# Production of Dissolving Grade Pulp from Tobacco Stalk Through $SO_2$-ethanol-water Fractionation, Alkaline Extraction, and Bleaching Processes

Caoxing Huang,[a,b,c] Runkun Sun,[c] Hou-min Chang,[c] Qiang Yong,[a,b] Hasan Jameel,[c,]* and Richard Phillips [c]

The objective of this study was to evaluate the possibility of producing dissolving grade pulp from tobacco stalk through combining $SO_2$-ethanol-water (SEW) fractionation, alkaline extraction, and bleaching with oxygen (O), chlorine dioxide (D), alkaline extraction with hydrogen peroxide (Ep), and hydrogen peroxide (P) ($OD_0(Ep)D_1P$). The results showed that the optimum SEW cooking condition to remove the original xylan and lignin in tobacco stalk to an acceptable level was 6% $SO_2$ charge (by weight) at 135 °C for 180 min. A bleachable pulp (Kappa number of 21.5) was produced from the SEW-treated tobacco stalk *via* a subsequent 1% NaOH extraction. After the $OD_0(Ep)D_1P$ sequence bleaching, the bleached pulp showed a high brightness (88.1% ISO) and a high α-cellulose content (94.9%). The viscosity (15.8 cP) and the residual xylan content (4.4%) of the pulp were within acceptable levels for dissolving pulp production. Thus, tobacco stalk was shown to be a viable raw material for dissolving pulp production following a SEW treatment, alkaline extraction, and a conventional bleaching sequence.

*Keywords: Tobacco stalk; $SO_2$-ethanol-water fractionation; Alkaline extraction; Bleaching; Dissolving pulp*

*Contact information: a: Key Laboratory of Forestry Genetics & Biotechnology (Nanjing Forestry University), Ministry of Education, Nanjing Forestry University, Nanjing 210037, China; b: Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China; c: Department of Forest Biomaterials, North Carolina State University, Campus Box 8005, Raleigh, NC 27695-8005 USA;*
** Corresponding author: jameel@ncsu.edu*

## INTRODUCTION

Dissolving pulp is a cellulose product that has high cellulose content (> 90%), high brightness (> 90% ISO), and low amounts of inorganic and organic non-cellulosic compounds. It can be used to produce viscose, cellulose acetate, cellulose nitrate, and cellulose ether (Tang *et al*. 2014; Liu *et al*. 2016). Traditionally, the main fibrous raw materials for dissolving pulp production are from hardwoods, softwoods, and cotton linters. Market studies indicate that the increasing demand for dissolving pulps will continue to increase during the next few decades (Sixta *et al*. 2013). Additionally, the costs of wood and cotton linters have increased. Low-price and suitable plant fibers are an appropriate biomass for dissolving pulp production in the future.

Tobacco (*Nicotiana tabacum* L.), such as burley tobacco and flue-cured tobacco, is an important commercial crop in the US (Lewis and Nicholson 2007). After harvesting, the high-quality leaves of tobacco are used for cigarette manufacturing, while the stalks are incorporated into soil or burned in the field (Shakhes *et al*. 2011). Tobacco stalk contains comparable amounts of the major constituents common to wood species (cellulose, hemicellulose, and lignin). On average, tobacco stalk are comprised of 30 to 40% cellulose, 10 to 20% hemicellulose, and 20 to 30% lignin on a dry mass basis. The hemicellulose and lignin can be removed by various technologies, resulting in the cellulose rich residues for dissolving pulp production. Therefore, it has been processed into chemical pulps using conventional pulping processes since the 1960s. Utilization of the tobacco stalk for dissolving pulp production not only solves tobacco disposal issues, but may also address fiber shortages that are anticipated to arise in the future.

Traditionally, dissolving pulp is produced by acid sulfite pulping or prehydrolysis kraft pulping. Acid sulfite pulping is performed under acidic conditions, where most of the hemicelluloses and some cellulose with low molecular weights are removed, resulting in an unbleached pulp with a high cellulose content (Annergren and Rydholm 1959; Yang *et al*. 2013; Ren *et al*. 2018). Currently, prehydrolysis kraft pulping is popular in new dissolving pulp mills due to its intrinsic advantages associated with capital investment, operation, and environmental compatibility (Sixta *et al*. 2013). During prehydrolysis, short-chain carbohydrates and hemicelluloses are hydrolyzed because they are under acidic conditions (Huang *et al*. 2016). Therefore, most hemicelluloses are extracted from the chips prior to kraft pulping. After pulping, bleaching is carried out to increase purity, adjust viscosity, tune the molecular weight distribution of the cellulose, and modify the reactivity of the dissolving pulp to meet the requirements of premium end-use products. Currently, the main bleaching methods are a combination of oxygen delignification (O), chlorine dioxide delignification (D), and hydrogen peroxide bleaching (P) (Batalha *et al*. 2011; Chi *et al*. 2014; Ma *et al*. 2015). After bleaching, post-treatments are carried out to reduce the amount of residual hemicelluloses in the pulp, including a hot caustic extraction, a cold alkaline extraction, or both.

The industrial concept of repurposing a kraft mill to a biorefinery has been proposed for many years (Sixta *et al*. 2013; Zhao *et al*. 2018; Chen *et al.* 2019). It requires the development of novel process concepts that allow for both the realization of advanced biorefinery concepts and the manufacture of pure cellulose pulps with a quality profile comparable to cotton linters. The existing dissolving pulp processes, acid sulfite and prehydrolysis kraft, constitute commercially attractive biorefinery platforms. The $SO_2$-ethanol-water (SEW) fractionation is an attractive biorefinery process for dissolving pulp production and has been proposed for many years (Iakovlev and van Heiningen 2011; Iakovlev *et al*. 2014; Huang *et al*. 2018a; Yadollahi *et al*. 2018). The SEW process is a cooking process that allows a fractionation of woody and non-woody biomass into cellulose, hemicellulose, and lignin (Iakovlev *et al*. 2009). The SEW fractionation is like acid sulfite pulping because it displays a similar liquor pH and process temperatures, but it uses sulfur dioxide instead of sulfite. In SEW cooking, the acidity comes from dissolved $SO_2$ and the formed lignosulfonic acid. An acidic environment leads to the hydrolysis of the hemicelluloses and the subsequent dissolution in the form of monosaccharides and low-molecular-weight oligosaccharides. The oligosaccharides can be recovered and used as animal feed formulations and as ingredients for functional foods for human consumption (Huang *et al*. 2018b). Meanwhile, the lignin is removed from the biomass *via* the acid-catalyzed sulfonation of *a*-carbon atoms located in the lignin structure producing lignosulfonic acid groups. After pulping, the ethanol and unreacted $SO_2$ are recovered through distillation. During the recovery of ethanol and $SO_2$, the oligosaccharides in the spent fractionation liquid are hydrolyzed and become monomeric sugars (Sklavounos *et al*. 2011). These sugars are excellent substrates for biofuel production using the acetone-butanol-ethanol (ABE) fermentation process. The sulfonated lignin (lignosulfonate) is recovered from the fermentation solution through ultrafiltration, water evaporation, or both to remove the ethanol or ABE solution (Sharazi *et al*. 2018). The SEW process has been employed by American Process Inc. (Atlanta, GA, USA) in a patent-pending biorefinery process (AVAP) and is used as a pulping technology for spruce. No studies have been conducted to understand if SEW technology is suitable for agricultural residues, such as tobacco stalk, to produce dissolving pulps.

