Integrated Biorefinery for Production of Biodegradable Film, Bioethanol, and Soda Pulp from Corn Stalks

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In traditional pulping, black liquor is burned in an alkali recovery system to produce energy. According to the integrated forest biorefinery (IFBR) concept, hemicellulose is partially pre-extracted prior to pulp production to generate value-added products. Corn stalks have a remarkable carbohydrate content (75% w/w), and thus were examined in this study in terms of the IFBR concept. The hemicelluloses were pre-extracted with hot water (90, 120, 135, and 150 °C), NaOH, and NaOH + $NaBH_4$ (50, 70, and 90 °C) for 4 h. NaOH charges of 16.7, 26.7, and 33.3% were explored. The extracts were utilized to produce bioethanol and biodegradable films, and papermaking pulps were produced from the solid fractions. Differences among groups were identified *via* analysis of variance, and the Duncan's test was applied to determine those differences that were significant. The results showed that the alkaline pre-extraction (26.7% NaOH at 50 °C) removed 35.6% of the xylose from the stalk structure. The liquid fraction collected from the hot water pre-extraction at 150 °C gave a 14.7% (g/100 g soluble material) yield of bioethanol. Moreover, the theoretical ethanol yield was calculated as 89.4%. The addition of gluten and nanocellulose to the xylan enabled the production of high-quality biodegradable films. Furthermore, the pulps produced from the hot water pre-extracted solid fractions were comparable in yield and pulp properties to the control soda pulp.

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INTRODUCTION

The importance of lignocellulosic biomass has been increasing due to its promising potential as a source of economically valuable chemicals and biofuels along with papermaking pulp. In conventional pulping, the black liquor mostly includes lignin and some hemicelluloses, which are burned in an alkali recovery system to produce steam and electricity. In contrast, the heating value of hemicelluloses is low (van Heiningen 2006) and thus the hemicelluloses can be pre-extracted to produce chemicals and biofuels. Therefore, the newly developed concept of an integrated forest products biorefinery (IFBR) involves pre-extracting some hemicelluloses prior to pulping (van Heiningen 2006). This approach is also expected to provide additional income for pulp and paper mills.

The alkaline technique that has been commonly used, based on chemical pretreatment, is known to dissolve much of the hemicelluloses from the structure, degrade lignin, and to conserve most of the cellulose in the structure. In addition, alkaline pretreatment techniques do not require adjusting the pH or washing the chips before

alkaline pulping and use much milder treatment conditions: temperature, pressure, and chemical dosages (Chong *et al.* 2017; Wang *et al.* 2020; Wu *et al.* 2021). Yuan *et al.* (2016) studied an alkaline pre-extraction of bamboo to completely extract silica and partially extract hemicelluloses prior to kraft pulping. They obtained similar pulp yield and also the drainage resistance was slightly improved when compared with the control. Çöpür and Tozluoğlu (2008) and Çöpür *et al.* (2012) modified their alkaline pre-extraction by adding a small amount of sodium borohydrate ($NaBH_4$), and the results showed that this modification improved the pulping selectivity by preventing peeling reactions *via* lower hemicelluloses degradation and providing higher delignification.

It should be noted that hot water extraction (also called autohydrolysis) could be considered an effective and environmentally friendly technique (Özyürek and van Heiningen 2018) because no chemicals are used. Yoon *et al.* (2011) examined hot water pre-extraction of pine and observed almost the same pulp yield when compared with the control cook.

Hemicellulose pre-extraction techniques applied before pulping have been investigated using the woody biomass of eucalyptus sawdust (Goash *et al.* 2021), poplar (Chen *et al.* 2017), and loblolly pine (Yoon *et al.* 2011). However, studies using corn stalks/stover in this context have been more limited (Jahan and Rahman 2012; Resalati *et al.* 2012; Cheng *et al.* 2014). Studies using agricultural residues have focused mostly on hemicellulose pre-extraction, but have not examined the subsequent pulping process and pulp properties. Wheat straw (Feng *et al.* 2014), corn stalks (Egüés *et al.* 2012), and sugarcane bagasse (Batalha *et al.* 2015) have been studied in terms of hemicellulose extraction only.

Corn stalks have little economic value and are a cheap and abundant feedstock in Turkey. They are mostly burnt or left in the field after harvest and thus may create environmental pollution. Corn stalks have a high carbohydrate content (75% w/w) and consequently they possess considerable potential for bioethanol and biodegradable films production as well as for papermaking pulp. Therefore, this study aimed to determine the technical feasibility of IFBR that uses feedstock corn stalks. Therefore, this study aimed to determine the technical feasibility of IFBR that uses feedstock corn stalks. In addition, hot water, alkali (NaOH), and modified alkali (NaOH and $NaBH_4$) pre-extraction techniques were applied and to investigate the effect of hemicellulose pre-extraction on the properties of soda pulp such as yield, freeness, viscosity, kappa number, sugar compositions, tensile, tear, and burst strength indices and brightness and opacity by comparing with the properties of the control pulp. A mass balance of the main components from hot water pre-extraction (120 °C for 4 h) to soda pulping was calculated.

EXPERIMENTAL

Materials

Corn stalks (*Zea mays* subsp. *indurata* Sturtev.) were obtained from local sources in Düzce Province, Turkey. A garden chopper was used to cut the corn stalk (does not include corn leaves and straw) into 2 to 3 cm pieces, which were then left to dry at room temperature. The moisture content of the air-dried material was measured according to the TAPPI T412 om-11 (2011) standard. Sealed plastic bags were used to store the material at room temperature.

Methods

Hot water and alkali (NaOH) pre-extraction techniques were performed for this study. In addition, the alkaline extraction method was modified with the addition of a small amount of $NaBH_4$. The extracted liquids were hydrolyzed and fermented to produce ethanol. The solid fractions were further chemically or mechanically pulped.

Pre-extractions

Pre-extractions were all carried out in a 3-L rotating digester using the hot water and alkali techniques to obtain the pre-extracted liquids. In the hot water pre-extractions, for the equivalent of 150 g of oven-dry (OD) stalks, the liquid-to-stalk ratio (L/S) was 10:1 L/kg OD. The stalks were treated at temperatures of 90, 120, 135, and 150 °C for 4 h, with the maximum temperature being reached in 30 min and the H factor was 1, 40, 170, and 670 respectively.

In the alkaline pre-extractions, the L/S was 4:1 L/kg OD. The digester was heated to the maximum temperature in 30 min and then kept at the maximum treatment temperature for 4 h. Varying NaOH concentrations (16.7, 26.7, and 33.3% w/w) and treatment temperatures (50, 70, and 90 °C) were investigated. The optimal alkaline pre-extraction conditions were determined for the ratio of carbohydrates to lignin in the solid residues. In addition, the alkaline technique was modified by adding 0.1, 0.5, 2, and 4% $NaBH_4$ for the optimal condition (26.7% NaOH w/w, at 50 °C for 4 h). After all pre-extractions, the liquid and residual solids were collected by filtration using a cloth filter. All pre-extractions were performed in duplicate.

Analysis of pre-extracted liquids

The solids were precipitated from the pre-extracted liquids by centrifuging at 5000 × g. To hydrolyze the oligomers into monomeric sugars, 1000 mL of 4% sulfuric acid was added to 50 mL of these liquids and then placed in an autoclave to incubate at 121 °C for 1 h (Li *et al.* 2010). Sufficient NaOH was added to neutralize the liquids to pH 7, and analysis of the monomeric sugar in the liquids was then performed *via* high performance liquid chromatography (HPLC) (Agilent 1200 series, Agilent Technologies, Santa Clara, CA, USA). Thus, the total sugar content of the liquids was determined prior to fermentation.

