such as scaling of the evaporator and forming glass on the lime particles (Cardoso et al., 2009; Le et al., 2015; Pekarovic et al., 2005). Silica in the final dissolving pulp also interferes with the downstream conversion into high-value products such as cellulose acetates (He et al., 2008; He et al., 2009). In addition, silica in the water stream also causes several complications such as membrane fouling and pipeline scaling (Le et al., 2015; Negro et al., 2001). Therefore, the removal of silica from the raw material could be the ideal method in solving the silica challenges when processing bamboo in biorefineries, especially in pulp and paper industry.

Most of silica accumulated as amorphous hydrate silica (SiO₂·H₂O) in bamboo with little crystalline phases (Motomura et al., 2006; Sterling, 1967). Thus, bamboo silica can be a valuable by-product such as amorphous nanosilica particles. Nanosilica, an essential starting material, is widely used for the production of thixotropic agents, pharmaceuticals, film substrates, electric and thermal insulators, composite fillers, etc. (Barik et al., 2008; Sun & Gong, 2001). Currently, amorphous nanosilica is mainly made from relatively expensive sources such as tetraethoxysilane and tetramethoxysilane under high temperature treatment (> 1300°C) (Chruściel & Ślusarski, 2003). In consequence, it would be useful and economical to fabricate nanosilica from renewable silica-containing biomasses such as bamboo in a cost-effective way.

In our earlier study, it was observed that low temperature alkaline pre-extraction of bamboo prior to pulping extracted all silica and up to 50% of hemicellulose into the bulk liquor, which also improved subsequent delignification and preserved pulp yield without affecting papermaking properties (Yuan et al., 2016). The alkaline pre-extraction liquor (APEL) cannot be directly added into the black liquor generated from kraft pulping for conventional chemical recovery circle to recover energy and alkali, because if we do so we are back to square one with silica problems. Within this context, the dissolved materials in APEL, e.g. silicates and hemicelluloses, should be isolated prior to processing for alkali recovery. Moreover, the recovered silica and hemicelluloses can be utilized for production of various high-value products such as nanosilica, ethanol, xylitol, bio-polymeric films (Jun et al., 2012; Huang et al., 2008; Schild et al., 2010). Thus, the recovery of these valuable dissolved materials, silica and hemicelluloses, from the

APEL in an economical and eco-friendly manner is critical to their downstream processing and utilization for value-added products.

Among the chemicals used for the precipitation of silica from alkali aqueous media (Minu et al., 2012; Zhang et al., 2013), CO₂ present in the waste flue gas from the energy plant of biorefinery mill (Seabra et al., 2010) or chemical recovery circle of pulp mill (Hektor & Berntsson, 2007), provides a convenient option. The utilization of waste gas can also, to some extent, alleviate environmental problems by reducing pulp mill greenhouse gas emissions. Another advantage of the alkaline pre-extraction lies in the fact that the APEL contains very low lignin content, thus, lignin co-precipitation, which normally occurs during the desilication of black liquor by lowering the pH with CO₂ or other mineral acids (Minu et al., 2012; Kopfmann & Hudeczek, 1988), will be significantly lower and as a result, pure silica can be separated. After silica removal, relatively clean hemicellulose can also be obtained from the residual APEL. Moreover, the silica associated challenges in chemical recovery of black liquor can be resolved.

In this study, a novel and green concept is proposed for the production of pure silica nanoparticles and polymeric hemicelluloses from bamboo, which at the same time solves the silica problems in processing bamboo in pulp industries and provides a mill a green pathway to manufacture high-value products from the pre-extracted silica and hemicelluloses.

Materials and Methods

Raw materials

Bamboo chips (*Neosinocalamus affinis* Keng) prepared were provided by Lee & Man Paper Manufacturing Ltd. The obtained chips were washed with distilled water for 10 min at a liquid-to-wood (based on the oven dry weight

of wood) ratio of 20 L/kg using a laboratory mixer. The washed chips were air dried for approximately 24 h and stored at 4°C until used. The moisture content of the washed and air-dried bamboo chips was 22.3%. All chemicals used in this study were reagent grade and were purchased from Fisher Scientific, Canada.

Preparation of alkaline pre-extraction liquor (APEL)

Different from the earlier study (Yuan et al., 2016), the reactor was routinely rotated at 50 rpm throughout the reaction process to simulate for the commercial process. Air-dried bamboo chips equivalent to 300 g oven dried (o.d.) mass were extracted with NaOH at the liquid-to-wood ratio of 8 L/kg in a 5 L stainless steel digester (Aurora Products, Savona, BC, Canada). Chips were treated at temperature of 90°C with various NaOH charges (10, 12 and 14% on o.d. chip mass) for 3 h. Upon completion of the extraction, the reactor was rapidly cooled to room temperature in a cold water bath. The liquor (APEL) was separated from the chips through vacuum filtration and collected for the experiments on the recovery of silica and hemicelluloses. The treated chips were stored at 4°C for further measurement and utilization. To prepare enough liquor for the study, several extraction runs were conducted. The obtained APEL obtained under the same conditions were mixed well in a large container and stored at 4°C until further used.

Preparation of silica particles from the APEL

The mechanisms for the liquor neutralization and silica precipitation with carbon dioxide CO₂ are shown in Eq 1 and 2. The apparatus was constructed to measure the effects of CO₂ treatment time and temperature on the silica precipitation from the APEL and analyze the compositions of all coexisting gases via an online gas chromatograph (Fig 1). Glass reactors with the ratio of length to diameter of 6 were used (No. 7 apparatus in Fig 1).

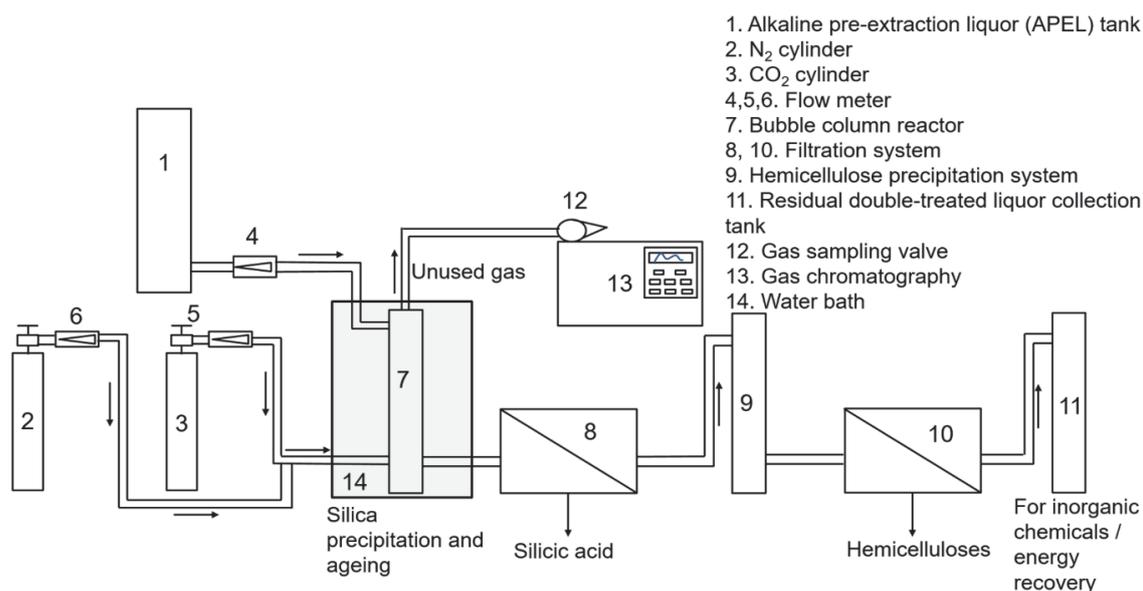
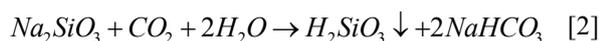
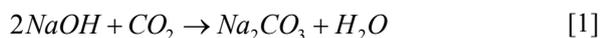


