

Ethanol Precipitation of Hetero-Polysaccharide Material from Hardwood by Alkaline Extraction Prior to the Kraft Cooking Process

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Hemicellulose material is an abundant and relatively under-utilized hetero-polysaccharide material present in lignocellulosic materials. In this study, an alkaline treatment was applied to sweetgum and *Eucalyptus globulus* chips to extract hemicelluloses prior to kraft pulping to subsequently evaluate the final product and process. An alkaline extraction (10 and 50% NaOH by weight on wood) for 60 min at 100 °C followed by precipitation in ethanol recovered 4.3% of the biomass as a predominantly xylan material (sweetgum 50% NaOH) with an average degree of polymerization around 250 and functional groups similar to a commercial xylan (sweetgum 10% NaOH). This process in comparison to autohydrolysis (water extraction at 100 °C) produced a much higher molecular weight and more pure hemicellulose. The results obtained indicate a promising combination between the effective extraction of hemicellulose from wood and a distillation process that recovers the ethanol, which may be an attractive alternative to recover liquor and ethanol after hemicellulose precipitation. Hemicellulose from sweetgum showed more thermal stability with high molecular weight compared to the hemicellulose extracted from *Eucalyptus globulus*. An attractive alternative looks to be to recover liquor and ethanol after hemicellulose precipitation.

Keywords: Xylan; Biorefinery; Alkaline extraction; Sweetgum; *Eucalyptus globulus*

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INTRODUCTION

Today, the United States' pulp and paper industry is facing increasing challenges from tropical pulp manufacturers who have low-cost wood and labor advantages. One response to the global competition is to develop green fuels and chemicals as byproducts from pulp and paper. To remain viable, the integrated forest biorefinery has become an important concept that can provide carbohydrates, oils, lignin, and other materials from biomass and convert them into a wide of valuable products with a sustainability approach in mind (Fig. 1). During the kraft pulping process, much of the lignin and hemicelluloses (40 to 50%) are dissolved in the black liquor (Mendes *et al.* 2011; Magaton *et al.* 2009) and sent to the recovery system to be burned in the recovery boiler. For carbohydrates, burning in the recovery system is not efficient because of a low heating value (14 MJ/kg) compared to lignin (25 MJ/kg) and issues in the efficiency of burning the black liquor (Colodette *et al.* 2011).