Fermentation and ethanol production

To produce bioethanol, the liquids were subjected to further fermentation in a bioreactor (Stedim Biotech Fermenter, Sartorius, Göttingen, Germany). During the fermentation process, 0.5 M NaOH and 0.5 M HCl were automatically added to maintain the pH at 6.0, along with the addition to the medium of 1.70 g/L $(NH_4)_2SO_4$, 0.96 g/L K_2HPO_4, 0.17 g/L $MgSO_4.7H_2O$, 0.23 g/L $CaCl_2.2H_2O$, and 0.02 g yeast extract. *Pichia stipitis* was cultured overnight and then added to the mixture to be incubated in the bioreactor, with fermentation carried out for 48 h at 100 rpm and 30 °C. After 3, 6, 12, 24, and 48 h, samples were taken and centrifuged for 10 min at 10,000 × g. The resulting supernatants were subsequently passed through filters (0.45-µm) and kept at -20 °C for later HPLC analysis. All experimental fermentation procedures were performed twice.

Biodegradable film production

The liquids from the pre-extractions were prepared for biodegradable film production by completely filtering out the solid particles and then centrifuging them at

5000 × g for 5 min. To precipitate the hemicelluloses, 2500 mL of cooled acetic acid-ethanol (1:10 v/v) were added to the liquid. For desalting, the precipitates were then washed three times with a solution of 200 mL deionized water and 600 mL ethanol and the residue was dried at room temperature.

The xylan precipitate (0.7 g) was mixed with xylitol (0.4 g) and stirred in deionized water (15 mL). The resulting solutions were distributed into 9-cm polystyrene Petri dishes, which were placed in a conditioned room and left to dry for three days at 50% relative humidity and 23 °C. In addition, to investigate the improvement of mechanical properties, other biodegradable film samples produced from gluten (0.10 g) and nanocellulose (0.025 g) were also prepared.

All film samples underwent conditioning in accordance with the TAPPI T402 sp-08 (2008) standard. A digital micrometer (40 EXL; Mahr GmbH, Esslingen am Neckar, Germany) with 0.1 μm sensitivity was used to measure the thickness of the films. The Zwick/Roell Z250 (Zwick GmbH & Co., Z5.0 TH, Ulm, Germany) strength tester (100 N/10 kN load cell) was used for tensile strength testing of the samples prepared according to the TAPPI T494 om-96 (1996) standard. The values for elastic modulus and tensile strength were also recorded for the samples.

Pulping

The control soda pulp was cooked from corn stalks to compare with the pulps prepared from the stalks subjected to hot water (120 °C) pre-extraction. Because the alkaline and modified alkaline ($NaBH_4$) pre-extraction of stalks delivered lower yields, the method reported by Chang *et al.* (2012) was applied to produce mechanical pulps.

The soda pulps, at the L:S ratio of 10:1 L/kg OD, were cooked at an alkali charge of 16.7%. The samples were cooked to the H factor target of 104 for 90 min at 140 °C, reaching the maximum temperature after 30 min. After the hot water pre-extraction H factor was calculated, it was excluded from the total H factor. The pulps from each cook were then defiberized in a laboratory defibrator (Waring Commercial, Torrington, CT, USA) and placed on a 200-mesh screen, followed by a thorough washing using tap water.

For the determination of the paper properties, the hot water pre-extracted and control pulps underwent a refining process for 0, 2, and 4 min using a Waring blender (HGB2WTS3, Waring Commercial, Torrington, CT, USA) (Shaw 1984; French and Maddern 1994; Chang *et al.* 2011, 2012). The refining response was evaluated in terms of the freeness levels of the pulps in accordance with ISO 5267-1 (1999) standard. A Rapid-Köthen sheet former (PTI, Vorchdorf, Austria) was used to produce handsheets according to the relevant methods of ISO 5269-2 (2004) standard. The physical properties of the paper were tested using the TAPPI T220 sp-01 (2001) method and the optical properties of the pulps were assessed using the ISO 2469 (2014) and ISO 2471 (2008) standard methods.

Analytical Tests

The corn stalks for the study were sampled and prepared according to the TAPPI T257 sp-14 (2014) standard method for analytical testing. The ash content was determined by the TAPPI T211 om-16 (2016) standard and the solubility properties were examined according to the TAPPI T204 cm-17 (2017) for alcohol-benzene, TAPPI T207 cm-08 (2008) for hot water, and TAPPI T212 om-12 (2012) for 1% NaOH.

The stalk dry weight and the initial sample weight were used to calculate the yield based on the gravimetric measurements. The samples were dried at 105 °C to constant weight to determine the dry solid contents. The TAPPI T236 om-99 (1999) standard and

SCAN-CM 15:99 (1999) standard methods were applied to determine the kappa number and the viscosity of the pulps, respectively.

The samples were subjected to the National Renewable Energy Laboratory (NREL) analytical procedures to determine their glucose, xylose-arabinose, and acid-soluble/ insoluble lignin contents (Sluiter *et al.* 2011). For determination of the sugar and ethanol contents, the samples were analyzed *via* the HPLC Agilent 1200 system equipped with a Shodex SH1011 sugar column (mobile phase: 5 mM H_2SO_4, flow rate: 0.5 mL/min, and column temperature: 60 °C) and refractive index detector. The solid samples were weighed to reveal the amount of acid-insoluble lignin, which was subsequently analyzed against blank deionized water at 320 nm adsorption.

The percentage of solids recovered was determined on an OD basis as seen in Eq. 1,

$$\text{Percentage of solids recovered} = (W_2 \div W_1) \times 100 \quad (1)$$

where W_1 is the sample dry weight before pretreatment (g) and W_2 is the treated sample dry weight (g).

The decrease in lignin was calculated according to the initial lignin dry weight in untreated material (LU) and the post treatment lignin dry weight in the remaining solids (LP). The percentage of lignin reduction was found using Eq. 2,

$$\text{Percentage of lignin reduction} = [(\text{LU} - \text{LP}) \div \text{LU})] \times 100 \quad (2)$$

where LP is the pre-treated sample lignin dry weight and LU is the lignin dry weight in the untreated biomass.

Furthermore, in the same way, the glucan and xylan solubilization in the pre-treated samples was calculated by substituting the relevant percentages for those of glucan and xylan.

The ethanol yield during fermentation was found by calculating it as a percentage of the theoretical maximum yield (Kim and Lee 2005) using Eq. 3,

$$\text{Percentage of theoretical ethanol yield} = E \div (X \times 0.511) \times 100 \quad (3)$$

where E is the ethanol (g) produced during fermentation and X is the xylose (g) in the liquids. The constant 0.511 was found as the theoretical ethanol yield from xylose.

Statistical analysis

The data obtained were statistically analyzed *via* the SPSS packet program (SPSS Inc., version 20 Chicago, IL, USA). Analysis of variance (ANOVA) was used to identify significant differences and the differences between groups were determined *via* Duncan's test.

RESULTS AND DISCUSSION

Chemical Composition of Corn Stalks

The chemical composition determined for the corn stalks and the literature values for hardwood and softwood (Fengel and Wegener 1989) are given in Table 1. The corn stalks were higher in carbohydrate and extractive contents but lower in lignin than hard wood or softwood. Moreover, for the corn stalks, all solubility values were significantly greater than those of hardwood or softwood.