Fig 1 - A schematic of experimental set-up for recovering silica and hemicelluloses from the APEL and measuring CO₂ adsorption.

The composition of residual gas was analyzed on a CX-3400 gas chromatograph (GC) (Varian Canada Inc., Mississauga, Ontario) equipped with a thermal conductivity detector (TCD) and flame ionization detector along with a CP-PoraPLOT U capillary column. Ultra-high purity Helium (He) was used as carrier gas. The gas sample was collected with a 1/8" stainless steel sampling valve (Agilent Technologies, Inc., Model 8134). The sampling valve was flushed out three times with He before collecting a sample for analysis.



Two separate studies were conducted in this work. In the first study, a series of CO₂ treatment experiments were carried out over various temperatures (20-100°C) and times (5-120 min). The temperature of the single experiment was maintained in an electrically heated water bath. For a silica precipitation run, 200 mL APEL was added into the reactor before placing in the water bath for 15 min to reach the desired temperature. Then, the CO₂ was introduced into the bottom of the reactor at the flow rate of 0.1 L/min. Upon completion of an experimental run, the reactor was taken out from the water bath and aged for 24 h. The precipitate was washed several times with distilled water and carefully collected. The collected precipitate was initially dried at 120°C in the oven for 24 h. The moisture free samples were used for FTIR analysis. Then, the sample was incinerated in a muffle furnace at 700°C for 4 h to completely remove any adsorbed organics. In the second study, the mixture gas of CO₂ and N₂ was used to simulate for the waste flue gas under conditions (such as temperature) optimized by the first study. The flow rates of CO₂ and N₂ were 0.1 and 0.2 L/min, respectively. The treatment time was set to 5-120 min at the fixed temperature. After each treatment, gas samples (300 µL) were taken for analysis with the Gas Chromatography (GC). The precipitate was collected as previously described.

Isolation of hemicelluloses

The separation of hemicelluloses from the CO₂ treated APEL was achieved by precipitation and filtration. In the precipitation process, 95% ethanol was slowly added to the filtrate obtained from the silica isolation with a volumetric ratio of 3 while stirring. The stirring was stopped after another 5 min after final addition. The mixture was kept at 20°C for 24 h to allow the formed precipitate to settle. Then, the hemicelluloses were recovered by centrifugation (3000 rpm, 10 min) and washed with 95% ethanol until the supernatant became colorless. Finally, the obtained hemicellulose particles were vacuum dried at 45°C for 36 h.

Analytical methods

Total solid content of the extracts and black liquors was determined by vacuum drying at 45°C for 48 h. Silica content of liquors was measured by using the silicon molybdenum blue photometric method (Tong et al., 2005). For the determination of lignin and carbohydrates content of the extracts, the filtered APELs were neutralized using dilute sulfuric acid. Then the samples

were auto-claved with 4% (w/w) H₂SO₄ for 60 min. Then, quantitative determination of dissolved organics was carried out following National Renewable Energy Laboratory (NREL) standard protocols (Sluiter et al., 2012). For polysaccharide analysis, acid hydrolysates (liquid samples) were recovered by filtration through medium porosity filtering crucibles (Fisher Scientific Co., ON, Canada), and an internal standard, fucose, added. These samples were re-filtered using 0.2 µm syringe filters (Chromatographic Specialties, Inc. ON, Canada) for HPLC. A Dionex ICS 5000+ HPLC system fitted with an AS-AP autosampler was used to separate the monomeric sugars in the samples at 45°C, against sugar standards, on a Dionex CarboPac SA10 analytical column. 1 mM NaOH at 1 mL/min flow was the mobile phase, and the sugars were quantified using electrochemical detection and Chromeleon software (Thermo Fisher Scientific, MA, USA). High purity monomeric sugar standards, arabinose, galactose, glucose, xylose and mannose were purchased from Sigma-Aldrich (ON, Canada). Acid soluble lignin in the two-step hydrolysate was measured at wavelength 205 nm using a UV-Visible spectrophotometer (Dence, 1992). Acid insoluble lignin was determined gravimetrically according to NREL methods (Sluiter et al., 2012).

Mineral composition of the silica powders obtained after incineration at 700°C was determined by atomic emission measurements using an iCP spectrometer (iCAP 6000 Series, Thermo Scientific, MA, USA) by using nitric acid (HNO₃) to prepare testing solutions. Fourier transform infrared spectroscopy experiments of silica particles and hemicelluloses were carried out on a Cary 630 FTIR Spectrometer (Agilent Technologies, ON, Canada) using the ATR model. The absorption spectra were recorded in the absorption band mode in the range of 4000 to 500 cm⁻¹. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of hemicelluloses were determined by size exclusion chromatography (SEC) with a DAWNEOS-Optilab rEX (Wyatt Technology Inc., USA) equipped with a high performance liquid chromatography (HPLC) pump (Waters Corp., USA) and two columns, TSK-GELG-4000 PWx1 (7.8 × 300 mm) and TSK-GEL G-2500 PWx1 (7.8 × 300 mm). The eluent phase used was 0.02 mol/L potassium dihydrogen phosphate (KH₂PO₄). The flow rate was 0.5 mL/min, and the operating temperature was 35°C. The solution was filtered with 0.45 µm membrane and injected in the SEC system for analysis, the glucan was used calibration standards. Alkali concentration was measured using titration method (TAAPI T-625 cm-85). The brightness was measured according to the TAPPI T452 om-08.

Results and Discussion

Generation of alkaline pre-extraction liquor (APEL)

The raw bamboo feedstock used in this study contained 47.3% glucan, 21.8% hemicellulose (20.3% xylan, 0.7% galactan, 0.8% arabinan, mannan undetected), 25.3% lignin (sum of acid-soluble and insoluble lignin), 4.6% extractives, 2.01% ash and 1.12% silica on a dry basis. Based on our previous study on alkaline pretreatment of

Table 1 - Chemical composition of alkaline pre-extraction liquor (APEL).