The feasibility of producing valuable dissolving pulp from tobacco stalk (TS) was evaluated by a sequence of SEW, alkaline extraction, and bleaching with oxygen (O), chlorine dioxide (D), alkaline extraction with hydrogen peroxide (Ep), and hydrogen peroxide (P) ($OD_0(Ep)D_1P$). In addition, NaOH extraction and autohydrolysis were performed on TS to show if the pre-removal of hemicellulose/lignin is necessary before SEW fractionation. The effects of the $SO_2$ charge, cooking time, and temperature on the chemical and viscosity properties of tobacco SEW pulps were evaluated to choose an optimum condition for further bleaching.

## EXPERIMENTAL

### Materials

Burley tobacco stalks (TS) were provided by R. J. Reynolds Tobacco Company (Winston-Salem, NC, USA). The TS were cleaned from the leaves, roots, and soil. The stalks were cut into chunks of roughly 4 to 5 cm in length and air-dried until an approximate 10% moisture content was reached. The air-dried TS were kept in a plastic bag to stabilize the moisture content. To determine the chemical composition, roughly 40- to 60-mesh fractions were selected.

The amounts of extracted TS in water and benzene-ethanol were determined according to the TAPPI methods of TAPPI T207 (1999) and TAPPI T204 (1997), respectively. The primary chemical components of the TS were analyzed according to the procedure developed by the National Renewable Energy Laboratory (NREL) (Sluiter *et al*. 2008).

### Methods

*Alkaline extraction and autohydrolysis*

The alkaline extraction and autohydrolysis were performed in an M/K Digester (1/K409; MK Systems Inc., Peabody, MA, USA). For the alkaline extraction, the tobacco chips were soaked in a 1% NaOH solution with a liquor to wood ratio of 5:1 at 100 °C for 1 h. For autohydrolysis, the chips were cooked in water with a liquor to wood ratio of 5:1 at 170 °C for 1 h. Meanwhile, 4.76 g/(100 g TS) of $H_2SO_4$ was added into the water to achieve the final prehydrolysis pH of approximately 3.5. After pretreatment, the pretreated TS were collected and washed under running tap water overnight. The washed solids were then used for the SEW fractionation.

### *SEW fractionation*

The SEW fractionation liquor preparation comprised of injecting gaseous sulfur dioxide into an ethanol-water (ratio of 55:45, v/v) solution, and the $SO_2$ charge was controlled by increasing the weight of the solution (Iakovlev and van Heiningen 2012). The $SO_2$ charges in the liquors were 6%, 9%, and 12% (by weight). The liquor (liquor-to-wood ratio of 10:1) and 50.0 g (oven-dried) of the TS chips were loaded in a 1.0-L Parr reactor (Model C-276, Parr Instrument Company, USA) and were cooked at 135 °C, 150 °C, and 160 °C for 80 min, 120 min, and 180 min, respectively. Scaled-up SEW cooking was performed at the optimum conditions using a 10-L M/K Digester (1/K409; MK Systems Inc., Peabody, MA, USA). The solid residues were washed twice with 500 mL of the ethanol-water solution (ratio of 40:60, v/v) and then washed under running tap water overnight. After washing, the pulp was collected, centrifuged, and stored at 4 °C for subsequent experiments.

### *Post treatments of alkaline extraction and sulfomethylation*

The post-treatments of alkaline extraction and sulfomethylation were performed in a 1.0-L Parr reactor. For the alkaline extraction, the SEW pulp was soaked in a 1% NaOH solution with a liquor to wood ratio of 10:1 at 100 °C for 1 h. For sulfomethylation, the SEW pulp was soaked in sodium hydroxymethylsulfonate solution with a liquor to pulp ratio of 8:1 at 160 °C for 3 h to remove lignin. The sodium hydroxymethylsulfonate charge was based on the lignin content in SEW pulp, with the sodium hydroxymethylsulfonate/ lignin ratio of 0.4 mol/mol. After extraction, the pulp was washed, collected, centrifuged, and stored at 4 °C for subsequent experiments.

### *Pulp bleaching*

The bleaching technologies of $OD_0(Ep)D_1P$ were applied to bleach the SEW pulp at a 10% consistency in which O is oxygen bleaching (110 °C, 1 h, 2% (w/w) NaOH charge), $D_0$ is chlorine dioxide bleaching (70 °C, 1 h, Kappa factor 0.25), Ep is alkaline extraction with hydrogen peroxide bleaching (70 °C, 1 h, $H_2O_2$ charge 0.5%), $D_1$ is chlorine dioxide bleaching (70 °C, 3 h, $ClO_2$ charge 1.0%), and P is hydrogen peroxide bleaching (25 °C, 1 h, $H_2O_2$ charge 0.5%). The oxygen bleaching was performed in a 2.8-L reactor in an oven heated by hot air at 110 °C. The other bleaching stages were performed in polyethylene bags in a water bath. The pulps were washed with deionized water after each stage.

### *Evaluation of the pulp*

The handsheets (60 $g/m^2$) for testing the pulp properties were prepared based on the TAPPI T205 (1988) test method. The Kappa number, viscosity, α-cellulose, and brightness of pulp were tested in accordance with TAPPI T236 (1999), TAPPI T230 (1999), TAPPI T203 (1999), and TAPPI T452 (1998) standards, respectively.

### *Chemical composition analysis of pulp*

The compositions of the SEW pulps and bleached pulps were analyzed according to the procedure developed by the NREL for analyzing biomass materials (Sluiter *et al*. 2008). The monomeric sugars in the composition analysis liquor were measured using a high-performance liquid chromatography (HPLC) system (1200; Agilent Technologies

Inc., Santa Clara, CA, USA) equipped with an Agilent guard column, degasser, pump, and refractive index (RI) detector. Milli-Q water (HPLC-grade) was used as the eluent at a flow rate of 0.5 mL/min and at a column temperature of 80 °C.

## RESULTS AND DISCUSSION

### Characterization of TS and Pretreated TS

The chemical compositions and results from the extractions of TS are shown in Fig. 1. The weight percents of the major components of TS were 32.9% glucan, 13.0% xylan, 26.6% lignin (acid-insoluble and acid-soluble), and 7.4% ash. Like other non-woody biomasses, the ash content of TS is higher than that of wood (Agrupis and Maekawa 1999). The ash content in TS consists of different metal salts such as carbonates, silicates, oxalates and potassium phosphates of multivalent metal ions, including magnesium, calcium, iron, and manganese. As shown in Fig.1, the benzene-ethanol extractive of TS was 3.7 %, which could be waxes, fats, resins, photosterols, and non-volatile hydrocarbons (Shakhes *et al*. 2011). In addition, TS contained a remarkable higher content of soluble compounds in cold and hot water, 18.1% and 20.5%, respectively. The silica content in tobacco stalk was low since it is a dicot and not a monocot. The total ash content was 7.4% and most of it was potassium, calcium and magnesium. The ash content in the final product was less than 0.3%. Most of the ash components ended up in the liquid phase.