The total carbohydrate content of the biomass is important for the IFBR concept, and results showed that the corn stalks contained 47.7% glucose, 25.0% xylose, and a total polysaccharide content of 74.5%. The total carbohydrate content observed in this study was higher than that reported in the literature (Varga *et al.* 2002; Shi *et al.* 2014; Li *et al.* 2015) for corn stalks/stover. Although the total lignin content (22.1%) was similar, the ash content (2.61%) was lower (Varga *et al.* 2002; Shi *et al.* 2014; Li *et al.* 2015). The variations in these values might be attributed to the growth environment, the growing season and location, soil conditions, analytical techniques, or other causes (Utne and Hegbom 1992; Amores *et al.* 2013).

Table 1. Chemical Composition of Corn Stalks and Hardwood/Softwood

Chemical Composition	Raw Material (%)	
	Corn Stalks (Current Study)	Hardwood/Softwood
Extractives	10.2 ± 0.11	2 to 6/2 to 8
Hot Water Solubility	11.2 ± 0.14	2 to 7/3 to 6
1% NaOH Solubility	43.0 ± 0.07	14 to 20/9 to 16
Lignin	22.1 ± 0.10	30 to 35/25 to 35
Ash	2.61 ± 0.03	0.35/0.35
Glucose	47.7 ± 0.23	-
Xylose	25.0 ± 0.11	-
Arabinose	1.84 ± 0.17	-

Hot Water Pre-extractions

The weight, glucose, xylose, and lignin losses for the hot water pre-extraction of the corn stalks at the different treatment temperatures are given in Fig. 1. The temperature had a great impact, and more material was removed from the structure as temperatures increased. Up to 33.3% of the material was removed when the pre-extraction was performed at 150 °C.

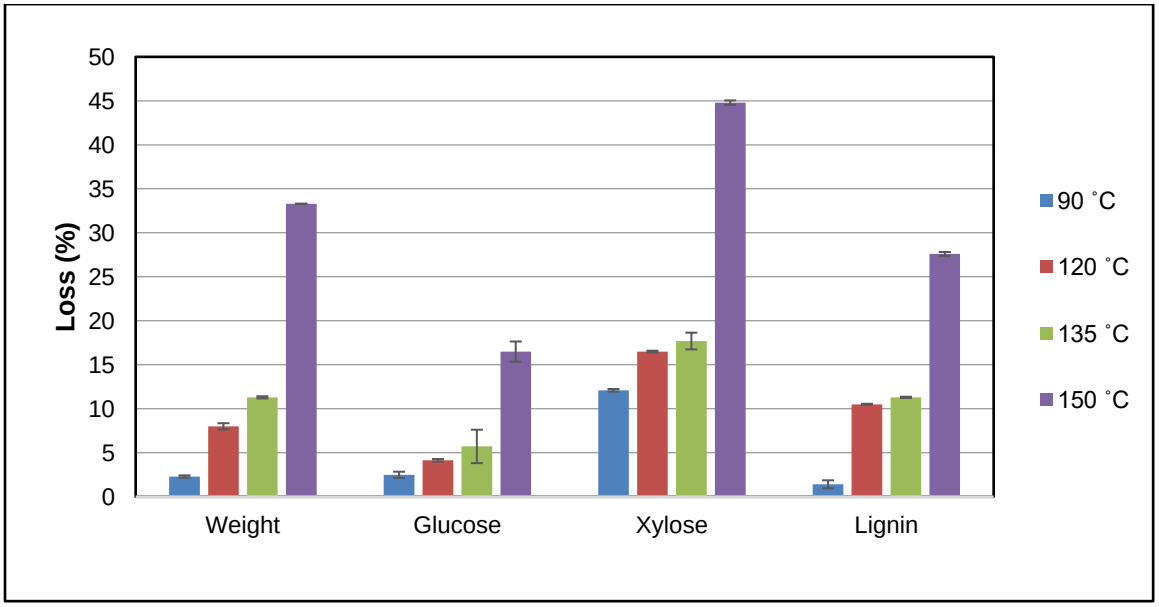


Fig. 1. Glucose, xylose, lignin, and weight loss for hot water pre-extraction of corn stalks at varying treatment temperatures

Results indicated that the weight loss in hot water pre-extraction was mainly due to the removal of hemicelluloses, along with some lignin and extraneous materials. Moreover, Jahan and Rahman (2012) also reported a pre-extraction weight loss (12.2%) when corn stalks were treated with hot water (150 °C) for 1 h. Tozluoğlu *et al.* (2015) observed a slightly higher weight loss (38.5%) with pre-extraction of wheat straw at 150 °C for 4 h. Consequently, the high amount of material removal seen in this study could have been caused by the lower degree of polymerization (DP) of the hemicelluloses in the stalk structure and the prolonged treatment time (240 min).

Compared to lignin, significantly higher xylose removal was observed for treatment temperatures of up to 135 °C. The highest xylose removal (44.8%) was seen when extraction was performed on the stalks at 150 °C. It should be noted that the removal of both components (xylose and lignin) was almost linear, although the removal ratio of xylose was higher compared to that of lignin. The removal of lignin with hemicellulose could have resulted from the xylan and lignin covalent bond chains in the structure of the corn stalks (Yoon *et al.* 2008).

The HPLC results indicated that this was not a case of the hydrolyzation of xylan to hydrolyzed xylose and its further degradation products of furfural, hydroxymethyl furfural (HMF), organic acids, *etc*. This could have been due to the mild treatment temperatures applied in this study. Results showed that the highest treatment temperature (150 °C) damaged the cellulose fraction and removed 16.5% of the glucose from the stalk structure (Fig. 1). The high amount of glucose removal may have been caused by the lower DP and the more amorphous regions of the cellulose in the stalk structure. Moreover, the statistical analysis showed that the weight, glucose, xylose, and lignin losses obtained with hot water pre-extraction were statistically significant ($p < 0.001$).

Alkali (NaOH) Pre-extractions

In this work, the aim of alkali pre-extraction prior to soda pulping was to extract maximum lignin and part of hemicelluloses from corn stalks while minimizing the loss of cellulose. Possibly the major effect of the alkali (NaOH) pre-extraction was the removal of lignin and some hemicelluloses as well as acetyl and the various uronic acid groups from the stalk structure. The amounts of alkaline pre-extraction weight, glucose, xylose, and lignin losses from the corn stalk structure are tabulated in Table 2. Results showed that the alkali used in this study was capable of reducing the lignin and hemicelluloses under the applied treatment conditions. In this study, the alkaline pre-extraction under various conditions resulted in weight losses ranging from 28.7 to 43.5% (Table 2). The results indicated that treatment temperature and alkali charge produced a significant effect on the pre-extraction yield. An increase in both alkali charge and treatment temperature resulted in greater material removal. There was less of a difference in the extraction rates (weight loss) between the 26.7 and 33.3% concentrations than between those of 16.7 and 26.7% (Table 2). The statistical analysis indicated that the change in alkali concentration was significantly effective on weight losses ($p < 0.001$).

The pre-extraction in this study also removed some glucose and hemicellulose (xylose) (Table 2). The results showed that both alkali charges and treatment temperatures affected the xylan extraction and increases in both variables resulted in higher xylan extraction. An increase in alkali charge from 16.7 to 26.7% resulted in a higher xylan extraction ratio; however, the extraction ratio was lower for the higher (33.3%) alkali charge. The maximum xylan extraction of 50.5% (*i.e.*, approximately 12.6% based on the

original stalks) was observed when the pre-extraction of the stalks was carried out with 33.3% alkali (NaOH) charge at 90 °C.

Varga *et al.* (2002) reported that 88.2% of the hemicelluloses and 95.9% of the lignin had been extracted when ground corn stalks were treated with 10% (w/w) NaOH for 1 h at 120 °C. In the present study, the lower xylan extractions might be linked to the stalk size and the mild treatment temperature.