NaOH charge (%)	Biomass yield (%)	Solid content (%)	Silica (g/L)	Lignin (g/L)	Glucan (g/L)	Xylan (g/L)	Galactan (g/L)	Arabinan (g/L)	Acetic acid (g/L)	pH
10	88.8	3.26	1.45	1.42	1.24	8.78	0.21	0.32	2.76	12.97
12	87.5	3.31	1.73	1.74	1.29	9.26	0.22	0.41	2.77	13.12
14	86.6	3.32	1.70	1.99	1.46	9.97	0.34	0.45	2.74	13.28

Values are expressed as averages of three replicate measurements.

bamboo chips to extract the maximum silica and hemicellulose while minimizing the degradation of cellulose and lignin (Yuan et al., 2016), the APEL was produced from the alkaline extraction with a NaOH charge of 10-14% (based on o.d. chip mass) in the laboratory. *Table 1* shows the chemical composition of the obtained APELs. As shown in *Table 1*, with the increase of the NaOH charge, the biomass yield decreased due to the removal of more individual component from bamboo biomass. The residual alkali in the APEL can be recovered as NaOH after the removal of silica and hemicelluloses through the conventional black liquor recovery cycle used in a typical chemical pulp mill (Sixta, 2006).

The concentration of silica, released as soluble sodium silicate (Na_2SiO_3), was 1.45, 1.73 and 1.70 g/L in the APELs obtained from 10, 12 and 14% NaOH charges, respectively. Based on the silica concentration in the APEL, the liquid-to-wood ratio (8 L/kg) used for the extraction and the moisture content of treated chips (60-65%), it was calculated that up to 99% of silica in raw chips was removed with 12-14% NaOH, whereas about 86% of silica was removed with 10% NaOH charge (based on o.d. chip mass). This was further confirmed by the measurement of the silica content of extracted chips, which was 0.17% (w/w) in the case of 10% NaOH charge and less than 0.02% (w/w) with 12% and 14% NaOH charge.

The maximum lignin concentration of the liquors was 1.99 g/L; this means that only about 5.1% of initial lignin was removed during alkaline pre-extraction under the studied conditions. This could be due to the fact that delignification of bamboo normally starts at temperatures higher than 100°C (Sixta, 2006), hence, the lignin detected with UV-vis spectroscopy in the APEL could be mainly mono- or oligo-lignols (Arato et al., 2005). The extracted glucan in the liquors ranged from 1.24-1.46 g/L with increasing NaOH charge from 10-14% (based on o.d. chip mass), corresponding to 1.7-2.0% of the initial glucan. The low removal of cellulose can be attributed to its low reactivity with alkali and high crystallinity (Gupta & Lee, 2010). Thus, under the investigated conditions, most of the lignin and glucan were preserved in the treated solids, which maintained the heating value of black liquor and the pulp yield (Yuan et al., 2016).

Different from cellulose, hemicellulose is branched, amorphous polysaccharides composed of short lateral chains consisting of several different monosaccharides and functional groups (Trajano & Wyman, 2013); this makes hemicellulose much easier to be degraded and dissolved than cellulose. In the studied bamboo, xylan is measured to be the major constituent, which accounted

for about 93% of hemicellulose. In the liquors, xylan had a concentration of 8.78-9.97 g/L depending on NaOH charge, corresponding to about 30% of xylan being removed during alkaline pretreatment. Concentrations of galactan and arabinan in the APELs were 0.2-0.5 g/L, respectively, while acetic acid concentration was about 2.75 g/L, which can be due to the liberation of acetyl groups from the hemicelluloses chains. According to the measurements, the sum of biomass yield and dissolved materials in the APELs were calculated to be 98.5% for the treatments under the three NaOH charges (10-14% w/w). This 1.5% biomass loss might be due to other undetermined dissolved inorganics and degradation products. The pH of generated APELs were 12.97, 13.12 and 13.28 for 10%, 12% and 14% NaOH charges, respectively.

Based on the above experimental data, utilization of 12% NaOH charge (on o.d. chip mass) not only had the potential of removing all silica from bamboo chips but also could reduce the chemical consumption compared to that of 14% NaOH charge. Consequently, the APEL obtained from the pretreatment with 12% NaOH charge (on o.d. chip mass) was selected and subjected for the recovery of silica and hemicellulose.

Isolation of silica from APEL with pure CO_2

During CO_2 treatment of the APEL, soluble sodium silicate (Na_2SiO_3) is converted to the insoluble colloid silicic acid (H_2SiO_3), which can be removed from the liquor (see *Eq 2*). In this work, silica was recovered from the APEL by lowering its pH with CO_2 at different temperatures (20-100°C). *Fig 2* shows the effect of temperature and pH on the removal of silica from the APEL. Evidently, the temperature had a minor effect on the amount of silica precipitated from the APEL. At the five studied temperatures, the percentage of removed silica varied 93-97% at a final liquor pH of about 9.0. The amount of silica removed was increased slightly by increasing the temperature from 20 to 60°C. Increase in temperature to 100°C led to a small reduction in silica removal. The maximum silica removal was achieved at 60-80°C. Moreover, compared to low temperature (20-60°C), higher temperature (80-100°C) required more CO_2 to reach the same final pH. For example, it required about 120 min to decrease the pH of the APEL to 9.0 at 100°C at a 0.1 L/min CO_2 flow rate; in contrast, at 20°C with the same flow rate, pH 9.0 was reached in about 25 min. This is due to the decreasing solubility of CO_2 with increasing temperature of the solution, which means that the utilization of flue gas would be less efficient at higher temperatures. Therefore, it can be concluded that the optimum temperature for the precipitation and recovery

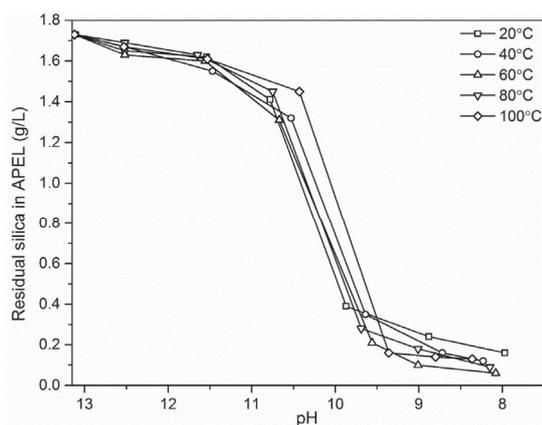


Fig 2 - Effect of temperature and pH on the precipitation of silica from the APEL.