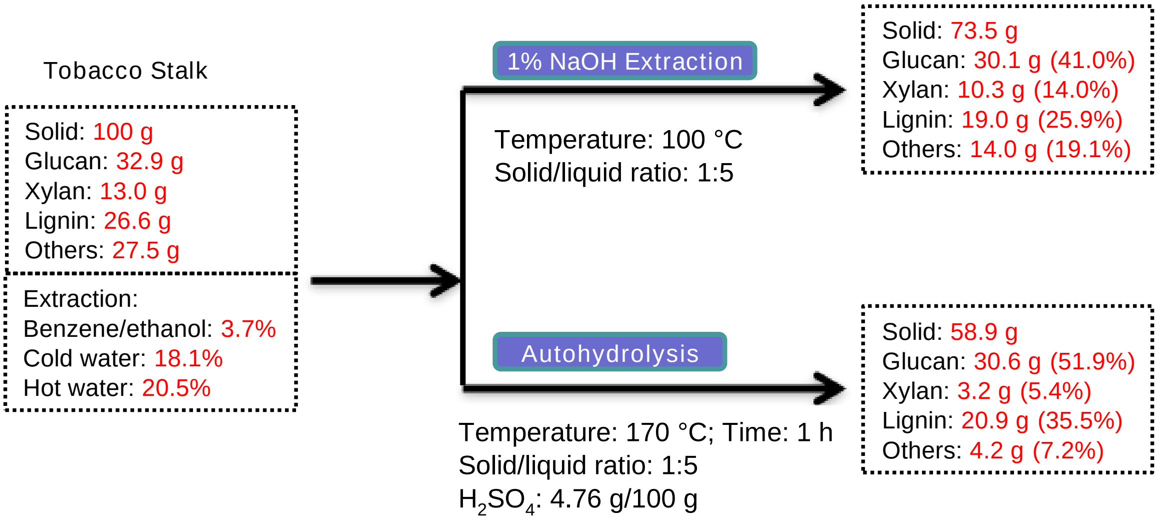

**Fig. 1.** The chemical compositions of TS, 1% NaOH extracted TS, and autohydrolyzed TS

The removal of hemicelluloses and lignin are key stages for dissolving pulp production before any pulping stage (Vila *et al*. 2011; Sixta *et al*. 2013). A 1% NaOH extraction and autohydrolysis were applied to pre-remove a part of xylan/lignin before the SEW fractionation. The components content and mass balance of the 1% NaOH extracted TS (TS-A) and the autohydrolyzed TS (TS-AH) are shown in Fig. °1. Under the present NaOH extraction conditions, the solid recovery yield of TS was 73.5%, mostly from removal of xylan and lignin. As shown in Fig. 1, 20.8% and 28.6% of xylan and lignin, respectively, were removed after the NaOH extraction. As a result, the component contents of glucan, xylan, and lignin in TS-A were 41.0%, 14.0%, and 25.9%, respectively. For the autohydrolysis process, xylan in TS decreased from 13.0 g (original material) to 3.2 g (TS-AH), which equated to a removal yield of 75.4%. Meanwhile, approximately 21.4% of original lignin was dissolved after autohydrolysis at 170 °C for 1 h. Overall, the 1% NaOH extraction and the autohydrolysis resulted in a partial removal of xylan and lignin for TS, which may favor the use of SEW fractionation to produce dissolving pulp.

## SEW Fractionation for Different Pretreated TS

After the 1% NaOH extraction and autohydrolysis, the SEW fractionation was applied to the pretreated TS (TS-A and TS-AH) to produce pulp. In addition, in order to understand whether the application of SEW pulping on unpretreated TS can achieve the pulp with similar property from pretreated TS (TS-A and TS-AH), the original TS was also pulped via SEW fractionation. The SEW fractionation was performed at 12% $SO_2$, 135 °C, and 80 min according to Iakovlev and van Heiningen (2012). The effects of SEW fractionation on the fractionation of the original TS (TS-SEW), the NaOH extracted TS (TS-A-SEW), and the autohydrolyzed TS (TS-AH-SEW) are shown in Fig. 2. All results in this work were reported in grams based on 100 g of raw, oven-dried TS.

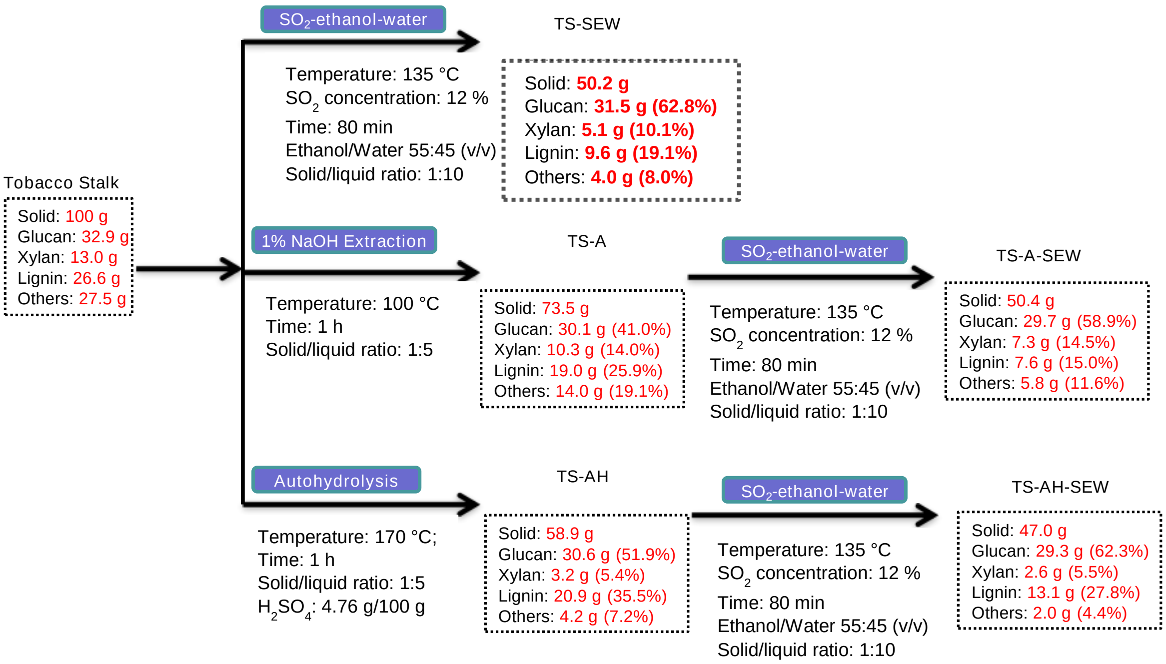

**Fig. 2.** The effects of SEW fractionation on the properties of TS, TS-A, and TS-AH

The TS-SEW and TS-A-SEW pulps had a similar solid recovery yield, 50.2% and 50.4%, respectively, while the solid recovery yield of TS-AH-SEW pulp was lower (47.0%). The solid recovery yields of the SEW pulps were lower than the woody biomass pulped by SEW. Iakovlev and van Heiningen (2011) reported that the recovery yields for the woody SEW-pulps were approximately a 60% yield for spruce and 56% to 60% yield for beech.