When the effect of the extraction temperature was considered, nearly linear xylan removal was observed by raising the treatment temperature from 50 to 90 °C. One aim in this study was to minimize the pulping yield loss after pre-extraction. Therefore, some hemicelluloses had to be preserved in the solid portion to produce pulp for paper with properties at least equal to those of the non-pre-extracted control soda pulp.

Table 2. Glucose, Xylose, Lignin, and Weight Losses in NaOH pre-extracted Corn Stalks at Different Temperatures and Alkali Concentrations

Temp. (°C)	NaOH Conc. (%)	Weight Loss (%)	Glucose Loss (%)	Xylose Loss (%)	Lignin Loss (%)
50	16.7	28.7 ± 0.44 a*	6.88 ± 0.13 a	25.6 ± 0.49 a	62.0 ± 0.26 a
	26.7	37.4 ± 0.73 d	7.60 ± 0.77 b	35.6 ± 0.73 c	73.2 ± 0.12 c
	33.3	39.5 ± 0.59 e	9.50 ± 0.65 d	45.2 ± 0.49 e	74.2 ± 0.18 d
70	16.7	34.3 ± 0.58 b	7.70 ± 0.63 b	31.7 ± 0.42 b	70.6 ± 0.14 b
	26.7	39.5 ± 0.29 e	8.43 ± 0.27 c	42.2 ± 0.35 d	75.9 ± 0.36 e
	33.3	41.7 ± 0.19 f	10.0 ± 0.07 e	49.0 ± 0.14 f	78.1 ± 0.22 f
90	16.7	35.4 ± 0.16 c	8.31 ± 0.71 c	34.9 ± 0.28 c	78.4 ± 0.00 f
	26.7	41.6 ± 0.28 f	9.16 ± 0.07 d	44.9 ± 0.35 e	83.7 ± 0.43 g
	33.3	43.5 ± 0.13 g	11.2 ± 0.14 f	50.5 ± 0.17 g	85.8 ± 0.82 h

*: Within each column, the factors followed by this letter were not significantly different according to Duncan's test ($p < 0.05$)

As with xylan, the increase in treatment temperature and alkali charge during pre-extraction removed more glucan from the stalk structure. The corn stalks were composed of 47.7% glucose (Table 1), and during pre-extraction, 6.88 to 11.2% (based on OD stalks) of the glucose was removed, depending on the treatment temperature and alkali charge (Table 2). Alkaline pre-extractions performed at lower than 100 °C caused some delignification and degradation reactions. The mild pre-extraction temperatures applied in this study may explain the lower glucan removal. The results obtained were comparable to the findings of Yuan *et al.* (2016). Cellulose degradation may significantly affect pulp and paper properties, and thus, the lower glucan degradation seen in the present study could enable the production of paper with better properties.

Higher lignin removal was observed when pre-extraction was performed on the stalks at higher temperatures and alkali charges (Table 2). The rate of lignin removal was significantly greater than that of xylan during alkaline pre-extraction. When the extraction rates of glucan, xylan, and lignin under varying extraction conditions were compared, it may be concluded that the treatment temperature, as opposed to the alkali (NaOH) charge, was more effective. This result is also compatible with the literature (Chen *et al.* 2017). Higher alkali concentrations removed more material possibly as a result of the more complete delignification reactions at higher alkali concentrations. In contrast, alkaline pre-extractions had a significant ($p < 0.001$) effect on weight, glucose, xylose, and lignin losses.

Optimized pre-extraction conditions could further be established as parameters for the dissolution of hemicelluloses, which might significantly affect paper properties.

Therefore, the optimum treatment condition for lignin and xylan removal rates was determined for extraction carried out on stalks using 26.7% alkali at 50 °C.

Modified Alkali Extraction ($NaBH_4$)

In alkali pulping, the pulping selectivity can be improved by adding $NaBH_4$ in small amounts to prevent peeling and degradation of hemicelluloses (Çöpür and Tozluoğlu 2008). The modification of alkaline pre-extraction with $NaBH_4$ was presumed to have conserved additional glucan and xylan and to have resulted in selective degradation of lignin (Çöpür *et al.* 2012). Consequently, more efficient delignification was achieved with the modification of the alkali extraction by the addition to OD material of 0.1, 0.5, 2, and 4% $NaBH_4$ for the optimal alkaline pre-extraction condition of 26.7% NaOH at 50 °C. Results showed that this modification affected the delignification and xylan degradation (Table 3). The xylan degradation could have been due to the lignin-xylan chemical bonds in the structure of the stalks (Yoon *et al.* 2008). Because only insignificant glucan loss was seen after modification, it was not included in the present study findings. However, delignification of the stalk structure was notably affected by the modification of an addition of 0.5% $NaBH_4$, which led to the removal of 2.30% of the lignin. Furthermore, modifying the extraction with 2% $NaBH_4$ resulted in 4.50% delignification; however, the xylan dissolution was higher (6.60%). The weight, lignin, and xylose losses for $NaBH_4$ modified pre-extraction were all statistically significant ($p < 0.001$).

Table 3. Lignin, Xylose, and Weight Losses for NaOH + $NaBH_4$ Pre-extraction of Corn Stalks

Temp. (°C)	NaOH - $NaBH_4$ Conc. (%)	Weight Loss (%)	Xylose Loss (%)	Lignin Loss (%)
50	26.7	37.4 a*	35.6 ± 0.73 a	73.2 ± 0.73 a
	26.7 to 0.1	40.0 b	37.5 ± 0.49 b	73.9 ± 0.19 a
	26.7 to 0.5	41.0 b	39.9 ± 0.21 c	75.5 ± 0.35 b
	26.7 to 2.0	43.5 c	42.2 ± 0.14 d	77.7 ± 0.12 c
	26.7 to 4.0	44.2 c	43.4 ± 0.07 e	80.2 ± 0.24 d

*: Within each column, the factors followed by this letter were not significantly different according to Duncan's test ($p < 0.05$)

Composition of Liquids and Ethanol Production

When the pre-extraction stalk liquids (hot water, alkali, and modified $NaBH_4$) were examined, they contained oligomers of glucan, xylan-arabinan, and lignin. Results showed that low levels of glucan were present in the liquid. This may be explained by the mild extraction conditions applied in this study, which produced unhydrolyzed glucan.

Pre-extraction of the stalks with hot water at 150 and 120 °C resulted in the recovery of nearly 71.8 and 69.1% of the xylan, respectively, as monomeric sugar (xylose). In contrast, the lowest xylose recovery (21.0%) was achieved with the 26.7% alkali treatment of the stalks (Table 4). This xylose recovery variability might have been linked to the solubilization of the lignin in the alkali and hot water pre-extractions. According to Mok and Antal (1992), the higher delignification in alkaline pre-extraction may impede the recovery of xylose sugars. In addition, mild alkaline extraction conditions might prevent the condensation of lignin and lead to high lignin dissolution. This may in turn inhibit the conversion of the degraded sugars to furfural, HMF, and organic acids (Chang and

Holtzapple 2000), which may have been the case in this study. The organic acids originating from the peeling reactions were probably retained.