of silica from the APEL was around 60°C. Additionally, since the temperature of the obtained APEL after pre-treatment (conducted at 90°C) was around 65°C, the proposed process would not require extra heat in the precipitation step. In contrast to temperature, the liquor pH plays a much more important role in silicic acid precipitation from the APEL. During the bubbling process, the pH of the APEL gradually decreased over time towards a plateau at all studied temperatures. As shown in Fig 2, in the pH range of 13.12 to 11.0, only about 4.8-8.7% of silica was precipitated from the APEL at all studied temperatures. However, when the pH of the liquor was decreased from 11.0 to 9.0 by bubbling CO₂ for a longer time (25-120 min), a sharp increase in the amount of precipitated silicic acid occurred; up to 93-97% of raw silica in the APEL was removed at the five treatment temperatures. For example, at 60°C, about 94% of silica was removed from the APEL by lowering the pH to 9.0. With continuous bubbling of CO₂ into the liquor, more carbonic acid is formed, and the pH drops as the acid concentration increases resulting in the rapid formation of the insoluble silicic acid at pH 11.0 to 9.0. About 2-5% of silica still remained dissolved in the APEL even when the pH was decreased to 8.2. This can be attributed to the solubility of silica even at pH 7 or lower, which means not all silica can be precipitated by lowering the pH of the solution (Icenhower and Dove, 2000). In addition, it should be noted that it was very difficult to reduce the pH of the APEL below 8.0 even at the lowest temperature (20°C) tested in this study, which might be due to the bicarbonate/carbonate buffering system formed in the APEL. In contrast, lowering the pH to 8.2 was much easier to achieve. Accordingly, the pH of silica precipitation from the APEL should be limited to about 8.2 in order to maintain mill efficiency.

The APEL after silica removal can be used as a raw feedstock for the recovery of hemicelluloses to produce ethanol, xylitol or polymeric films; so it is of great importance to minimize the loss of hemicelluloses during the CO₂ treatment stage. Analysis of the chemical composition of APEL recovered after maximum silica removal at 60°C showed that only about 4% of hemicelluloses was removed during the silica removal. The likely reasons for hemicellulose loss include the

potential co-precipitation of hemicellulose with silica as well as wash-off during the silica separation process. It can be concluded that the precipitation and filtration of silica from the APEL does not significantly influence the hemicellulose concentration in the supernatant, and will not have a large negative effect on subsequent hemicellulose recovery.

Capture of CO₂ from the CO₂/N₂ mixture

With the fundamental information obtained from the silica precipitation with CO₂ only, an attempt for developing the utilization of flue gas for recovering silica was initiated. Thus, a mixture gas of CO₂ (0.1 L/min) and N₂ (0.2 L/min) was used to simulate for the flue gas (Fan et al., 2009). During the treatment process, the unreacted gas mixture was released from the reactor to make the pressure in the reactor constant. The composition of the released gas was analyzed at different times (5-120 min), the CO₂ fraction is given in Table 2. The CO₂ fraction in the gas phase was found to gradually increase with increasing treatment time. This could be related to the fact that initially more CO₂ was dissolved and consumed by the reactions with chemicals such as NaOH and Na₂SiO₃ in the APEL; with prolonged treatment, the chemical reactions were completed and the content of CO₂ in the APEL reached saturation.

Table 2 - Gas phase CO₂ measurements during silica precipitation.

Time (min)	CO ₂ (%) (± 0.20)
0	33.33
5	18.21
10	20.34
15	20.56
20	20.78
25	20.91
30	21.43
35	22.44
40	22.53
45	23.02
50	23.59
55	24.51
60	25.25
65	25.89
70	26.43
75	27.10
80	27.42
85	27.78
90	28.19
95	28.42
100	28.73
105	28.95
110	29.15
115	29.35
120	29.52

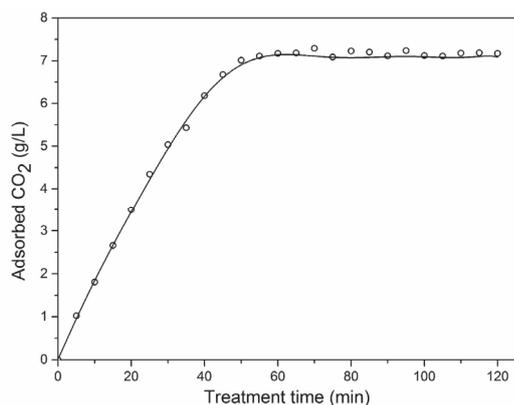


Fig 3 - CO₂ adsorption measurement curves during the precipitation of silica at 60°C.

Based on the compositional analysis of the residual gas phase, the actual adsorption or consumption of CO₂ for a period of 5-120 min was calculated. As shown in Fig 3, the adsorption/uptake of CO₂ by the APEL initially increased with increasing time, thereafter it reached a plateau. At 60 and 120 min, the pH of the treated APEL was determined to be 8.16 and 8.08, respectively. These results confirmed that it was very difficult to lower the pH of the APEL below 8.0 with CO₂. As illustrated in Fig 3, during the process of reducing the pH of APEL from 13.12 to 8.16, 1.94 L CO₂ (at a density of 1.842 g/L at 20°C) was consumed per 200 mL APEL. Thus, the adsorption of CO₂ is calculated to be 7.15 g CO₂ per liter of APEL (based on the 12% NaOH charge used in this study), the same liquor used in pure CO₂ treatment. Since the real flue gas might contain small amounts of other acidic compounds such as SO₂, NO_x or H₂S (Douskova et al., 2009), which will also be removed by the APEL, resulting in a relatively clean gas for emissions.

Compositional and FTIR analysis of silica powders

To remove organics (lignin and sugars) and prepare highly purified silica powder, oven dried silica samples were burnt at 700°C for 4 h. The weight percentages of the mineral ingredients present in the silica powders after burning were measured using an ICP spectrometer (Table 3). The impurities contained in the silica powders were calcium, manganese, iron, copper, magnesium, potassium and sodium; among which the concentration of calcium was the highest (0.12% w/w) while the total impurities accounted for about 0.16% (w/w). These results showed that the produced powders contained more than 99.8% (w/w) of silica, confirming the hypothesis that high purity silica could be produced from the APEL of bamboo. Such high purity of the precipitated porous silica particles makes it an excellent starting material for various high-value products such as pharmaceuticals that require silica purity higher than 99.7% (Morpurgo et al., 2010).

Fig 4 shows the FTIR spectra of the silica powders before (a) and after (b) high temperature (700°C) burning. As shown in Fig 4a, the two absorption peaks at 3408 cm⁻¹ and 1596 cm⁻¹ are principally attributed to stretching of -OH groups and bending modes of absorbed water in hemicelluloses, respectively. The predominant absorption

Table 3. Mineral composition of silica powder prepared from APEL.