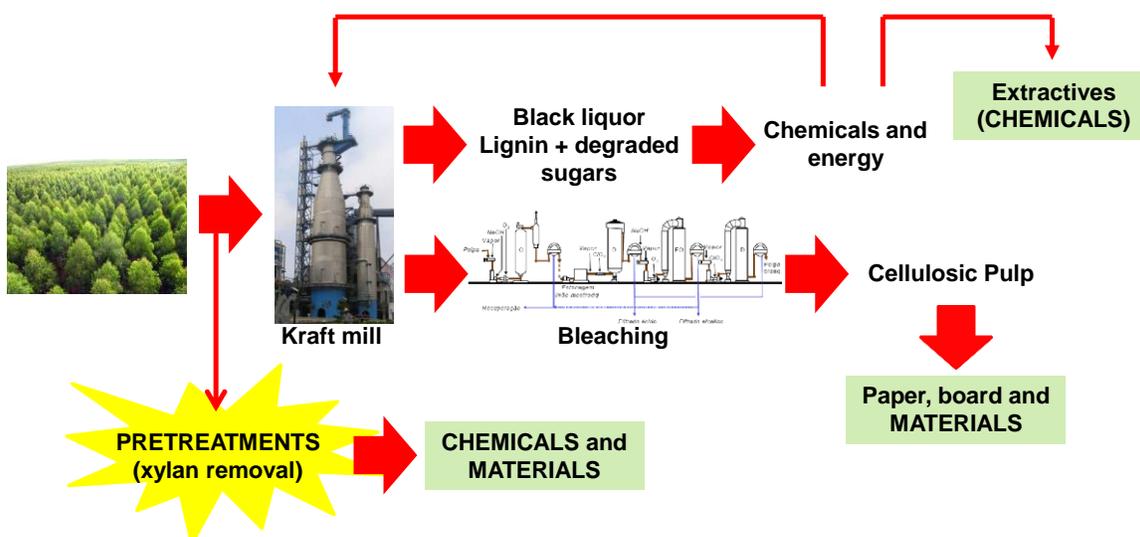


Fig. 1. Biorefinery concept

Hemicellulose, a class of hetero-polysaccharides present in the cell wall of wood and annual plants (Whistler *et al.* 1962; Sun and Cheng 2002) with a high molecular weight and a degree of polymerization between 80 and 425 (Bai *et al.* 2012), represents 20 to 35% of lignocellulosic biomass. It is the second most common polysaccharide in nature and is composed of a wide variety of monosaccharides, including xylose, arabinose, glucose, galactose, mannose, fructose, glucuronic acid, and galacturonic acid, depending on the source (Saha 2003). The most abundant hemicelluloses in trees are xylan in hardwoods and glucomannans in softwoods (Cousins 1978). In hardwoods, the major hemicellulose component is *O*-acetyl-4-*O*-methylglucuronoxylan, whereas in softwood species, *O*-acetyl-galactoglucomannan is predominant (Fengel and Wegener 1984).

Based on the billion-ton vision of the US Department of Energy (DOE), nearly 400 million tons of hemicellulose is available in the US per annum for bioprocessing to fuels and chemicals. In addition, every year, approximately 15 million tons of hemicellulose are produced by the pulp and paper industry alone, and according to preliminary results, this can yield in excess of 2 billion gallons of ethanol and 600 million gallons of acetic acid, with a net cash flow of \$3.3 billion. In some cases, such as for making dissolving pulps, hemicelluloses are already being removed to allow for the production of pure cellulose.

Investigations of hemicellulose isolation include alkaline extraction (Égües *et al.* 2012), alkaline peroxide extraction (Doner and Hicks 1997), liquid hot water extraction (Hasegawa *et al.* 2004), steam explosion-based extraction (Chen and Liu 2007), and others. The extensive hydrogen bonding between the individual polysaccharide cell wall components may impede the isolation of hemicellulose components (Hendriks and Zeeman 2009; Reddy and Yang 2005). Others studies have involved hot water extraction of hemicellulose sugars, mainly as low-molecular weight oligomers, as a starting material for ethanol production (Pu *et al.* 2011). However, to most effectively exploit their polymeric properties, the hemicelluloses can be converted directly in polymeric form for novel industrial applications such as biopolymers, hydrogels, and thermoplastic xylan derivatives.

Hydroxide ions cause swelling of cellulose, hydrolysis of ester linkages, and disruption of intermolecular hydrogen bonds between cellulose and hemicellulose, solubilizing a portion of the hemicellulosic material into solution. Alkaline extraction has been shown to be very effective for the removal of hemicellulose (Égües *et al.* 2012).

In this research, attention is focused on the extraction of hemicellulose with NaOH, a chemical that is already used and recovered in conventional kraft-based pulp and paper mills. The aim of this research is to demonstrate the characteristics and material balance of the xylans extracted from different hardwood species, *Eucalyptus globulus* and sweetgum, under different extraction conditions. In addition, important aspects of the recovery and re-use of the processing liquids used to isolate hemicellulose are investigated. The results can be used in the development of an efficient hemicellulose extraction system within the boundaries of a biorefinery.

MATERIALS AND METHODS

Materials

Two different types of hardwood chips, one from the Chilean pulp and paper industry (*Eucalyptus globulus*) and the other from the Southeast United States (*Liquidambar styraciflua*, called sweetgum), were used in this work. Both samples were chipped, dried, screened (bars screen from 4 to 8 mm), and then stored in plastic bags. The moisture content of the air-dried materials was measured by oven drying at 105 °C until constant weight was achieved. All chemicals and reagents used in this study were purchased from Sigma-Aldrich and Fisher Chemical companies and used as received.

Methods

Wood pretreatment

A quantity of 150 (oven dry, OD) g of wood chips was placed in an M/K digester model 1/K409 with 7-L capacity, temperature controller, and liquor circulation system. The conditions for the alkaline pretreatments and auto-hydrolysis are shown in Table 1. These conditions were chosen according some references with focus on xylans extraction (Pu *et al.* 2011; Al-Dajani and Tschirner 2007).