Table 4. Sugars in Pre-extraction Solids and Liquids

Pre-extraction Conditions	Solids				Liquids		
	Sample	Untreated Stalks (g)	Extracted Solids (g)	Loss (%)	Sample	Extracted Liquids (%)	Recovery (%)
120 °C	Yield	100	92.0	8.00			
	Xylan	25.0	20.8	16.8	Xylose	11.6	69.1
150 °C	Yield	100	66.7	33.3			
	Xylan	25.0	13.8	44.8	Xylose	32.2	71.8
26.7% NaOH	Yield	100	62.6	37.4			
	Xylan	25.0	16.1	35.6	Xylose	7.50	21.0

The xylose in the extraction liquids was fermented to produce bioethanol. Consequently, the theoretical ethanol yield for pre-extraction of the stalks was 83, 89.4, and 80.7% for the 120 °C hot water, 150 °C hot water, and 26.7% alkaline methods, respectively. In this investigation, liquids obtained from hot water (120 and 150 °C) pre-extraction of the stalks resulted in ethanol yields of 4.91 and 14.7 g (g/100 g soluble material), respectively. The liquid portion of the alkaline pre-extraction of the stalks (26.7% NaOH at 50 °C) yielded 7.66 g (g/100 g soluble material) of ethanol. The lower ethanol yield in the alkaline pre-extraction samples could be explained by the lower xylose recovery and the alkali media of the samples. Another possible reason is the presence of lignin, which inhibits fermentation.

Biodegradable Films

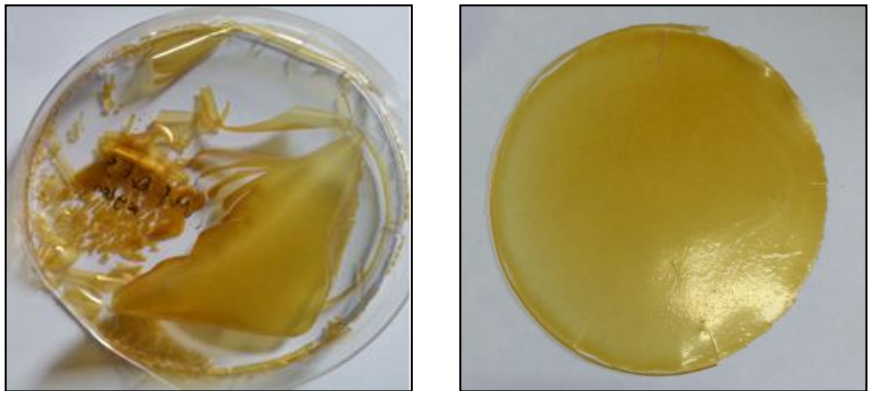
In addition to bioethanol, biofilm production was examined in this study. Biofilm samples produced using solely xylan resulted in crack formation (Fig. 2). This finding was also observed by Gabrielii and Gatenholm (1998) and Göksu (2005). To eliminate this problem, xylitol (Seber 2010; Gonçalves 2011) was added to the mixture and this resulted in a good biofilm construction (Fig. 2).

The produced biofilms were tested to determine their mechanical properties; however, the results showed them to be poor. To improve the mechanical properties, gluten and nanocellulose were added to the mixture (Table 5). Results showed that the addition of gluten improved the tensile strength, whereas a dramatic increase (more than two-fold) in tensile strength was observed when small amounts of nanocellulose were added to the mixture (Table 5).

The results also indicated that biofilms produced from corn stalks, when compared to those from wheat straw (Tozluoğlu *et al.* 2015), gave better (almost 2 to 3 times greater) mechanical strength values. In the literature, films with additions of corncob xylan exhibited a more regular surface compared to the other films, thus explaining the high stretchability feature of corncob xylan films. Films including grass xylan resulted in a surface marred by small globular forms, whereas birchwood xylan produced more heterogeneous films (Göksu 2005).

Table 5. Thickness and Mechanical Properties of Biodegradable Films

Biofilm Composition	Thickness (mm)	Elastic Modulus (N/mm^2)	Tensile Strength (N/mm^2)
Control (Xylan + Xylitol)	0.151 ± 0.02	171 ± 17.5	3.60 ± 0.22
Control + Gluten	0.141 ± 0.02	214 ± 10.7	4.07 ± 0.28
Control + Nanocellulose	0.133 ± 0.01	341 ± 33.6	7.78 ± 0.37



(a) **(b)**

Fig. 2. (a) Films obtained using only extracted xylan; (b) extracted xylan and xylitol

Pulp and Paper Properties

This study included chemically pulped soda (control) and hot water (120 °C) pre-extracted pulps together with mechanically pulped alkaline (26.7% NaOH) and modified alkaline (0.1% $NaBH_4$) pre-extracted pulps (Table 6).

Table 6. Data on Pulps

Pre-extractions	Yield (% of OD Stalks)	Reject (% of OD Stalks)	Kappa (mL/g)	Viscosity (cm^3/g)	Glucose (% of OD Pulp)	Xylose (% of OD Pulp)	Lignin (% of OD Pulp)
Control	53.6	3.00	12.2 ± 0.05 a*	1031 ± 0.04 b	64.2 ± 1.19 b	24.5 ± 0.85 ab	3.47 ± 0.44 a
Hot Water 120 °C	52.9	3.34	13.1 ± 0.00 b	967 ± 0.07 a	64.7 ± 1.20 b	24.9 ± 0.42 b	6.33 ± 0.24 b
26.7% NaOH	62.6	-	-	-	60.3 ± 0.77 a	25.7 ± 0.73 b	8.94 ± 0.12 a
+ 0.1% $NaBH_4$	60.0	-	-	-	63.7 ± 0.49 b	22.7 ± 0.49 a	8.77 ± 0.19 b

*: Within each column, the factors followed by this letter were not significantly different according to Duncan's test ($p < 0.05$)

Similar to the findings of Yoon *et al.* (2011), the hot water pre-extraction samples gave a slightly lower pulp yield (52.9% OD stalks) compared to the control soda pulp (53.6% OD stalks). However, Jahan and Rahman (2012) reported lower pulp yields (around 49%) when hot water pre-extraction corn stalks were cooked using the soda-AQ method. In contrast, a significant reduction in the pulp yield of pre-extraction corn stover was

observed by Cheng *et al.* (2014). Furthermore, the hot water pre-extracted pulp had a slightly higher reject content (3.34% OD stalks) (Table 6). The chemical compositions of both pulps were analyzed and the results showed that both pulps had similar amounts of glucose and xylose. The hot water pre-extracted soda pulp had a slightly higher kappa number compared to the control soda pulp. Cheng *et al.* (2014) also observed similar results. However, Jahan and Rahman (2012) found a lower kappa number compared to the present findings. In contrast to the control, the hot water pre-extracted soda pulp exhibited slightly lower viscosity, which could have occurred because the stalk structure was open to the cooking chemicals and thus resulted in more cellulose degradation (Yoon *et al.* 2011). Consequently, the hot water pre-extraction created a more porous structure that may have increased the ability of the cooking chemicals to reach the inner structures, resulting in improved lignin reactivity and hemicelluloses degradation. The higher yield reported in this study compared to the findings of Cheng *et al.* (2014) could be due to the mild cooking conditions applied in this study. The observed values for kappa ($p < 0.001$), viscosity ($p < 0.001$), xylose ($p < 0.05$), glucose ($p < 0.01$), and lignin ($p < 0.001$) were all statistically significant.

The alkaline (26.7% OD stalks) and modified alkaline (0.1% $NaBH_4$ OD stalks) mechanical pulps had similar yields. The results showed that the $NaBH_4$ modified pulp had higher cellulose (63.7% OD pulp) but lower lignin (8.77% OD pulp) contents. Prior to handsheet preparation, the chemical soda pulps of the control and the hot water pre-extracted pulps were refined for 0, 2, and 4 min. Additionally, the mechanical pulps were fiberized for 1 min using a Waring blender. Table 7 presents the results of the freeness test and the tensile, tear, and burst (mechanical) tests as well as the (physical) properties determined for brightness and opacity of the pulps.