Element	Weight percentage (%)
Ca	0.12
Mn	0.0026
Fe	0.0071
Al	ND
Cu	0.0097
Mg	0.0075
K	0.0057
Na	0.0034
Sum	0.156

ND: not detected.

band at 1074 cm⁻¹ can be assigned to Si-O-Si asymmetric stretching and, absorbance peaks at 794 cm⁻¹ is due to the symmetric Si-O-Si bond (Nagaraja & Venkateswara, 2006). Peaks of Fig 4a (before high temperature burning) confirmed that very little hemicelluloses co-precipitated during the silicic acid precipitation process. Comparison of the FTIR spectra 4b (after burning at 700°C) and 4a shows the disappearance of the two absorption peaks at 3408 cm⁻¹ and 1596 cm⁻¹ upon burning, indicating the complete removal of organics and water producing high purity silica powders. Other absorbance bands at 1084 cm⁻¹ and 792 cm⁻¹ (Fig 4b) are also assigned to Si-O-Si asymmetric stretching and symmetric Si-O-Si bond, respectively (Nagaraja & Venkateswara, 2006). The shift in the 1074 cm⁻¹ peak in Fig 4a to 1084 cm⁻¹ in Fig 4b is likely due to the elimination of the hydrogen bond (O-H) and the weakening of Si-O-Si after high temperature treatment. The IR bands of silica powder investigated in this study were similar to those reported in other investigations (Barik et al., 2008; Kalapathy et al., 2002). Also, the absence of peaks at around 1510 cm⁻¹ and 2930 cm⁻¹ in the FTIR analysis confirmed that lignin did not co-precipitate with silica during APEL processing (Liu et al., 2008). Therefore, alkaline pre-extraction effectively decouples desilication from the major delignification reactions of kraft pulping. This is a significant benefit in kraft pulping because, with a pre-extraction step, silica does not fractionate into the black liquor during the kraft cook. Scaling and other problems that occur during kraft chemical recovery are hence eliminated. Moreover, if necessary, cleaner lignin fractions with lower ash, can be recovered from black liquor.

Isolation and characterization of hemicelluloses from the treated APEL

The hemicelluloses recovery was conducted on the APEL after silica removal at optimum conditions (CO₂ treatment at 60°C to pH 8.2). Chemical composition analysis of the isolated hemicelluloses showed that the total sugar content was 92.2%, in which xylan, galactan, arabinan and glucan contents were 78.1%, 2.1%, 1.8%, and 10.2%, respectively. The measured lignin and ash contents were 2.7% and 1.1%, respectively. The uronic acid content was determined to be 4.0%, which was in good accordance with reports that about 4-5% of uronic acid appeared as 4-O-methyl-D-glucuronic acid residues in bamboo feedstocks (Billa et al., 1996). In the literature,

similar composition results have been reported for alkaline extracted hemicellulose from hardwood and sugar cane bagasse (Jun et al., 2012; Peng et al., 2010). Due to the co-precipitation of lignin and possibly extractives, the isolated hemicelluloses had a brightness of 32.6% ISO. After hemicelluloses precipitation, the residual liquor can be sent to the traditional kraft chemical recovery process to recover inorganics such as sodium hydroxide for alkaline pre-extraction or kraft cooking.

Fig 5 shows the FTIR spectra of the isolated hemicellulosic fraction. The strong broad band at 3419 cm^{-1} is attributed to the stretching of O-H bond. The absorbance at 2920 cm^{-1} was due to the C-H stretching vibration. The absorbance at 1611 cm^{-1} can be assigned to absorbed water in hemicelluloses (Wen et al., 2011). The prominent absorption peak of 1044 cm^{-1} is due to C-O stretching in C-O-C linkages. The absorption bands of 1385, 1329, and 1246 cm^{-1} are characteristic of hemicelluloses obtained by alkali extraction (Xu et al. 2007). The absorbance at 897 cm^{-1} can be assigned to β -glycosidic linkages between the sugar units (Liu et al., 2011). The small absorption peak of 1513 cm^{-1} is characterized by aromatic skeleton vibrations belonging to lignin (Peng et al., 2010).

To further characterize the isolated hemicelluloses, size exclusion chromatography (SEC) was used to determine the average molecular weight. The measured weight-average (M_w) and number-average (M_n) molecular weights were 26,770 and 18,920 g/mol, respectively, indicating the hemicellulose in the alkaline hydrolysate was mainly in the polymeric form. The values of M_w and M_n indicate a uniform molecular weight distribution, which is favorable for downstream applications such as production of hemicellulose-based bio-polymeric films.

Potential of the proposed technology

Based on our findings, we propose a process that integrates alkaline extraction and the recovery of silica and hemicellulose from the APEL into commercial kraft

pulping process where high-value products are manufactured from lignocellulosic feedstocks (Fig 6).

In the proposed process, a sequential route involving carbon dioxide (CO_2) precipitation and ethanol treatment was developed. CO_2 , a waste gas readily available as flue gas in kraft pulp mills (Hektor & Berntsson, 2007), was used to convert the soluble silicates into insoluble silicic acid, which is isolated via filtering. Then, the filtered samples were dried and burnt at 700°C to remove any residual organics and produce silica particles. The obtained amorphous silica particles can be easily pulverized to nanosilica for various applications (Liu 2004). Ethanol was then added to the CO_2 -treated APEL to precipitate the hemicellulose. Then, the CO_2 and ethanol treated APEL will be mixed with black liquor and sent to the traditional, well-established chemical recovery circuit to recover spent chemicals.

Based on 100 g original o.d. chip mass, taking the alkaline pretreatment at 90°C with 12% NaOH for 3 h and the optimized CO_2 treatment conditions (at 60°C to final pH of 8.2) for silica precipitation as an example, the mass balance of silica and hemicellulose around the proposed process was determined. Moreover, the adsorption of CO_2 can also be measured according to bubbling time and flow rate (Fig 3). Mass balance of each fraction is expressed in terms of dried material mass. The analysis of the APEL showed that about 28.9% of hemicelluloses (mainly xylan) and 99% of silica contained in raw bamboo chips were extracted and about 1.06 g silica was produced with the adsorption of 4.06 g CO_2 . The CO_2 treated liquor was used for hemicellulose recovery, in which the precipitated hemicellulose was determined to be 4.94 g. The masses of obtained silica (1.06 g) and hemicelluloses (4.94 g) corresponded to 95.5% and 94.8% of the two components in the APEL, respectively. The losses of silica and hemicelluloses during the recovery process might be due to the solubility of silica even at low pH and hemicellulose separation during CO_2 treatment process, respectively.