For the pulp production, the amount of cellulose (glucan) retained in the solid is one of main indices for pulping success. The amount of original glucan in the TS-SEW was 31.5 g, which indicated that only 4.3% of the original glucan was dissolved during the SEW fractionation. In comparison, TS-A-SEW and TS-AH-SEW showed higher glucan loss with the recovery yields of original glucans of 90.3% and 89.1%, respectively. The lower glucans remaining in the TS-A-SEW and TS-AH-SEW pulps after the NaOH and autohydrolysis treatments of the SEW cooking could be explained by the cellulose chains becoming more susceptible to degradation during SEW cooking as the xylan layer covering the cellulose fibrils is partially removed (Colodette *et al.* 2011; Batalha *et al.* 2012). From the perspective of high cellulose recovery, directly applying SEW fractionation technology was better, compared to the pre-removal of xylan, lignin, or both through NaOH extraction or autohydrolysis.

Figure 2 also shows that combining autohydrolysis and SEW removed 80.0% of the original xylan in TS. Only 43.8% and 60.8% of the original xylan in TS were removed from TS-SEW and TS-A-SEW, respectively. In addition, SEW fractionation showed an excellent performance of delignification for the original TS and TS-A with a delignification degree of 63.9% and 71.4%, respectively. The lignin in the prehydrolysis solid was difficult to remove by SEW fractionation, only 50.1% of the original lignin was dissolved. Compared to other lignocellulosic materials, the SEW fractionation showed a lower efficiency for TS for lignin removal at the same pulping conditions. In Iakovlev and van Heiningen's (2011) work, they show that the SEW cooking conditions of 135 °C, 12% $SO_2$ charge, and 80 min cooking time (the same as in this study) give the lignin contents of 6.4% and 4.2% in spruce pulp and wheat straw pulp, respectively, and that they are remarkably lower than that of the tobacco stalk pulp. The delignification with tobacco stalk was lower because the ash might be buffering the reaction system (Wu *et al.* 2019).

Based on the principles of low cellulose degradation and the high removal yields of xylan and lignin for the pretreated substrate, SEW fractionation without the pre-removal of xylan, lignin by prehydrolysis or NaOH extraction was the most cost-effective method to produce dissolving pulp from TS. This was because almost all of the cellulose was retained in the residual pulp without pre-extraction, and acceptable removal yields (over 60%) of xylan and lignin were achieved. The remaining xylan and lignin can be removed at the bleaching and post-treatment stages (Sixta *et al*. 2013; Huang *et al*. 2019).

### Optimum Conditions for SEW Fractionation to Produce an Acceptable Pulp

In the aforementioned result, it is found that only 43.8% of xylan and 63.9% of lignin were removed from the TS by SEW fractionation with the selected condition (135 $^{o}$C, 12% $SO_2$ for 80 min). To determine an optimum condition of SEW fractionation to produce an acceptable pulp from TS, different cooking times, temperatures, and $SO_2$ charges of SEW fractionation were investigated in an effort to effectively remove lignin and xylan. Table 1 shows the effects of the cooking temperature and the $SO_2$ charge on the pulp properties of total yield, removal yield of xylan, degree of delignification, Kappa number, and viscosity.

The pulp yields decreased with increased $SO_2$ charge and increased cooking temperature. When the $SO_2$ charge was increased from 6% to 12%, the pulp yield decreased 3%, 2%, and 8% at 135 °C, 150 °C, and 160 °C, respectively. The decreased pulp yields were due to the degradation of glucan, xylan, and lignin. Almost no glucan was further degraded when the $SO_2$ charge increased from 6% to 12% at 135 °C, whereas at 150 °C and 160 °C, the degradation of glucan showed degradation yields of 4.9% to 8.2% and 7.3% to 20.4%, respectively. For xylan, a higher removal was measured with increased cooking temperature and increased $SO_2$ charge. The removal yield of xylan increased from 46.9% to 60.8% when the $SO_2$ charge increased from 6% to 12% at 135 °C. Increased degradation of glucan, xylan, or both can be from the acid-depolymerization of cellulose, hemicellulose, or both under acidic conditions (Wu *et al.* 2015). When the $SO_2$ charge increased from 6% to 12%, the initial pH of the SEW cooking liquor decreased from 1.81 to 1.55. This is more favorable for the acid-hydrolysis of the glycosidic linkages of glucan and xylan (Iakovlev and van Heiningen 2012).

**Table 1.** The Effects of SEW Fractionation Conditions (Cooking Temperature and $SO_2$ Charge) on the Pulp Properties of TS

| Temp. (°C) | $SO_2$ (%) | Time (min) | Recovery Yield (%) | | Removal Yield (%) | | Kappa Number | Viscosity (cp) |
|---|---|---|---|---|---|---|---|---|
| | | | Pulp | Glucan | Lignin | Xylan | | |
| 135 | 6 | 80 | 53.2 | 96.7 | 52.3 | 46.9 | 81.7 | Insoluble |
| 135 | 9 | 80 | 52.7 | 96.4 | 56.8 | 53.8 | 74.1 | 16.2 |
| 135 | 12 | 80 | 50.2 | 95.7 | 63.9 | 60.8 | 68.7 | 8.1 |
| 150 | 6 | 80 | 42.2 | 95.1 | 81.2 | 75.4 | 58.1 | 14.2 |
| 150 | 9 | 80 | 40.4 | 93.6 | 82.7 | 75.4 | 53.9 | 6.7 |
| 150 | 12 | 80 | 40.1 | 91.8 | 83.8 | 87.7 | 50.3 | 3.1 |
| 160 | 6 | 80 | 40.4 | 92.7 | 79.7 | 88.5 | 74.6 | 3.5 |
| 160 | 9 | 80 | 35.3 | 82.4 | 85.3 | 94.6 | 55.1 | 3.4 |
| 160 | 12 | 80 | 32.5 | 79.6 | 88.7 | 94.8 | 43.1 | 2.9 |

Delignification to low Kappa numbers can be achieved for SEW pulp from spruce (33.5) and wheat straw (29.8) at 135 °C with 12% $SO_2$ for 80 min (Iakovlev and van Heiningen 2011). In this work, it was found to be difficult to achieve a low Kappa number (~30) for the TS pulp with the SEW cooking at the same cooking conditions, which only produced a Kappa number of 68.7. As shown in Table 1, despite different $SO_2$ charges at 135 °C, 150 °C, and 160 °C, the SEW fractionation did not provide bleachable grade pulps from TS; the Kappa numbers ranged from 81.7 to 43.1. In addition, the viscosity of the SEW pulp dropped from 16.2 cP to 8.1 cP, from 14.2 cP to 3.1 cP, and from 3.5 cP to 2.9 cP, when the $SO_2$ charge increased from 9% to 12% at 135 °C, 150 °C, and 160 °C cooking temperatures, respectively. The SEW pulp at 135 °C showed the highest pulp viscosity compared to 150 °C and 160 °C, which suggested lower damage on fiber. Although the Kappa number of the pulp can be reduced to a low number at the 12% $SO_2$ charge, the viscosity of the pulp was 2.9 cP to 8.1 cP, which may not be suitable for producing dissolving pulp (Kirci and Akgul 2002; Andrade and Colodette 2014). Pulp viscosity is an important indicator of pulp damage with different pulping methods (Silva *et al.* 2010). Therefore, SEW cooking with a 6% $SO_2$ charge at different cooking times and temperatures were investigated (Table 2) to obtain an acceptable pulp with a low Kappa number and high viscosity.