Table 1. Pretreatment Conditions Used in this Study

Pretreatment	Autohydrolysis (AH)	Alkaline (ALK)
Reaction time, (min)*	30	60
Temperature, (°C)	170	100
Chemical charge, (%)**	water	10 and 50% NaOH
Liquor : wood ratio (m ³ /ODt)	10 : 1	10 : 1
*Heating-up/cooling down periods were 30 and 5 min, respectively.		
**Based on original wood		

After the reaction was completed, the liquors were collected. Ethanol was added overnight to the alkaline liquor at a ratio of 1:1 by volume. The liquor was centrifuged, and the solid phase (ethanol precipitation material - EPM) was separated from the liquid

phase (ethanol and sodium hydroxide). The EPM was washed several times with ethanol before drying to avoid the material becoming difficult to dissolve during the characterization step.

The liquid phase containing the residual NaOH and degraded wood was distilled at 80 to 85 °C to investigate the possibility of recovering both ethanol and NaOH. A 100-mL sample of liquor was placed in a 500-mL Erlenmeyer flask linked to a 50-mL Soxhlet apparatus to collect the condensed phase. The apparatus was placed in a laboratory furnace with temperature control. After collecting 50 mL of condensate from the initial liquor, the distillation was stopped and both solutions (ethanol and NaOH phases) were collected. The NaOH liquid phase was titrated to determine the NaOH concentration after distillation. The ethanol liquid phase from the distillation process was submitted to a density test using a laboratory balance. Then, 10 mL of liquors and pure ethanol (references) and 10 mL of liquors collected after distillation were placed in a 30-mL beaker to check the water/ethanol ratio in the phases. The water fraction in the phases was determined by comparing the density of the pure compounds (references) and the density of the ethanol phase. Phenolphthalein was added to check for the presence of NaOH in the recovered ethanol.

The chips were washed with excess water, dried, ground in a Wiley mill, and sieved, and the fraction that passed through a 40-mesh screen but was retained by a 60-mesh screen was collected. The wood meals were Soxhlet-extracted overnight with benzene:ethanol 2:1 (v/v), dried, and used for lignin and sugar analysis. Those treatment conditions were established based on the literature (Colodette *et al.* 2011; Al-Dajani and Tschirner 2008; Pu *et al.* 2011).

Lignin content and sugar analysis

The lignin and sugar compositions were determined using extractive free wood meal before/after acid and alkaline hydrolysis. Also, this analysis was done in the EPM samples. The EPM samples were washed several times with ethanol (to remove residual NaOH) until neutral pH (around 8) before sugar/lignin analyses. Ash content on EPM samples was determinate before ethanol washing. These analyses were used to determine the precipitation process yield and material/xylan recovered after extraction based on wood.

Approximately 0.1 g of sample was hydrolyzed with 1.5 mL of 72% H₂SO₄ at room temperature for 90 min. The mixture was then diluted to 3% H₂SO₄ using deionized water, transferred to a vial, sealed, and heated to 122 °C for 90 min. Klason lignin and acid-soluble lignin were determined for each species (Lin and Dence 1992). The sum of Klason lignin and acid-soluble lignin is reported as the total lignin content. The resulting suspension was filtered, and the filtrate was analyzed for monomeric sugar content. Fructose was used as an internal standard.

The monomeric sugar content was determined by injecting 2.5-mL samples into a high-performance anion-exchange chromatography with pulsed amperometric detection (HPAE-PAD) on a Dionex IC-3000 chromatography system. Sugars were separated using a Carbo-Pac PA1 guard and analytical columns connected in series. Water was used as the eluent at the flow rate of 3.0 mL/min, and the column temperature was 18 °C. A post-column base of 400 mM NaOH was added to improve detection by pulsed amperometry. The post-column flow rate was 3.0 mL/min.