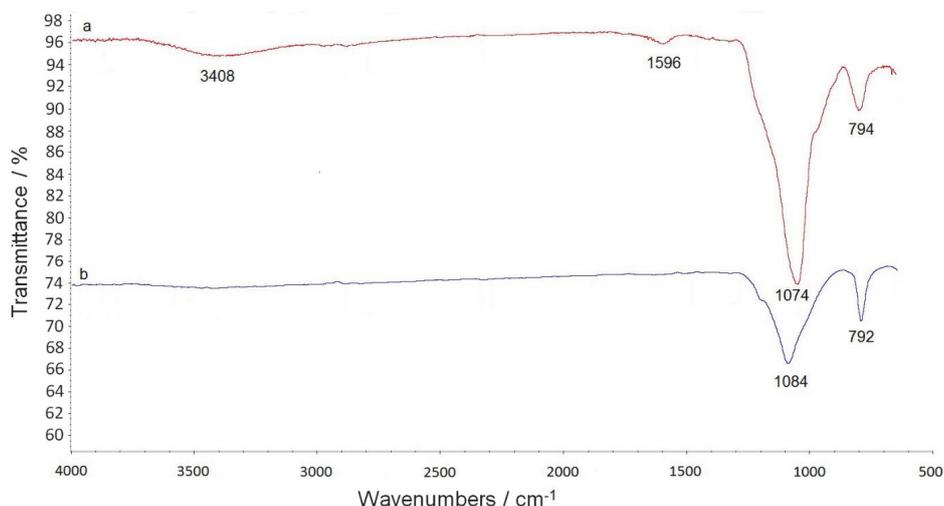


Fig 4 - Fourier transform infrared (FTIR) spectra of silica produced from the APEL of bamboo (a: before burning; b: after burning at 700°C).

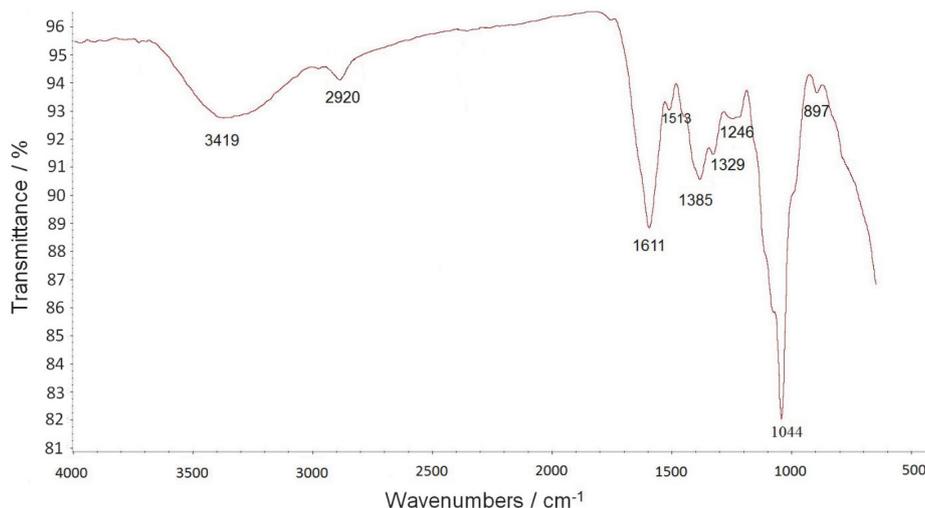


Fig 5 - Fourier transform infrared (FTIR) spectra of hemicelluloses produced from APEL.

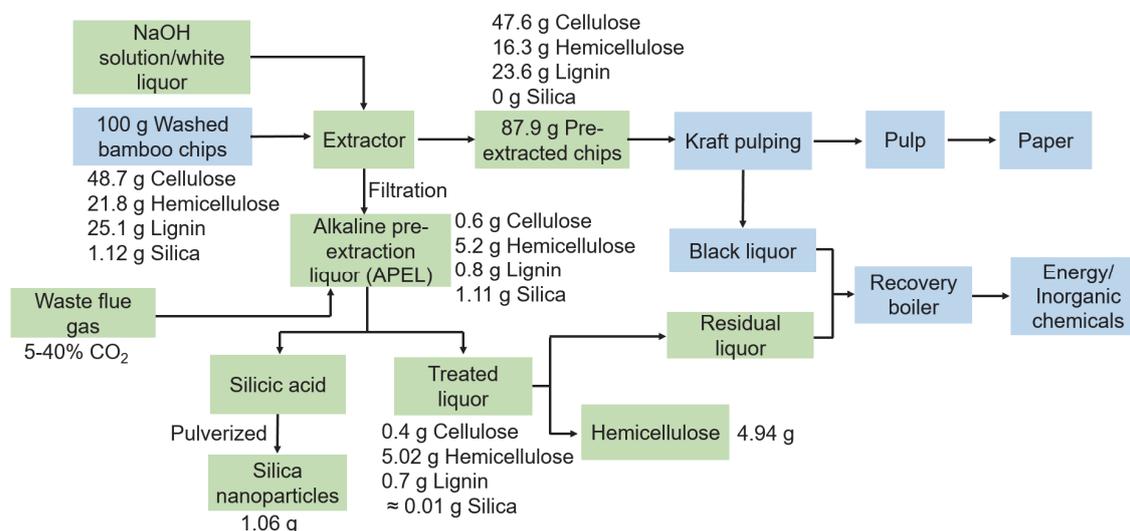


Fig 6 - Proposed process for extracting and recovering silica and hemicelluloses and its integration into kraft pulping.

Moreover, one of the most important observations was the adsorption of CO₂ in a cost-effective way, which transferred the industrial waste (flue gas) to a valuable starting material; this has the potential for lowering capital and operating costs and reducing pulp mill greenhouse gas emissions. In using silica-rich biomasses for pulp and biorefineries, this proposed process has several advantages, for example, it creates a silica-free substrate with high digestibility and increases the revenue to the industrial mill by recovering silica and hemicelluloses for various consumer products. It also reduces the emissions of CO₂ by converting waste industrial flue gas to a valuable starting material. Moreover, during the subsequent processing of alkaline extracted chips, lower chemical or enzyme charge could be expected (Ko et al., 2009; Kumar et al., 2009; Jun et al., 2012; Huang et al., 2008). Additionally, a relatively clean lignin fraction could be obtained from the spent liquor after cooking silica-free bamboo chips.

To investigate the feasibility of the proposed technology, a classic kraft pulping scheme was used as an

example, in which extracted chips were used as the starting material for kraft cooking (cooked with NaOH and sodium sulfide) to produce kraft pulp or dissolving-grade pulp. For a biomass-to-pulp plant that has a capacity of 600-700 tons bleached kraft pulp per day, about 1500 o.d. tons of bamboo chips are required. With the studied bamboo, about 16.8 tons/day of silica is processed into the pulping scheme, which causes serious problems in chemical recovery circuit and quality of final pulp. With the proposed technology, alkaline pretreatment of bamboo chips carried out with a liquid-to-wood ratio of 8 L/kg at 90°C and 12% NaOH charge (based on o.d. chip mass) for 3 h, about 9500 m³/day APEL will be generated. To precipitate the dissolved silica in the APEL, about 67.9 tons/day of CO₂ is required, which will might improve the handling of acidic compounds in the mill waste gas. Moreover, the separation of the maximum amounts of silica from the APEL significantly improves the recovery of residual alkali and lime mud in the chemical recovery cycle of a typical kraft pulping process. The extraction of silica

prior to pulping increases the evaporation efficiency by lowering the viscosity of black liquor obtained from kraft pulping and eliminating the scale buildup in the evaporators (Cardoso et al., 2009). In addition, the pre-extraction of silica from bamboo chips also makes the generated lime mud (CaCO₃) from causticizing recyclable in the lime kiln, avoiding disposal of large amounts of solid waste and the requirement for purchase of fresh lime (Pekarovic et al., 2005).