Table 2 shows the effects of different cooking times and temperatures on the total yield, removal of xylan, degree of delignification, Kappa number, and viscosity of the SEW pulps. At 135 °C, an increased cooking time from 80 min to 180 min resulted in a pulp with a lower Kappa number and a relatively high viscosity (> 18.7 cP). The Kappa number increased and the viscosity decreased when the cooking time was prolonged between 150 °C and 160 °C. This may have been because of the severe cooking conditions of 150 °C and 160 °C for 120 min and 180 min, because a portion of the pulp was carbonized and thus affected the determination of the Kappa number. Additionally, the condensation of lignin may have been another reason for the high Kappa number.

The viscosity and the Kappa number of the pulp were sensitive and dependent on the chosen pulping methods. Therefore, it is important to choose the proper chemicals and conditions for SEW fractionation based on the viscosity and Kappa number (Loureiro *et al*. 2011). In this work, the pulps produced from the cooking conditions of 135 °C, 6% $SO_2$ charge, for 180 min (termed TS-SEW-1) and 150 °C, 6% $SO_2$ charge, for 80 min (termed TS-SEW-2) had comparable Kappa numbers and viscosities. Although the removal yields of the xylan and lignin of TS-SEW-1 were slightly lower than that of TS-SEW-2, it was possible to obtain a comparable xylan and lignin content with a post-alkaline treatment on these two pulps (Gehmayr *et al*. 2011). Hence, based on the pulp properties with similar Kappa number and viscosity, these two cooking conditions were considered the optimum SEW fractionation methods for TS to prepare dissolving pulp.

**Table 2.** The Effects of SEW Fractionation Conditions (Cooking Time and Cooking Temperature) on the Pulp Properties of TS

| Temp. (°C) | $SO_2$ (%) | Time (min) | Recovery Yield (%) | | Removal Yield (%) | | Kappa Number | Viscosity (cp) |
|---|---|---|---|---|---|---|---|---|
| | | | Pulp | Glucan | Lignin | Xylan | | |
| 135 | 6 | 80 | 53.9 | 96.7 | 52.3 | 46.9 | 81.7 | Insoluble |
| 135 | 6 | 120 | 47.9 | 90.3 | 62.4 | 63.8 | 68.1 | 20.4 |
| **135** | **6** | **180** | **40.8** | **86.0** | **73.3** | **69.2** | **56.8** | **18.7** |
| **150** | **6** | **80** | **42.2** | **96.0** | **81.2** | **75.4** | **58.1** | **14.2** |
| 150 | 6 | 120 | 39.2 | 90.6 | 82.0 | 80.8 | 59.5 | 7.0 |
| 150 | 6 | 180 | 36.6 | 87.5 | 81.2 | 90.0 | 64.9 | 2.9 |
| 160 | 6 | 80 | 40.4 | 92.7 | 79.7 | 88.5 | 74.6 | 3.5 |
| 160 | 6 | 120 | 37.1 | 83.6 | 78.9 | 93.8 | 78.8 | 2.3 |
| 160 | 6 | 180 | 33.9 | 78.1 | 72.9 | 97.7 | / | 2.2 |

### Effects of Post Alkaline Treatment on the Properties of SEW Pulp

An alkaline-based treatment can be used to convert paper-grade pulps to dissolving pulps by extracting hemicelluloses and lignin (Ibarra *et al*. 2010; Gehmayr *et al*. 2011; Schild and Sixta 2011). In addition, because sulfite pulps are easily bleached with peroxide, the sulfomethylation of kraft pulp prior to bleaching was considered as one of the possible approaches. Therefore, two alkaline-based methods, 1% NaOH extraction and sulfomethylation, were applied on the SEW TS-SEW-1 and TS-SEW-2 pulps to obtain bleachable pulps through removal of the xylan and lignin. The effects of the treatments on the properties of SEW pulps are shown in Fig. 3.

With sulfomethylation, the viscosity of the SEW pulps declined from 18.7 cP to 12.2 cP for TS-SEW-1 and from 14.2 cP to 11.2 cP for TS-SEW-2. Compared to sulfomethylation, the NaOH extraction reduced the pulp's viscosity, but the magnitudes of reduction were smaller (less than 2 cP). This implied that NaOH did not have a large effect on the pulp viscosity during extraction. Additionally, the NaOH extraction more effectively removed the xylan and lignin in the SEW pulps. For NaOH extracted pulps, TS-SEW-1-A and TS-SEW-2-A had a similar amount of xylan (0.9 g), comparable amounts of lignin (2.1 g and 2.0 g) and glucan (23.9 g and 25.9 g), and had comparable Kappa numbers (21.5 and 19.2), respectively. The viscosity of the TS-SEW-1-A pulp gave the highest value of 17.5 cP, which was higher than that of TS-SEW-2-A (12.3 cP). Hence, the TS-SEW-1-A pulp was chosen as the pulp for bleaching to produce dissolving pulp.