Byproducts content in autohydrolysis liquor

Furfural, hydroxymethyl furfural (HMF), formic acid, and acetic acid were determined inserting the autohydrolysis liquor (after AH treatment) in a Dionex HPLC System (Dionex, Sunnyvale, CA), which consisted of an ASI-100 automated sample injector, solvent rack SOR-100 module, P680 HPLC pump, and UVD170U multi-wavelength ultraviolet detector. Chromatographic separation was achieved using a 4.0 mm x 250 mm Acclaim® organic acid column (5 mm, Dionex, Sunnyvale, CA) coupled to an Acclaim® organic acid-guard column (5 mm, Dionex, Sunnyvale, CA). Non-linear gradient separations were carried out using 2.5 mmol.L⁻¹ methanesulfonic acid and water/acetonitrile (10/90, v/v) as mobile phase A and mobile phase B solvents, respectively. The concentrations of formic acid and acetic acid in the samples were measured at 210 nm, and HMF and furfural concentrations were determined at 227 nm. 4-tert-butylphenoxiacetic acid was used as an internal standard (Chen *et al.* 2006; Lee *et al.* 2010). Standard curves were made for each byproduct using a six-point calibration. All the standard points were dissolved in ACS grade methanol, and 4-tert-butylphenoxiacetic acid was used as an internal standard. Methanesulfonic acid and acetonitrile were used as eluents with flow rates of 1 mL/min.

FTIR analysis

The FTIR analysis were determined using EPM samples. The FTIR spectra were recorded on a NEXUS 670 FTIR spectrophotometer using a KBr disc containing 10% finely ground sample particles. All the spectra were obtained by accumulating 256 scans, with a resolution of 4 cm⁻¹, from 400 to 4000 cm⁻¹.

Thermal analysis

Thermogravimetric analysis was performed with a TGA Q500 (TA Inc., New Castle, DE), and 5 mg of EPM was used for each experiment under a nitrogen atmosphere. The temperature range and heating rate were 30 to 600 °C and 10 °C/min, respectively, followed by isothermal heating at 600 °C for 5 min. Each sample was tested in triplicate, and the average was used. The thermal transitions of the samples were studied using differential scanning calorimetry (DSC). The instrument used was a DSCQ100 (TA Inc., New Castle, DE) with a hermetic pan (T090127). Samples were subjected to a 10 °C/min temperature ramp. Before analysis, the samples were dried at 50 °C under vacuum overnight. The samples were heated from 40 to 200 °C, and an empty pan was used as a reference.

Acetylation of hemicellulose

The hemicellulose acetate was synthesized by reaction with acetic anhydride using N-bromosuccinimide (NBS) as a catalyst in an almost solvent-free system. The details of the acetylation of the hemicelluloses are as follows: dry hemicelluloses powder (0.66 g of EPM, equal to 0.005 mol of anhydroxylose unit and 0.01 mol of hydroxyl functionality in hemicelluloses) in 10 mL of distilled water was heated to 80 °C under magnetic bar stirring until completely dissolved (~10 min). A 5-mL volume of dimethylformamide (DMF) was added, and the mixture was stirred for about 5 min. The water and DMF were removed from the swollen gel by repeated distillation (rotating evaporator). The hemicellulose was then added to a mixture of 30 mL of acetic anhydride and 0.3 g of NBS. The reaction mixture was stirred for 2 h at 70 °C with a magnetic stirrer. Upon completion of the reaction, the reaction mixture was cooled to room temperature and then

slowly poured into 120 mL of 95% ethanol with stirring. The separated product from the solution was filtered off and collected.

Gel permeation chromatography (GPC)

The molecular-average weights of the acetylated hemicelluloses (EPM) were determined by gel permeation chromatography using water as a mobile phase. The samples were dissolved in tetrahydrofuran (THF) at a concentration of 0.1%, and a 200- μ L sample in solution was injected. GPC measurements for molecular weight calculation were carried out with a Waters GPC 510 pump equipped with UV and RI detectors using THF as the eluent at a flow rate of 0.6 mL/min at room temperature. Two Ultrastyrigel linear columns linked in series (Styrigel HR 1 and Styrigel HR 5E) were used for the measurements. Standard mono-disperse polystyrenes with molecular weight ranges from 0.82 to 1860 kg/mol were used for the calibration. The number- and weight-average molecular weights were calculated using the Millenium software by Waters. The repeat unit molecular weight was estimated to be 164 g.mol⁻¹. For reference, some authors have reported that a native hemicellulose with a degree of polymerization of 200 corresponds to a molecular weight of 32,800 g.mol⁻¹. (Palm and Zacchi 2003).

The intrinsic viscosity of extracted hetero-polysaccharides was also determined at 25 °C with an Ubbelohde-type viscometer for the measurement of molecular weight (Koshijima *et al.* 1965). EPM were dissolved with 0.04 M cupriethylenediamine (CED). An amount of 7.2 mL of the solution was added to a viscometer (Number 50) by pipet. Suction was then applied to force the solution into the bulb about 2 cm above capillary tube. The vacuum was removed and the solution was allowed to flow down through capillary by the force of gravity. The time it took for the solution to flow through the capillary was then recorded as the efflux time.