Table 7. Paper Properties

Pre-extractions	Refining (min)	SR (mL)	Tensile Index (Nm/g)	Tear Index (mNm^2/g)	Burst Index ($kPam^2/g$)	Brightness (% ISO)	Opacity (% ISO)
Control*	0	24	58.4 ± 0.51 b***	8.25 ± 0.03 b	2.73 ± 0.51 b	35.3 ± 0.33 e	90.7 ± 0.89 d
	2	55	95.0 ± 0.34 e	8.17 ± 0.06 b	5.67 ± 0.25 f	33.8 ± 1.07 d	84.4 ± 0.63 a
	4	72	100 ± 0.17 f	7.41 ± 0.04 a	5.79 ± 0.56 g	32.9 ± 0.20 c	80.6 ± 0.27 b
Hot Water 120 °C*	0	22	46.1 ± 0.13 a	8.11 ± 0.04 b	2.04 ± 0.19 a	33.9 ± 0.44 d	94.4 ± 0.56 e
	2	52	80.5 ± 0.20 c	7.84 ± 0.04 b	4.77 ± 0.11d	31.8 ± 0.50 b	88.8 ± 0.40 c
	4	66	81.4 ± 0.18 c	7.76 ± 0.05 b	4.84 ± 0.43 d	30.2 ± 0.27 a	84.2 ± 0.81 a
26.7%NaOH**	1	33	93.1 ± 0.31 d	9.83 ± 0.03 c	4.93 ± 0.41e	30.6 ± 0.47 a	87.4 ± 0.27 b
+0.1%$NaBH_4$**	1	37	81.9 ± 0.22 c	12.2 ± 0.04 d	3.80 ± 0.50 c	30.0 ± 0.64 a	87.0 ± 0.42 b

*: Pre-extracted soda chemical pulps; **: Pre-extracted mechanical pulps
***: Within each column, the factors followed by this letter were not significantly different according to Duncan's test ($p < 0.05$)

Compared to the control soda pulp, the hot water pre-extracted pulp exhibited a lower refining response. This may be attributed to the lower hemicellulose content, resulting in lower swellability of the fibers (Yoon and van Heiningen 2008; Helmerius *et al.* 2010; Yuan *et al.* 2016).

The tensile and burst (mechanical) properties of the chemical pulps were improved by the refining, which might be ascribed to fiber fibrillation during refining. However, the value of the tear index was slightly reduced, subject to the refining intensity. The tensile and burst features found in the control soda pulp were higher than in the hot water pre-extracted soda pulp, which could have been caused by the damage wrought on individual fibers. The higher fiber flexibility and increased inter-fiber bonding could account for the higher tensile and burst index values (Çöpür 2007; Yuan *et al.* 2016). A comparison of the chemical and mechanical pulps revealed that lower tensile and burst index values were exhibited by the mechanical pulps. The mechanical pulps had a higher lignin content, which produced stiff fibers, and thus caused lower inter-fiber bonding. One possible reason is the lesser hemicellulose content in modified alkali extracted pulps, resulting in less bonding (Çöpür 2007; Yuan *et al.* 2016).

The tear value is chiefly determined by the strength of individual fibers and rarely on the extent of inter-fiber bonding. Therefore, compared to the chemical pulps, the mechanical pulps presented higher tear index values. The control soda pulp, with a relatively undamaged structure, resulted in a better tear index value compared to the hot water pre-extracted soda pulp.

A comparison of their physical properties demonstrated that the control pulp yielded a slightly better brightness value than the other pulps, whereas the opacity value was the reverse. The refining diminished both brightness and opacity due to the larger optical contact area between the fibers (*i.e.*, higher fiber bonding). The statistical analysis implied that the pre-extractions had a significant ($p < 0.001$) effect on the tensile index, burst index, opacity, and brightness, whereas no significant differences ($p > 0.05$) were found for the tear indices.

Mass Balance Observation on Pre-Extraction

The mass balance was calculated according to the solid recovery, soda pulp, soluble sugars in liquid, and ethanol yield on the basis of 100 kg OD corn stalks, which was extracted with hot water under the conditions of 120 °C for 4 h (Fig. 3). The results showed that roughly 1.34 kg of xylan could be extracted from 100 kg of OD corn stalks. On the other hand, 0.33 kg of glucan was lost and 0.84 kg of lignin was delignified during the pre-treatment. The dissolved sugars were fermented to get bio-ethanol; 0.40 kg of ethanol was produced in this work.

The extracted solid part was cooked with the soda method, and 49 kg of corn stalks pulp was produced. The pulp consisted of 31.7 kg of glucan, 12.2 kg of xylan, and 3.1 kg of lignin. Conversely, 56.2 kg of soda pulp was obtained when the control cook was accomplished for the equivalent H factor of the pre-extracted soda cook. The control pulp had 36.1 kg of glucan, 13.8 kg of xylan, and 1.95 kg of lignin in the structure. In comparison to the control pulp, the hot water pre-extracted pulp had almost 12% lower xylan in the structure. Moreover, the hot water pre-extraction resulted in 49 kg of soda pulp in addition to the 0.40 kg of ethanol.

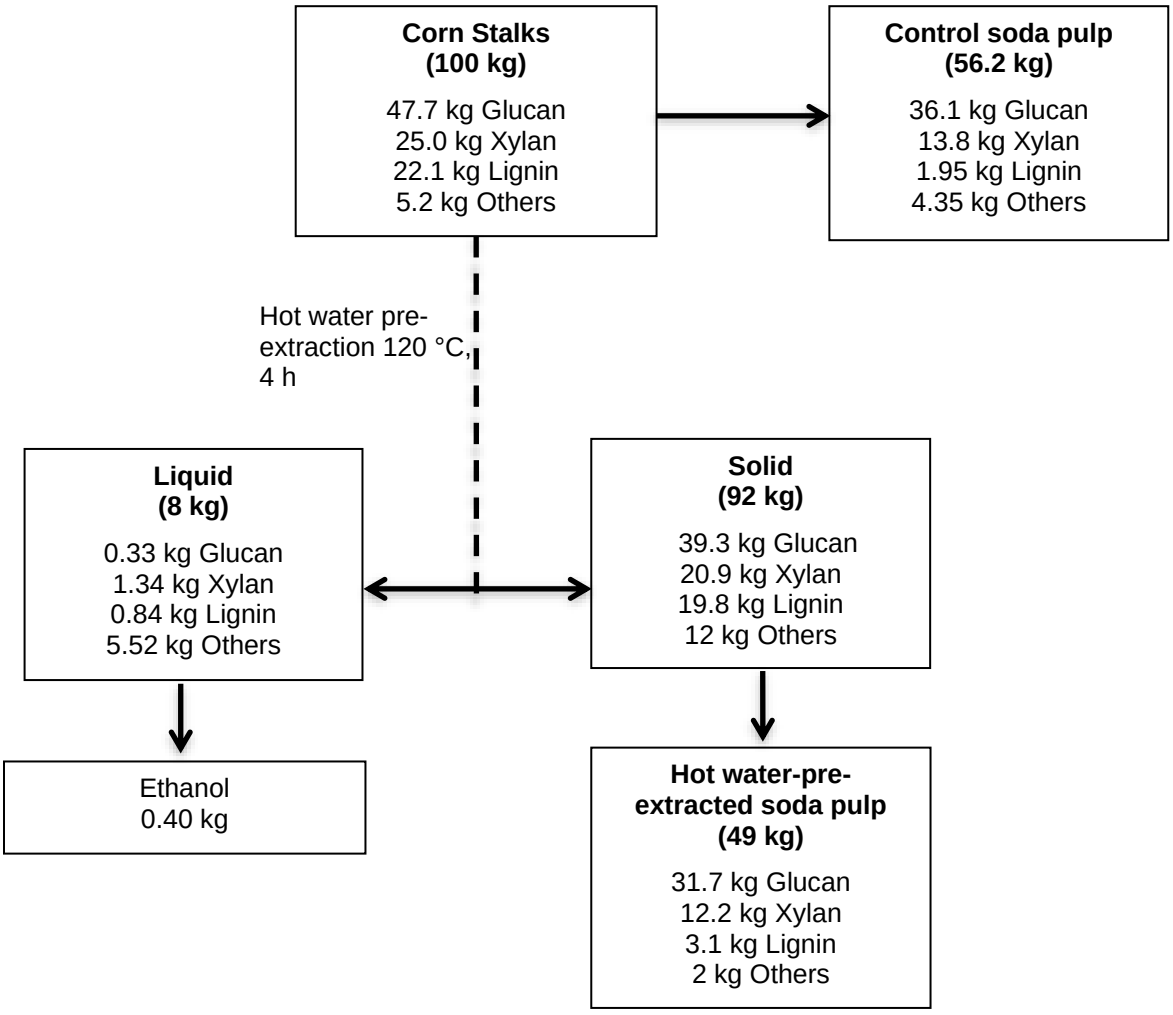


Fig. 3. Mass balance analysis of hot water pre-extraction, soda pulping and ethanol fermentation