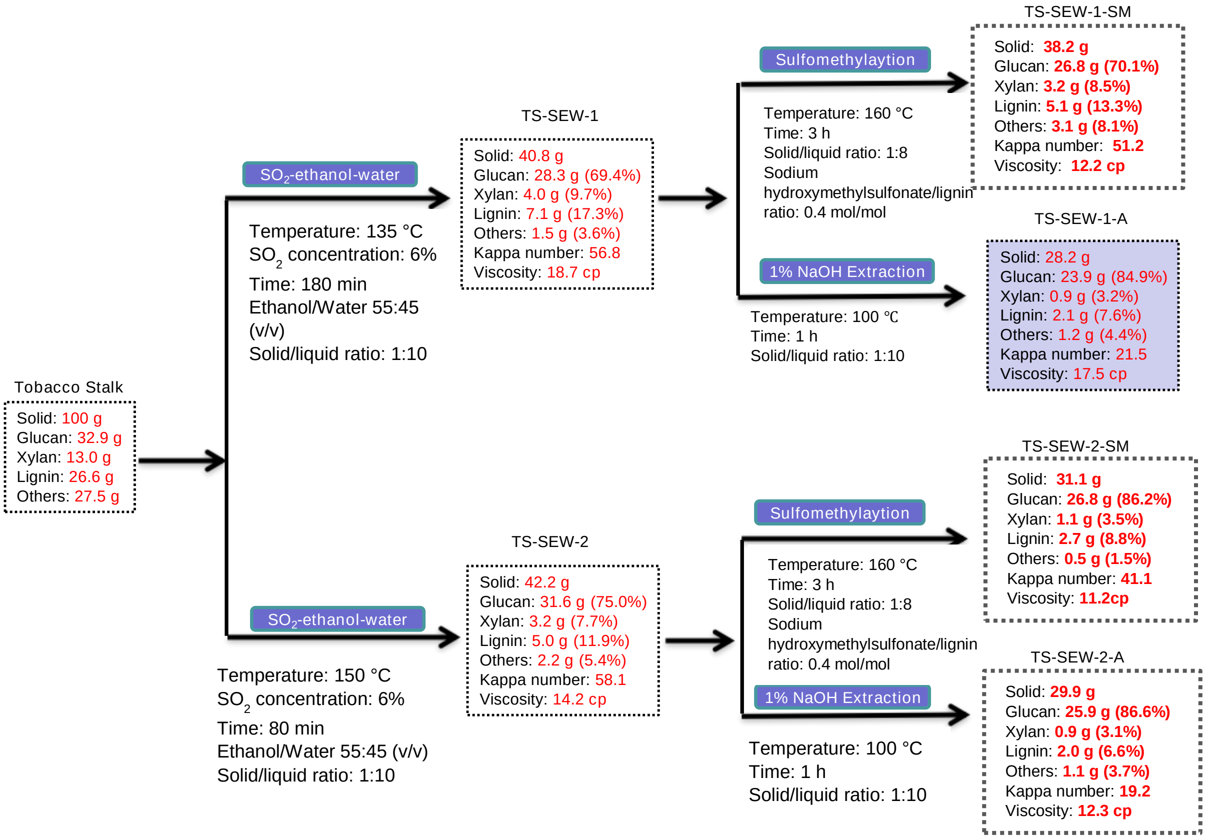

**Fig. 3.** The effects of NaOH extraction and sulfomethylation on the properties of SEW pulps

## Bleaching Process

In this work, scaled-up SEW cooking and NaOH extraction experiments were performed using an M/K Digester (10-L) to obtain a sufficient pulp for bleaching. The properties of the resulting pulp were different than the pulp produced using the Parr reactor (1-L). The Kappa number and viscosity of this pulp (TS-SEW-A) were 19.4 and 17.9 cP, respectively.

The bleaching process to produce dissolving pulp from tobacco stalk are shown in Fig. 4. It can be seen that both the brightness and delignification were improved after the $O_2$ bleaching. The Kappa number of TS-SEW-A decreased from 19.4 to 10.9 and the brightness increased from 48.7% to 64.2%. Although $O_2$ bleaching reduced the pulp viscosity, the magnitude of reduction was small as shown by the decrease from 17.9 cP to 17.4 cP. After subsequent bleaching using $D_0$, Ep, and $D_1$, 0.6 g of the original glucan was dissolved, and the resulting content of the original glucan in the pulp was reduced from 24.5 g (TS-SEW-A) to 23.9 g (TS-SEW-A-O-B). Meanwhile, the viscosity of the pulp decreased from 17.9 cP to 16.8 cP. This may have been due to the generation of free radicals from the decomposition of hydrogen peroxide during the alkaline stage (Ep). The free radicals can attack the cellulose fibers and reduce the viscosity of the pulp (Andrade and Colodette 2014). The bleached pulp (TS-SEW-A-O-B) contained 94.3% *a*-cellulose, had a brightness of 86.3% ISO, and 1.4 g of the original xylan (5.5%) remained in the pulp.

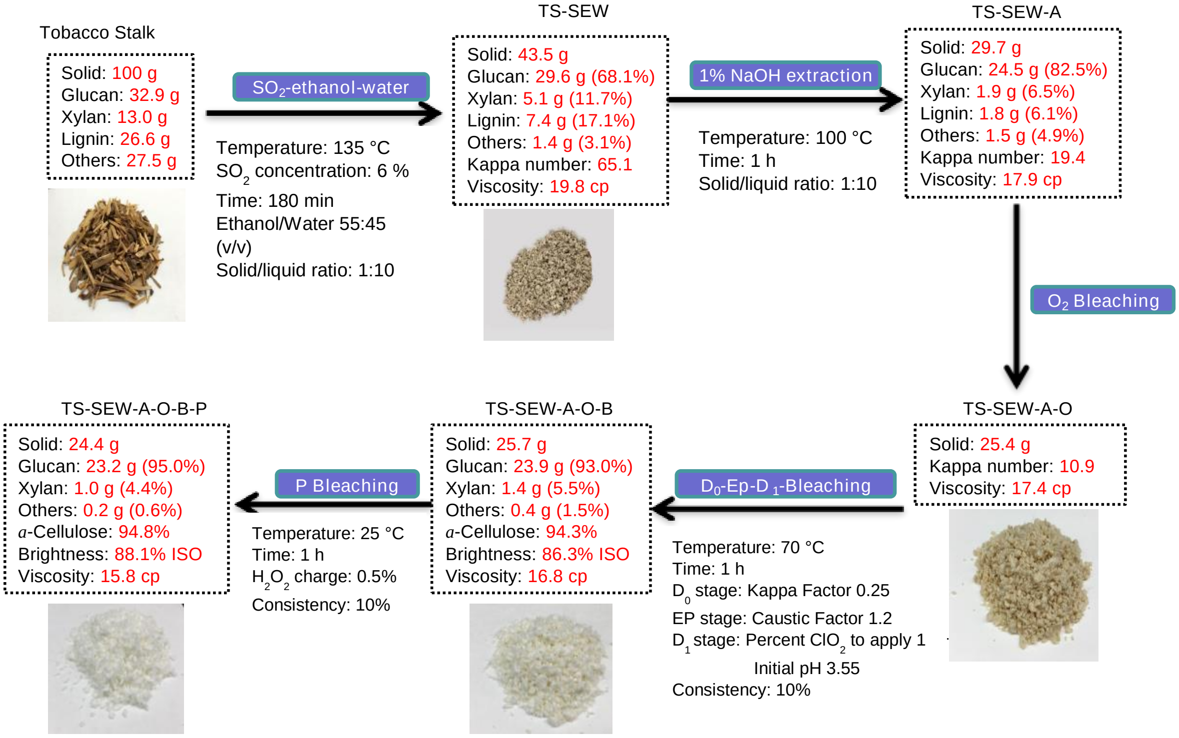

**Fig. 4.** The whole process of dissolving pulp production from tobacco stalk

A peroxide stage (P) was applied on the bleached pulp to remove residual xylan and increase the brightness of the pulp (Wu *et al*. 2019). As shown in Fig. 4, the amount of *a*-cellulose, brightness, and xylan removal improved after the P stage. The $OD_0(Ep)D_1P$ bleaching allowed for the conversion of a T S-SEW-A pulp to a dissolving pulp with a hemicellulose (xylan) content lower than 5%, a 94.8% content of *α*-cellulose, 88.1% ISO brightness, 15.8 cP viscosity, and 0.2% ash content. These properties of the TS-SEW-A-O-B-P make it acceptable for most dissolving pulp applications for viscose (Henriksson *et al*. 2005; Kvarnlof *et al*. 2006).