Intrinsic viscosity [μ] was determined as the product of elution time (sec) and the viscosity meter constant. The Standing-Mark-Houwink equation used for the xylan solution in cupriethylenediamine was,

$$[\mu] = 2.2 \times 10^{-2} \times Pn^{-0.72} \quad (1)$$

where Pn is the degree of polymerization (DP) and Total Molecular Weight is the degree of polymerization times the molecular weight of the monomer unit.

RESULTS AND DISCUSSION

Wood Composition

The wood composition results are shown in Table 2 and expressed in percentages based on the original wood. AH pretreatments were more efficient than ALK pretreatments for both woods, including the 50% NaOH pretreatment, although both pretreatments can be considered sufficient to remove significant quantities of xylan from the wood. According to xylose removal, the AH pretreatment for *Eucalyptus globulus* (49.4%) was more efficient than that using sweetgum (36.5%). Concerning sweetgum wood, AH (36.5%) and SG 50% NaOH (33.9%) pretreatments removed almost the same amount of xylose. For both types of wood (EG and SG), the AH extraction removed more glucose (about 15% for both types) than did the ALK extraction (7.8% and 8.7%, respectively), showing a higher selectivity for the ALK extraction process. ALK

pretreatments using 10% NaOH were not as efficient in xylan removal as were the other pretreatments due to the low concentration of NaOH. The ash content of the wood was significantly higher after ALK pretreatments due to the high NaOH charge used.

Table 2. Wood Characterization for Reference Wood and Wood after Pretreatment

Sample	Xyl (%)	Glc (%)	Total Sugar (%)	Total Lignin (%)	Ash (%)	Total (%)	Yield (%)
EG REF	16.0	46.1	67.1	25.9	0.3	93.3	100.0
EG AH	8.1	39.5	48.9	22.3	0.2	71.4	84.0
EG ALK 10	13.8	45.0	60.1	24.5	2.4	87.0	92.8
EG ALK 50	10.7	42.5	54.6	20.4	9.0	84.0	82.8
SG REF	18.9	43.7	66.3	24.6	0.2	91.1	100.0
SG AH	12.0	36.8	49.8	21.2	0.1	71.1	79.1
SG ALK 10	17.4	41.9	60.3	23.3	2.7	86.3	89.2
SG ALK 50	12.5	39.9	53.3	21.6	10.3	85.1	81.9

EG = *Eucalyptus globulus*; SG = sweetgum; Xyl = xylan; Glc = glucan
All results are expressed in % based on original wood.

Characterization of Autohydrolysis Liquor

During the AH processes, water under high temperature and pressure penetrates into the wood, causing partial hydrolysis of cellulose, dissolving part of the hemicelluloses, and removing a portion of lignin (Taherzadeh and Karimi 2008). Normally, four main byproducts may be found in the liquor after AH pretreatment: furfural, hydroxymethylfurfural (HMF), acetic acid, and formic acid, with concentrations depending on the wood species. However, due to the high liquor:wood ratio (10:1), some of these components were not found in the liquor of this study (HMF and formic acid). SG showed a higher concentration in acetic acid (0.58%) than did EG (0.13%), whereas both woods showed similar furfural concentrations (0.05% for EG and 0.06% for G), as shown in Table 3. These values are low compared to a study using autohydrolysis of a mixed hardwood material (Pu *et al.* 2011). In addition to the different wood types, this difference could be due to the high liquor:wood ratio used here for the AH process.

Also, the HMF polymerizes with itself or its precursors by forming solid materials during hydrolysis (McKibbins *et al.* 1962). So, the low concentration of degradation products (furfural, HMF and formic acid) in the AH liquor could also be due to condensation of degradation products with themselves and lignin.