CONCLUSIONS

1. The pre-extraction of corn stalks with hot water (150 °C) removed up to 44.8% of the xylose from the structure. The ratio of xylose removal was higher than that of lignin for all hot water pre-extractions.
2. The increase in alkali concentration removed more material from the structure. Modified alkali ($NaBH_4$ + NaOH) pre-extraction increased the lignin removal.
3. Bioethanol was obtained from the extracts. The pre-extraction of the stalks with hot water at 150 °C produced 14.7 g (g/100g OD) of ethanol. Moreover, the theoretical ethanol yield was calculated as 89.4%.
4. The pre-extracted xylan was used to produce biodegradable films. Pure xylan did not form a self-supporting biofilm; however, adding xylitol, gluten, and nanocellulose resulted in self-supporting film formation with sufficient mechanical properties.

5. Lastly, the pulp properties and yield of the hot water pre-extracted and the control soda pulps were comparable.

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REFERENCES CITED

Amores, I., Ballesteros, I., Manzanares, P., Sáez, F., Michelena, G., and Ballesteros, M. (2013). "Ethanol production from sugarcane bagasse pretreated by steam explosion," *Electron. J. Energy. Environ.* 1(1), 25-36. DOI: 10.7770/ejee-V1N1-art519

Batalha, L. A. R., Han, Q., Jameel, H., Chang, H., Colodette, J. L., and Gomes, F. J. B. (2015). "Production of fermentable sugars from sugarcane bagasse by enzymatic hydrolysis after autohydrolysis and mechanical refining," *Bioresource Technol.* 180, 97-105. DOI: 10.1016/j.biortech.2014.12.060

Chang, X. F., Bridges, C., Vu, D., Kuan, D., Kuang, L., Olson, J. A., Luukonen, A., and Beatson, R. P. (2011). "Saving electrical energy by alkaline peroxide pretreatment of TMP prior to low consistency refining," *Pul. Pap.-Canada* 112(4), 21-27.

Chang, V. S., and Holtzapple, M. T. (2000). "Fundamental factors affecting biomass enzymatic reactivity," *Appl. Biochem. Biotechnol.* 84-86(1-9), 5-37. DOI: 10.1385/ABAB:84-86:1-9:5

Chang, X. F., Olson, J. A., and Beatson, R. P. (2012). "A comparison between the effects of ozone and alkaline peroxide treatments on TMP properties and subsequent low consistency refining," *BioResources* 7(1), 99-111. DOI: 10.15376/biores.7.1.0099-0111

Chen, J., Jia, T., Yang, G., and He, M. (2017). "Pre-extraction of hemicelluloses from poplar chips and effect on kraft pulping," *Journal of Korea TAPPI* 49(2), 30-40. 2017. DOI : 10.7584/JKTAPPI.2017.04.49.2.30

Cheng, H., Li, J., Feng, Q., Zhan, H., and Xie, Y. (2014). "Hot water extraction of corn stover: Hemicellulose fractionation and its effect on subsequent soda-AQ pulping," *BioResources* 9(2), 2671-2680. DOI: 10.15376/biores.9.2.2671-2680

Chong, G.-G., He, Yu-C., Liu, Q-X., Kou, X.-Q., Huang, X.-J., Di, J.-H., Ma, C.-L., (2017). "Effective enzymatic in situ saccharification of bamboo shoot shell pretreated by dilute alkalic salts sodium hypochlorite/sodium sulfide pretreatment under the autoclave system," *Bioresource Technol.* 241, 726-734. DOI: 10.1016/j.biortech.2017.05.182.

Çöpür, Y. (2007). "Refining of polysulfide pulps," *J. Appl. Sci.* 7(2), 280-284. DOI: 10.3923/jas.2007.280.284

Çöpür, Y., and Tozluoğlu, A. (2008). "A comparison of kraft, PS, kraft-AQ and kraft-$NaBH_4$ pulps of Brutia pine," *Bioresource Technol.* 99(5), 909-913. DOI: 10.1016/j.biortech.2007.04.015

Çöpür, Y., Tozluoğlu, A., and Özyürek, Ö. (2012). "Sodium borohydrate ($NaBH_4$) pretreatment for efficient enzymatic saccharification of wheat straw," *Bioresource Technol.* 107, 258-266. DOI: 10.1016/j.biortech.2011.12.076

Egüés, I., Sanchez, C., Mondragon, I., and Labidi, J. (2012). "Effect of alkaline and autohydrolysis process on the purity of obtained hemicelluloses from corn stalks," *Bioresource Technol.* 103(1), 239-248. DOI: 10.1016/j.biortech.2011.09.139

Feng, L., Qin, L., Liu, Z.-H., Dong, C.-Y., Li, B.-Z., and Yuan, Y.-J. (2014). "Combined severity during pretreatment chemical and temperature on the saccharification of wheat straw using acids and alkalis of differing strength," *BioResources* 9(1), 24-38. DOI: 10.15376/biores.9.1.24-38

Fengel, D., and Wegener, G. (1989) *Wood—Chemistry, Ultrastructure, Reactions* (2nd ed.), Walter de Gruyter, Berlin, Germany.

French, J., and Maddern, K. N. (1994). "A mini pulp evaluation procedure," *Appita. J.* 47(1), 38-44.

Gabrielii, I., and Gatenholm, P. (1998). "Preparation and properties of hydrogels based on hemicelluloses," *J. Appl. Polym. Sci.* 69(8), 1661-1667. DOI: 10.1002/(SICI)1097-4628(19980822)69:8<1661::AID-APP19>3.0.CO;2-X

Goash, D., Tanner J., Lavoie, J.-M., Garnier, G., and Patti, A. F. (2021). "An integrated approach for hemicellulose extraction from forest residue," *BioResources* 16(2), 2524-2547. DOI: 10.15376/biores.16.2.2524-2547

Gonçalves, A. M. C. (2011). *Preparation and Evaluation of Material Properties of Biofilms from Spruce Xylan*, Master's Thesis, Chalmers University of Technology, Göteborg, Sweden.

Göksu, E. I. (2005). *Hemicellulose Based Biodegradable Film Production*, Master's Thesis, Middle East Technical University, Ankara, Turkey.

Helmerius, J., von Walter J. V., Rova, U., Berglund, K. A., and Hodge, D. B. (2010). "Impact of hemicellulose pre-extraction for bioconversion on birch kraft pulp properties," *Bioresource Technol.* 101(15), 5996-6005. DOI: 10.1016/j.biortech.2010.03.029

ISO 2469 (2014). "Paper, board and pulps -- Measurement of diffuse radiance factor (diffuse reflectance factor)," International Organization for Standardization, Geneva, Switzerland.