This proposed technology could be used to convert the existing kraft-based pulping mills into a biorefinery unit. Moreover, the proposed approach may work for a bioethanol plant as well with using high-silica biomasses.

Conclusions

All silica, and a part of the hemicelluloses in bamboo chips were fractionated into an alkaline pre-extraction liquor (APEL) during alkali pre-treatment of bamboo chips. A sequential route involving carbon dioxide (CO₂) and ethanol precipitation was developed to recover silica and hemicellulose from the APEL. Up to 97% of silica dissolved in the APEL was recovered by treating the APEL at 60°C with CO₂ (flue gas could be used in pulp mills) to a final pH of 8.2. The CO₂ adsorption capacity of the APEL was determined to be 7.15 g CO₂ per liter APEL. The precipitated silica nanoparticles had a purity of 99.8%, indicating that the isolated silica can be used as the starting material for various high-value products. The hemicelluloses isolated from the CO₂-treated APEL had a uniform molecular weight distribution, showing their potential for downstream conversion into high-value bio-products.

Through this study, an economical and environmentally friendly way to produce pure silica and polymeric hemicelluloses from bamboo has been developed. In addition, the removal of silica prior to pulping solves the problems created by silica. The proposed use of mill waste gas containing CO₂ would reduce mill greenhouse gas emissions and contribute to reduce global warming.

Acknowledgements

The authors are grateful to Jimmy Lowe, British Columbia Institute of Technology, Vancouver, for providing devices and technical support in this study.

Literature

Arato, C., Pye, E.K. & Gjennestad, G., (2005): The lignol approach to biorefining of woody biomass to produce ethanol and chemicals. *Applied Biochemistry and Biotechnology*, 123 (1-3), 871-882.

Barik, T.K., Sahu, B. & Swain, V., (2008): Nanosilica-from medicine to pest control. *Parasitology Research*, 103(2), pp. 253-258.

Billa, E., Tollier, M.T. & Monties, B., 1996. Characterisation of the monomeric composition of in situ wheat straw lignins by alkaline nitrobenzene oxidation: effect of temperature and reaction time. *Journal of the Science of Food and Agriculture*, 72(2), pp. 250-256.

Cardoso, M., de Oliveira, É.D. & Passos, M.L., 2009. Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills. *Fuel*, 88(4), pp. 756-763.

Chruściel, J. & Ślusarski, L., 2003. Synthesis of nanosilica by the sol-gel method and its activity toward polymers. *Material Sci*, 21, pp. 461-468.

Dence, C.W., 1992. The determination of lignin. In: *Methods in Lignin Chemistry*. Berlin New York: Springer-Verlag, pp. 33-61.

Ding, T.P., Zhou, J.X., Wan, D.F., Chen, Z.Y., Wang, C.Y. & Zhang, F., 2008. Silicon isotope fractionation in bamboo and its significance to the biogeochemical cycle of silicon. *Geochimica et Cosmochimica Acta*, 72(5), pp. 1381-1395.

Douskova, I., Doucha, J., Livansky, K., Machat, J., Novak, P., Umysova, D., Zachleder, V. & Vitova, M., 2009. Simultaneous flue gas bioremediation and reduction of microalgal biomass production costs. *Applied Microbiology and Biotechnology*, 82(1), pp. 179-185.

Fan, S., Li, S., Wang, J., Lang, X. & Wang, Y., 2009. Efficient capture of CO₂ from simulated flue gas by formation of TBAB or TBAF semiclathrate hydrates. *Energy and Fuels*, 23(8), pp. 4202-4208.

Gupta, A. & Verma, J.P., 2015. Sustainable bio-ethanol production from agro-residues: a review. *Renewable and Sustainable Energy Reviews*, 41, pp. 550-567.

Gupta, R. & Lee, Y.Y., 2010. Investigation of biomass degradation mechanism in pretreatment of switchgrass by aqueous ammonia and sodium hydroxide. *Bioresource Technology*, 101(21), pp. 8185-8191.

He, J., Cui, S. & Wang, S., 2008. Preparation and crystalline analysis of high-grade bamboo dissolving pulp for cellulose acetate. *Journal of Applied Polymer Science*, 107(2), pp. 1029-1038.

He, J., Zhang, M., Cui, S. & Wang, Y. 2009. High-quality cellulose triacetate prepared from bamboo dissolving pulp. *Journal of Applied Polymer Science*, 113(1), pp. 456-465.

Hektor, E. & Berntsson, T., 2007. Future CO₂ removal from pulp mills-process integration consequences. *Energy Conversion and Management*, 48(11), pp. 3025-3033.

Huang, H.J., Ramaswamy, S., Tschirner, U.W. & Ramarao, B.V., 2008. A review of separation technologies in current and future biorefineries. *Separation and Purification Technology*, 62(1), pp. 1-21.

Icenhower, J.P. & Dove, P.M., 2000. The dissolution kinetics of amorphous silica into sodium chloride solutions: effects of temperature and ionic strength. *Geochimica et Cosmochimica Acta*, 64(24), pp. 4193-4203.

Jun, A., Tschirner, U.W. & Tauer, Z., 2012. Hemicellulose extraction from aspen chips prior to kraft pulping utilizing kraft white liquor. *Biomass and Bioenergy*, 37, pp. 229-236.

Kadla, J.F., Kubo, S., Venditti, R.A., Gilbert, R.D., Compere, A.L. & Griffith, W., 2002. Lignin-based carbon fibers for composite fiber applications. *Carbon*, 40(15), pp. 2913-2920.

Kalapathy, U., Proctor, A. & Shultz, J., 2002. An improved method for production of silica from rice hull ash. *Bioresource Technology*, 85(3), pp. 285-289.

Kapu, N.S. & Trajano, H.L., 2014. Review of hemicellulose hydrolysis in softwoods and bamboo. *Biofuels, Bioproducts and Biorefining*, 8(6), pp. 857-870.