Table 3. Byproducts from Acid Liquor after AH Pretreatment

Byproducts	Yield (%)*	
	EG	SG
Acetic acid	0.13	0.58
Furfural	0.05	0.06

*Based on original wood

Characterization of Ethanol Precipitated Material (EPM)

After separation by centrifugation, the EPM was dried using a vacuum oven (model 280A-Fisher Scientific) at 30 °C, and the yield was determined, as shown in Table 4. The yield of EPM was higher with increased NaOH concentration, which may be explained by the strong ability of NaOH to cleave the ester bonds and provide swelling properties. The EPM yield from the initial wood using 50% NaOH was 1.6 and 4.3% for EG and SG, respectively, while the liquor from pretreatment using only 10% NaOH showed 0.3 and 1.1% for EG and SG, respectively. The EPM was solubilized in water and inserted in the HPLC to check the monomer content on the material, but no spectra were observed, which means, after alkaline pretreatment, all materials precipitated were oligosaccharides.

The majority of the oligosaccharide was xylose, with a smaller amount of galactan detected (Table 4). The 50% NaOH pretreatments resulted in higher yields of xylans (53.1 and 52.8% for EG and SG, respectively). The EPM from pretreatment using 50% NaOH showed less lignin content (4.4 and 3.2% for EG and SG, respectively) than pretreatment using 10% NaOH (12.5 and 8.5%, respectively). The ash content in the EPM was high, which would require extensive washing in practice.

Table 4. EPM Composition of *Eucalyptus globulus* (EG) and Sweetgum (SG)

Samples	Yield (%) [*]	Oligo-xylans (%)	Oligo-glucan (%)	Oligo-galactan (%)	Total Oligos (%)	Total Lignin (%)	Ash (%)	Total Material (%)
EG 10	0.3	29.3	2.5	4.2	39.3	12.5	36.2	87.9
EG 50	1.6	53.1	0.8	3.2	58.6	4.4	23.2	86.2
SG 10	1.1	27.2	34.0	2.7	66.6	8.5	14.5	89.6
SG 50	4.3	52.8	10.8	1.3	66.4	3.2	19.6	89.2

^{*}Based on original wood (EPM from alkaline liquor)

It is important to consider the large part of dissolved material present in the alkaline liquor and that was not precipitated with ethanol. That soluble fraction is composed from a variety of non-precipitated carbohydrates and especially carbohydrate degradation products such as monocarboxylic and dicarboxylic hydroxy acids, together with formic and acetic acids, and lignin fragments. Also, during the alkaline treatment, the carbohydrate components in wood are subjected to degradation through the hydrolysis of acetyl groups, the dissolution of low weight carbohydrates, peeling reaction, and alkaline hydrolysis (Tunc and van Heiningen 2011; Sjöström 1993).

Recovering Sodium Hydroxide and Ethanol After EPM Separation

After separation of the liquid (ethanol + sodium hydroxide) and solid (EPM) phases, the liquid phase was submitted to a distillation process to recover ethanol and sodium hydroxide. The pH values and NaOH residual mass from liquors before distillation are shown in Table 5 along with the pH of the ethanol liquor.

The pH showed no difference before and after the distillation process. Also, the pH values of recovered ethanol (EtOH_{rec}) were around 7.7 to 8.8, higher than the pure ethanol. The recovered solution with ethanol was submitted to a phenolphthalein test, which did not detect any presence of NaOH (Table 5).

Table 5. Parameters Indicating the Possibility of Recovering Both Ethanol and NaOH after EPM Production

Material	pH		Density (g/cm ³)		NaOH residual (g)		EtOH/liquor ratio	
	EG	SG	EG	SG	EG	SG	EG	SG
¹ Lq 10	12.7	12.8	1.011	1.011	2.6	1.8		
¹ Lq 50	13.2	13.1	1.050	1.050	35.4	38.3		
² EtOH _{pure}	6.9		0.785					
³ Lq 10 AD	12.8	12.7	0.992	0.980	1.8	0.7	14 / 86	8 / 92
³ Lq 50 AD	13.3	12.9	1.034	1.038	35.6	38.1	5 / 95	6 / 94
⁴ EtOH _{Rec} 10	7.7	8.8	0.829	0.815			87 / 13	80 / 20
⁴ EtOH _{Rec} 50	8.1	8.5	0.828	0.819			87 / 13	84 / 16
¹ Liquor after ALK pretreatment (before distillation process)								
² Commercial ethanol used in laboratory								
³ Liquor after distillation								
⁴ Ethanol recovered after distillation								

Residual NaOH in the liquor before and after distillations was very similar, indicating that the majority of the NaOH was preserved in the liquor phase and could be utilized again in an extraction. A small difference was found with 10% NaOH pretreatment before and after distillation.