## CONCLUSIONS

1. The optimum SEW cooking (135 °C, 6% $SO_2$ charge, for 180 min) resulted in an acceptable Kappa number (56.8) and viscosity (18.7 cP).
2. The SEW fractionation was followed by a 1% NaOH extraction to further decrease the lignin and the xylan content to prepare a bleachable pulp with an acceptable Kappa number and viscosity from tobacco stalk.

3. The SEW fractionation, NaOH post-extraction, and the $OD_0(Ep)D_1P$ bleaching sequence proved suitable to produce dissolving pulp from tobacco stalk and resulted in a bleached pulp of 94.8% $\alpha$-cellulose, 88.1% ISO brightness, 15.8 cP viscosity, 4.4% xylan, and 0.2% ash, which are acceptable values for many dissolving grade pulps.

## ACKNOWLEDGMENTS

The authors thank the Natural Science Foundation of Jiangsu Province (BK20180772) and National Natural Science Foundation of China (31800501) for supporting this work. This work was also supported by the funding from R. J. Reynolds Tobacco Company (Winston-Salem, NC, USA).

## REFERENCES CITED

Agrupis, S. C., and Maekawa, E. (1999). "Industrial utilization of tobacco stalks (1) Preliminary evaluation for biomass resources," *Holzforschung* 53(1), 29-32. DOI: 10.1515/HF.1999.005

Andrade, M. F., and Colodette, J. L. (2014). "Dissolving pulp production from sugar cane bagasse," *Ind. Crop. Prod.* 52, 58-64. DOI: 10.1016/j.indcrop.2013.09.041

Annergren, G. E., and Rydholm, S. A. (1959). "On the behavior of the hemicellulose during sulphite pulping," *Sven. Papperstidn.* 62(20), 737-742.

Batalha, L. A. R., Colodette, J. L., Gomide, J. L., Barbosa, L. C., Maltha, C. R., and Gomes, F. J. B. (2011). "Dissolving pulp production from bamboo," *BioResources* 7(1), 640-651. DOI: 10.15376/biores.7.1.640-651

Chen, W., Wang, X., Feizbakhshan, M., Liu, C., Hong, S., Yang, P., and Zhou, X. (2019). "Preparation of lignin-based porous carbon with hierarchical oxygen-enriched structure for high-performance supercapacitors," *J. Colloid Interf. Sci.* 540, 524-534.DOI: 10.1016/j.jcis.2019.01.058

Chi, C., Liu, M., Jameel, H., Zhang, S., and Zhang, Z. (2014). "Hydrothermal pretreatment of hardwood chips prior to alkaline pulping and $D_0(EP)D_1$ bleaching," *BioResources* 9(4), 6193-6204. DOI: 10.15376/biores.9.4.6193-6204

Colodette, J. L., Loungue, J. D., Pedrazzi, C., Oliveira, R. C., Gomide, J. L., and Gomes, F. J. B. (2011). "Pulpability and bleachability of xylan-depleted eucalyptus wood chips," *Ind. Eng. Chem. Res.* 50(4), 1847-1852. DOI: 10.1021/ie101799y

Gehmayr, V., Schild, G., and Sixta, H. (2011). "A precise study on the feasibility of enzyme treatments of a kraft pulp for viscose application," *Cellulose* 18(2), 479-491. DOI: 10.1007/s10570-010-9483-x

Henriksson, G., Chritiernin, M., and Agnemo, R. (2005). "Monocomponent endoglucanase treatment increases the reactivity of softwood sulphite dissolving pulp," *J. Ind. Microbiol. Biot.* 32(5), 211-214. DOI: 10.1007/s10295-005-0220-7

Huang, C., Jeuck, B., Du, J., Yong, Q., Chang, H. M., Jameel, H., and Phillips, R. (2016). "Novel process for the coproduction of xylo-oligosaccharides, fermentable sugars, and lignosulfonates from hardwood," *Bioresource Technol.* 219, 600-607. DOI: 10.1016/j.biortech.2016.08.051

Huang, C., Lin, W., Lai, C., Li, X., Jin, Y., and Yong, Q. (2019). "Coupling the post-extraction process to remove residual lignin and alter the recalcitrant structures for improving the enzymatic digestibility of acid-pretreated bamboo residues," *Bioresource Technol.* 285, 121355. DOI: 10.1016/j.biortech.2019.121355

Huang, C., Ma, J., Liang, C., Li, X., and Yong, Q. (2018a). "Influence of sulfur dioxide-ethanol-water pretreatment on the physicochemical properties and enzymatic digestibility of bamboo residues," *Bioresource Technol.* 263, 17-24. DOI: 10.1016/j.biortech.2018.04.104

Huang, K., Luo, J., Cao, R., Su, Y., and Xu, Y. (2018b). "Enhanced xylooligosaccharides yields and enzymatic hydrolyzability of cellulose using acetic acid catalysis of poplar sawdust," *J. Wood Chem. Technol.* 38(5), 371-384. DOI: 10.1080/02773813.2018.1500608

Iakovlev, M., Pääkkönen, T., and van Heiningen, A. (2009). "Kinetics of $SO_2$-ethanol-water pulping of spruce," *Holzforschung* 63(6), 779-784. DOI: 10.1515/HF.2009.109

Iakovlev, M., and van Heiningen, A. (2011). "$SO_2$-ethanol-water (SEW) pulping: I. Lignin determination in pulps and liquors," *J. Wood Chem. Technol.* 31(3), 233-249. DOI: 10.1080/02773813.2010.523161

Iakovlev, M., and van Heiningen, A. (2012). "Kinetics of fractionation by $SO_2$-ethanol-water (SEW) treatment: Understanding the deconstruction of spruce wood chips," *RSC Adv.* 2(7), 3057-3068. DOI: 10.1039/c2ra00957a

Iakovlev, M., You, X., van Heiningen, A., Sixta, H. (2014). "$SO_2$-ethanol-water (SEW) fractionation process: production of dissolving pulp from spruce," *Cellulose* 21(3), 1419-1429. DOI: 10.1007/s10570-014-0202-x

Ibarra, D., Köpcke, V., Larsson, P. T., Jääskeläinen, A. S., and Ek, M. (2010). "Combination of alkaline and enzymatic treatments as a process for upgrading sisal paper-grade pulp to dissolving-grade pulp," *Bioresource Technol.* 101(19), 7416-7423. DOI: 10.1016/j.biortech.2010.04.050

Kirci, H., and Akgül, M. (2002). "Production of dissolving grade pulp from poplar wood by ethanol-water process," *Turk. J. Agric. For.* 26(5), 239-245.

Kvarnlof, N., Germgard, U., Jonsso, L., and Soderlund, C. A. (2006). "Enzymatic treatment to increase the reactivity of a dissolving pulp for viscose production," *APPITA. J.* 59(3), 242-246.