ISO 2471 (2008). "Paper and board -- Determination of opacity (paper backing) -- Diffuse reflectance method," International Organization for Standardization, Geneva, Switzerland.

ISO 5267-1 (1999). "Pulps--Determination of drainability--Part 2: Schopper-Riegler method," International Organization for Standardization, Geneva, Switzerland.

ISO 5269-2 (2004). "Pulps -- Preparation of laboratory sheets for physical testing -- Part 2: Rapid-Köthen method," International Organization for Standardization, Geneva, Switzerland.

Jahan, M. S., and Rahman, M. M. (2012). "Effect of pre-hydrolysis on the soda-anthraquinone pulping of corn stalks and *Saccharum spontaneum* (kash)," *Carbohydr. Polym.* 88(2), 583-588. DOI: 10.1016/j.carbpol.2012.01.005

Kim, T. H., and Lee, Y. Y. (2005). "Pretreatment of corn stover by soaking in aqueous ammonia," *Appl. Biochem. Biotech.* 124, 1119-1131. DOI: 10.1385/abab:124:1-3:1119

Li, H., Saeed, A., Jahan, M. S., Ni, Y., and van Heiningen, A. (2010). "Hemicellulose removal from hardwood chips in the pre-hydrolysis step of the kraft-based dissolving pulp production," *J. Wood Chem. Technol.* 30(1), 48-60. DOI: 10.1080/02773810903419227

Li, R., Xie, Y., Yang, T., Li, B., Wang, W., and Kai, X. (2015). "Effects of chemical-biological pre-treatment of corn stalks on the bio-oils produced by hydrothermal liquefaction," *Energ. Convers. Manage.* 93, 23-30. DOI: 10.1016/j.enconman.2014.12.089

Mok, W. S. L., and Antal, Jr., M. J. (1992). "Uncatalyzed solvolysis of whole biomass hemicellulose by hot compressed liquid water," *Ind. Eng. Chem. Res.* 31(4), 1157-1161. DOI: 10.1021/ie00004a026

Özyürek, Ö., and van Heiningen, A. (2018). "Formic acid reinforced autohydrolysis of wheatstraw for high yield production of monosugars and minimal lignin precipitation," *Ind. Crop. Prod.* 112, 320-326. DOI: 10.1016/j.indcrop.2017.12.026

Resalati, H., Kermanian, H., Fadavi, F., and Feizmand, M. (2012). "Effect of hot-water and mild alkaline extraction on soda-AQ pulping of wheat straw," *Lignocellulose* 1(1), 71-80.

SCAN-CM 15:99 (1999). "Pulps – Viscosity in cupri-ethylenediamine solution," Scandinavian Pulp, Paper and Board Testing Committee, Stockholm, Sweden.

Seber, A. G. (2010). *Preparation of Antimicrobial Films from Agricultural Biomass*, Master's Thesis, Middle East Technical University, Ankara, Turkey.

Shaw, A. C. (1984). "Simulation of secondary refining," *Pulp Pap. Can.* 85(6), 107-112.

Shi, J., Yang, Q., and Lin, L. (2014). "The structural features of hemicelluloses dissolved out at different cooking stages of active oxygen cooking process," *Carbohydr. Polym.* 104, 182-190. DOI: 10.1016/j.carbpol.2014.01.004

Sluiter, A., Hamnes, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2011). *Determination of Structural Carbohydrates and Lignin in Biomass* (NREL/TP-510-42618), National Renewable Energy Laboratory, Golden, CO, USA.

TAPPI T204 cm-88 (2017). "Wood extractives in ethanol-benzene mixture," TAPPI Press, Atlanta, GA, USA.

TAPPI T207 cm-08 (2008). "Water solubility of wood and pulp," TAPPI Press, Atlanta, GA, USA.

TAPPI T211 om-16 (2016). "Ash in wood, pulp, paper and paperboard: Combustion at 525 °C," TAPPI Press, Atlanta, GA, USA.

TAPPI T212 om-12 (2012). "One percent sodium hydroxide solubility of wood and pulp," TAPPI Press, Atlanta, GA, USA.

TAPPI T220 sp-01 (2001). "Physical testing of pulp handsheets," TAPPI Press, Atlanta, GA, USA.

TAPPI T236 om-99 (1999). "Kappa number of pulp," TAPPI Press, Atlanta, GA, USA.

TAPPI T257 sp-14 (2014). "Sampling and preparing wood for analysis," TAPPI Press, Atlanta, GA, USA.

TAPPI T402 sp-08 (2008). "Standard conditioning and testing atmospheres for paper board, pulp handsheets and related products," TAPPI Press, Atlanta, GA, USA.

TAPPI T412 om-11 (2011). "Moisture in pulp, paper and paperboard," TAPPI Press, Atlanta, GA, USA.

TAPPI T494 om-96 (1996). "Tensile properties of paper and paperboard," TAPPI Press, Atlanta, GA, USA.

Tozluoğlu, A., Özyürek, Ö., Çöpür, Y., and Özdemir, H. (2015). "Integrated production of biofilm, bioethanol, and papermaking pulp from wheat straw," *BioResources* 10(4), 7834-7853. DOI: 10.15376/biores.10.4.7834-7853

Utne, B., and Hegbom, L. (1992). "Microscopy studies of wheat straw and rice straw as raw materials for the pulp and paper industry," in: *Second International Nonwood Pulping Conference*, Beijing, China, pp. 583.

van Heiningen, A. (2006). "Converting a kraft pulp mill into an integrated forest products biorefinery," *Pulp. Pap. Can.* 107(6), 38-43.

Varga, E., Szengyel, Z., and Réczey, K. (2002). "Chemical pretreatments of corn stover for enhancing enzymatic digestibility," *Appl. Biochem. Biotech.* 98, 73-87. DOI: 10.1385/abab:98-100:1-9:73

Wang, J., Wang, J., Lu, Z., Zhang J., (2020). "Adsorption and desorption of cellulase on/from enzymatic residual lignin after alkali pretreatment" *Ind. Crop. Prod.*, 155, 1-6. DOI: 10.1016/j.indcrop.2020.112811.

Wu, M., Gong, L., Ma, C., He, Yu-C., (2021). "Enhanced enzymatic saccharification of sorghum straw by effective delignification *via* combined pretreatment with alkali extraction and deep eutectic solvent soaking," *Bioresource Technol.* 340, 1-9. DOI: https://doi.org/10.1016/j.biortech.2021.125695.

Yoon, S.-H., Macevan, K., and van Heiningen, A. (2008). "Hot-water pre-extraction from loblolly pine (*Pinus taeda*) in an integrated forest products biorefinery," *TAPPI J.* 7(6), 27-31.

Yoon, S.-H., and van Heiningen, A. (2008). "Kraft pulping and papermaking properties of hot-water pre-extracted loblolly pine in an integrated forest products biorefinery," *TAPPI J.* 7(7), 22-27.

Yoon, S.-H., Tunc, M. S., and van Heiningen, A. (2011). "Near-neutral pre-extraction of hemicelluloses and subsequent kraft pulping of southern mixed hardwoods," *TAPPI J.* 10(1), 7-15. DOI: 10.32964/TJ10.1.7

Yuan, Z., Kapu, N. S., Beatson, R., Chang, X. F., and Martinez, D. M. (2016). "Effect of alkaline pre-extraction of hemicelluloses and silica on kraft pulping of bamboo (*Neosinocalamus affinis* Keng)," *Ind. Crop. Prod.*, 91, 66-75. DOI: 10.1016/j.indcrop.2016.06.019

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