Ko, J.K., Bak, J.S., Jung, M.W., Lee, H.J., Choi, I.G., Kim, T.H. & Kim, K.H., 2009. Ethanol production from rice straw using optimized aqueous-ammonia soaking pretreatment and

- simultaneous saccharification and fermentation processes. *Bioresource Technology*, 100(19), pp. 4374-4380.
- Kopfmann, K. & Hudeczek, W.**, 1988. Desilication of black liquor: pilot plant tests. *Tappi Journal*, 71(10), pp. 139-147.
- Kumar, R., Mago, G., Balan, V. & Wyman, C.E.**, 2009. Physical and chemical characterizations of corn stover and poplar solids resulting from leading pretreatment technologies. *Bioresource Technology*, 100(17), pp. 3948-3962.
- Le, D.M., Sørensen, H.R., Knudsen, N.O. & Meyer, A.S.**, 2015. Implications of silica on biorefineries-interactions with organic material and mineral elements in grasses. *Biofuels, Bioproducts and Biorefining*, 9(1), pp. 109-121.
- Liou, T.H.**, 2004. Preparation and characterization of nano-structured silica from rice husk. *Materials Science and Engineering: A*, 364(1), pp. 313-323.
- Liu, Q., Wang, S., Zheng, Y., Luo, Z. & Cen, K.**, 2008. Mechanism study of wood lignin pyrolysis by using TG-FTIR analysis. *Journal of Analytical and Applied Pyrolysis*, 82(1), pp. 170-177.
- Liu, Z., Ni, Y., Fatehi, P. & Saeed, A.**, 2011. Isolation and cationization of hemicelluloses from pre-hydrolysis liquor of kraft-based dissolving pulp production process. *Biomass and Bioenergy*, 35(5), pp. 1789-1796.
- Minu, K., Jiby, K.K. & Kishore, V.V.N.**, 2012. Isolation and purification of lignin and silica from the black liquor generated during the production of bioethanol from rice straw. *Biomass and Bioenergy*, 39, pp. 210-217.
- Morpurgo, M., Teoli, D., Pignatto, M., Attrezi, M., Spadaro, F. & Realdon, N.**, 2010. The effect of Na₂CO₃, NaF and NH₄OH on the stability and release behavior of sol-gel derived silica xerogels embedded with bioactive compounds. *Acta Biomaterialia*, 6(6), pp. 2246-2253.
- Motomura, H., Fujii, T. & Suzuki, M.**, 2006. Silica deposition in abaxial epidermis before the opening of leaf blades of *Pleioblastus chino* (Poaceae, Bambusoideae). *Annals of Botany*, 97(4), pp. 513-519.
- Nagaraja, D.H. & Venkateswara, R.A.**, 2006. Organic modification of TEOS based silica aerogels using hexadecyltrimethoxysilane as a hydrophobic reagents. *Applied Surface Science*, 253(3), pp. 1566-1572.
- Negro, C., Blanco, M.A., Lopez-Mateos, F., DeJong, A.M.C.P., LaCalle, G. & Van Erkel, J.**, 2001. Free acids and chemicals recovery from stainless steel pickling baths. *Separation Science and Technology*, 36(7), pp. 1543-1556.
- Pekarovic, J., Pekarovicova, A. & Joyce, T.W.**, 2005. Desilication of agricultural residues-the first step prior to pulping. *Appita Journal*, 58(2), pp. 130-134.
- Peng, F., Ren, J., Xu, F., Bian, J., Peng, P. & Sun, R.**, 2010. Fractional study of alkali-soluble hemicelluloses obtained by graded ethanol precipitation from sugar cane bagasse. *Journal of Agricultural and Food Chemistry*, 58(3), pp.1768-1776.
- Pye, E.K.**, 2008. Industrial lignin production and applications, in: Kamm, B., Gruber, P.R., Kamm, M. (Eds.), *Biorefineries-Industrial Processes and Products: Status quo and Future Directions*. United Kingdom: Wiley, pp. 165-200.
- Schild, G., Sixta, H. & Testova, L.**, 2010. Multifunctional alkaline pulping. Delignification and hemicellulose extraction. *Cellulose Chemistry & Technology*, 44(1), pp. 35-45.
- Scurlock, J.M.O., Dayton, D.C. & Hames, B.**, 2000. Bamboo: an overlooked biomass resource?. *Biomass and Bioenergy*, 19, pp. 229-244.
- Seabra, J.E., Tao, L., Chum, H.L. & Macedo, I.C.**, 2010. A techno-economic evaluation of the effects of centralized cellulosic ethanol and co-products refinery options with sugarcane mill clustering *Biomass and Bioenergy*, 34, pp. 1065-1078.
- Sixta, H.**, 2006. *Handbook of pulp*. Weinheim: Wiley-VCH.
- Sluiter, J.B., Ruiz, R.O., Scarlata, C.J., Sluiter, A.D., Templeton, D.W. & Crocker, D.**, 2012. *Determination of Structural Carbohydrates and Lignin in Biomass*. Version 2012. National Renewable Energy Laboratory, USA.
- Sterling, C.**, 1967. Crystalline silica in plants. *American Journal of Botany*, 54, pp. 840-844.
- Sun, L. & Gong, K.**, 2001. Silicon-based materials from rice husks and their applications. *Industrial & Engineering Chemistry Research*, 40(25), pp. 5861-5877.
- Tong, G.L., Lu, Q. & Wang, J.**, 2005. Spectrophotometric determination of silicon in rice straw and black liquor after rice straw alkaline pulping by silicomolybdate blue. *China Pulp & Paper Industry*, 26(8), pp. 64-66.
- Torelli, N. & Čufar, K.**, 1995. Mexican tropical hardwoods. Comparative study of ash and silica content. *Holz als Roh- und Werkstoff*, 53(1), pp. 61-62.
- Trajano, H.L. & Wyman, C.E.**, 2013. Fundamentals of biomass pretreatment at low pH. In: *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals*. United Kingdom: John Wiley & Sons, Ltd.
- Wen, J.L., Xiao, L.P., Sun, Y.C., Sun, S.N., Xu, F., Sun, R. & Zhang, X.**, 2011. Comparative study of alkali-soluble hemicelluloses isolated from bamboo (*Bambusa rigida*). *Carbohydrate Research*, 346(1), pp. 111-120.
- Xu, F., Sun, J.X., Geng, Z.C., Liu, C.F., Ren, J.L., Sun, R., Fowler, P. & Baird, M.S.**, 2007. Comparative study of water-soluble and alkali-soluble hemicelluloses from perennial ryegrass leaves (*Lolium perenne*). *Carbohydrate Polymer*, 67(1), pp. 56-65.
- Yuan, Z., Kapu, N.S., Beatson, R., Chang, X.F. & Martinez, D.M.**, 2016. Effect of alkaline pre-extraction of hemicelluloses and silica on kraft pulping of bamboo (*Neosinocalamus affinis* Keng). *Industrial Crops and Products*, 91, pp. 66-75.
- Zhang, X., Zhao, Z., Ran, G., Liu, Y., Liu, S., Zhou, B. & Wang, Z.**, 2013. Synthesis of lignin-modified silica nanoparticles from black liquor of rice straw pulping. *Powder Technology*, 246, pp. 664-668.

Manuscript received October 11, 2016

Accepted December 12, 2016