Lewis, R. S., and Nicholson, J. S. (2007). "Aspects of the evolution of *Nicotiana tabacum* L. and the status of the United States *Nicotiana* germplasm collection," *Genet. Resour. Crop. Ev.* 54(4), 727-740. DOI: 10.1007/s10722-006-0024-2

Liu, Y. S., Shi, L. X., Cheng, D., and He, Z. B. (2016) "Dissolving pulp market and technologies: Chinese prospective-A mini-review," *BioResources* 11(3), 7902-7916. DOI: 10.15376/biores.11.3.Liu

Loureiro, P. E., Evtuguin, D. V., and Carvalho, M. G. V. S. (2011). "The final bleaching of eucalypt kraft pulps with hydrogen peroxide: Relationship with industrial ECF bleaching history and cellulose degradation," *J. Chem. Technol. Biot.* 86(3), 381-390. DOI: 10.1002/jctb.2527

Ma, Q. Z., Wang, Q., Wang, C., Feng, N. J., Zhai, H. M. (2015). "Application of pure, thermostable, alkali-tolerant xylanase in bleaching of oxygen-delignified pine kraft pulp," *APPITA. J.* 14(11), 689-694.

Ren, J., Liu, L., Zhou, J., Li, X., and Ouyang, J. (2018). "Co-production of ethanol, xylo-oligosaccharides and magnesium lignosulfonate from wheat straw by a controlled magnesium bisulfite pretreatment (MBSP),"*Ind. Crop. Prod.* 113, 128-134. DOI: 10.1016/j.indcrop.2018.01.026

Schild, G., and Sixta, H. (2011). "Sulfur-free dissolving pulps and their application for viscose and lyocell," *Cellulose* 18(4), 1113-1128. DOI: 10.1007/s10570-011-9532-0

Shakhes, J., Marandi, M. A., Zeinaly, F., Saraian, A., and Saghafi, T. (2011). "Tobacco residuals as promising lignocellulosic materials for pulp and paper industry," *BioResources* 6(4), 4481-4493. DOI: 10.15376/biores.6.4.4481-4493

Sharazi, A. M., van Heiningen, A. R., Sumerskii, I., and Bacher, M. (2018). "Sugarcane straw lignin obtained by sulfur dioxide-alcohol-water (SAW) fractionation: Effect of solvent," *Ind. Crop. Prod.* 115, 235-242. DOI: 10.1016/j.indcrop.2018.02.039

Silva, T. C. F., Colodette, J. L., Lucia, L. A., Oliveira, R. C. D., Oliveira, F. N., and Silva, L. H. M. (2010). "Adsorption of chemically modified xylans on eucalyptus pulp and its effect on the pulp physical properties," *Ind. Eng. Chem. Res.* 50(2), 1138-1145. DOI: 10.1021/ie101960a

Sixta, H., Iakovlev, M., Testova, L., Roselli, A., Hummel, M., Borrega, M., and Schottenberger, H. (2013). "Novel concepts of dissolving pulp production," *Cellulose* 20(4), 1547-1561. DOI: 10.1007/s10570-013-9943-1

Sklavounos, E., Iakovlev, M., Yamamoto, M., Teräsvuori, L., Jurgens, G., Granström, T., and Heiningen, A. (2011). "Conditioning of $SO_2$-ethanol-water spent liquor from spruce for the production of chemicals by ABE fermentation," *Holzforschung* 65(4), 551-558. DOI: 10.1515/hf.2011.103

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2008). *Determination of Structural Carbohydrates and Lignin in Biomass* (NREL/TP-510-42618), National Renewable Energy Laboratory, Golden, CO.

Tang, Y., Yang, S., Zhang, N., and Zhang, J. (2014). "Preparation and characterization of nanocrystalline cellulose *via* low-intensity ultrasonic-assisted sulfuric acid hydrolysis," *Cellulose* 21(1), 335-346. DOI: 10.1007/s10570-013-0158-2

TAPPI T203 (1999). "Alpha-, beta-, and gamma-cellulose in pulp," TAPPI Press, Atlanta, GA.

TAPPI T204 (1997). "Solvent extractives of wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI T205 (1988). "Forming handsheets for physical tests of pulp," TAPPI Press, Atlanta, GA.

TAPPI T207 (1999). "Water solubility of wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI T230 (1999). "Viscosity of pulp (capillary viscometer method)," TAPPI Press, Atlanta, GA.

TAPPI T236 (1999). "Kappa number of pulp," TAPPI Press, Atlanta, GA.

TAPPI T452 (1998). "Brightness of pulp, paper, and paperboard (directional reflectance at 457 nm)," TAPPI Press, Atlanta, GA.

Vila, C., Romero, J., Francisco, J. L., Garrote, G., and Parajó, J. C. (2011). "Extracting value from Eucalyptus wood before kraft pulping: Effects of hemicelluloses solubilization on pulp properties," *Bioresource Technol.* 102(8), 5251-5254. DOI: 10.1016/j.biortech.2011.02.002

Wu, Q. Q., Ma, Y. L., Chang, X., and Sun, Y. G. (2015). "Optimization and kinetic analysis on the sulfuric acid – Catalyzed depolymerization of wheat straw," *Carbohyd. Polym.* 129, 79-86. DOI: 10.1016/j.carbpol.2015.04.053

Wu, X., Tang, W., Huang, C., Huang, C., Lai, C., and Yong, Q. (2019). "The effects of exogenous ash on the autohydrolysis and enzymatic hydrolysis of wheat straw." *Bioresource Technol.* 286, 121411. DOI: 10.1016/j.biortech.2019.121411

Wu, Y., Wu, J., Yang, F., Tang, C., and Huang, Q. (2019). "Effect of $H_2O_2$ bleaching treatment on the properties of finished transparent wood. *Polymers* 11(5), 776. DOI: 10.3390/polym11050776

Yadollahi, R., Dehghani Firouzabadi, M., Resalati, H., Borrega, M., Mahdavi, H., Saraeyan, A., Sixta, H. (2018). "$SO_2$-ethanol-water (SEW) and kraft pulping of giant milkweed (*Calotropis procera*) for cellulose acetate film production." *Cellulose* 25, 3281-3294. DOI: 10.1007/s10570-018-1802-7

Yang, L. F, Cao, J., Mao, J. Y., and Jin, Y. C. (2013). "Sodium carbonate-sodium sulfite pretreatment for improving the enzymatic hydrolysis of rice straw," *Ind. Crop. Prod.* 43, 711-717. DOI: 10.1016/j.indcrop.2012.08.027

Zhao, Z., Hayashi, S., Xu, W., Tanaka, S., Sun, S., Zhang, M., Kanayama, K., and Umemura, K. (2018). "A novel eco-friendly wood adhesive composed by sucrose and ammonium dihydrogen phosphate," *Polymers* 10(11), 1251. DOI: 10.3390/polym10111251

Article submitted: December 7, 2018; Peer review completed: March 2, 2019; Revised version received: May 23, 2019; Accepted: May 25, 2019; Published: May 29, 2019.
DOI: 10.15376/biores.14.3.5544-5558