Moreover, the quality of recovered ethanol (EtOH_{rec}) was estimated after distillation using the densities of liquor and pure ethanol. It was determined that the distillate ethanol had more than 80% ethanol by weight. Using the same procedure for liquor after distillation, the liquor had less than 15% ethanol in its composition. Therefore, the distillation process seems to be a reasonable approach to recycling alkaline-rich liquor streams and ethanol-rich streams. Further investigation is required to develop this process.

Characterization of the EPM

Analysis of the FT-IR data for all types of xylans extracted did not show bands due to vibrations of free hydroxyls (3500 to 3700 cm⁻¹), which indicated that all OH groups of the xylans were involved in H-bonds. The strongest absorption bands in the IR spectra of the examined xylans were observed at 3500 to 3000 cm⁻¹ and 1200 to 1000 cm⁻¹. These groups of bands were due to C–O–H vibrations. The higher frequency band with a maximum at 3410 cm⁻¹ corresponded to CO–H stretching vibrations (strong and broad), and the complicated absorption band with a principal maximum at 1042 cm⁻¹ corresponded to C–OH stretching vibrations (strong), typical of xylans (Xu *et al.* 2007; Buslov *et al.* 2009) and present in the commercial xylan sample (Fig. 2). In other words, this region is dominated by ring vibrations overlapped with stretching vibrations of C-OH side groups and C-O-C glycosidic bond vibrations (Xie *et al.* 2006). All the spectra were similar to the commercial xylan provided by Sigma-Aldrich.

The weight (*M_w*) and number (*M_n*) averages of molecular weight and polydispersity measured via GPC are listed in Table 6. These molecular weights were calculated based on the range from 200 g.mol⁻¹ and up, with material detected below this threshold not considered.

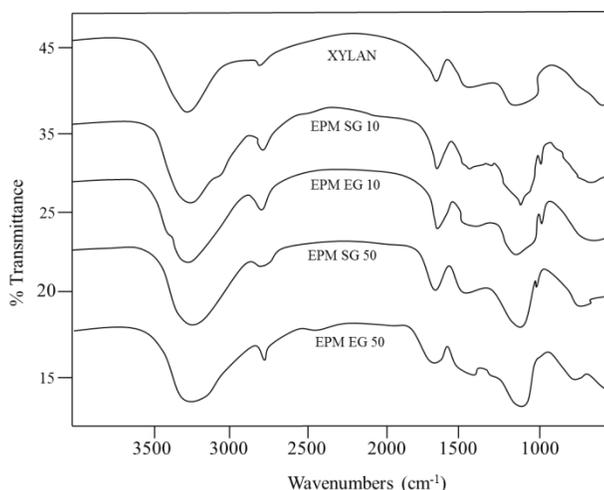


Fig. 2. FT-IR curves of different types of EPMs

Table 6. The Weight-Average (M_w) and Number-Average (M_n) Molecular Weight in $\text{g}\cdot\text{mol}^{-1}$ and the Polydispersity (M_w/M_n) of the Hemicellulosic Fractions Isolated from *Eucalyptus globulus* and Sweetgum with a Comparison to Hemicellulose Isolated from Sugar Beet Pulp using GPC and Intrinsic Viscosity Methods (Sun and Hughes 1998)

Molecular Weight from GPC				
Hemicellulose extraction conditions	M_w	M_n	$PD=M_w/M_n$	DP
10% NaOH, 100 °C, <i>Eucalyptus globulus</i>	41,000	18,000	2.27	250
50% NaOH, 100 °C, <i>Eucalyptus globulus</i>	16,000	7,000	2.28	97
10% NaOH, 100 °C, sweetgum	45,000	23,000	1.95	274
50% NaOH, 100 °C, sweetgum	14,500	5,100	2.84	88
Molecular Weight from Intrinsic Viscosity				
10% NaOH, 100 °C, <i>Eucalyptus globulus</i>	46,285	-	-	280
50% NaOH, 100 °C, <i>Eucalyptus globulus</i>	18,600	-	-	74
10% NaOH, 100 °C, sweetgum	50,106	-	-	305
50% NaOH, 100 °C, sweetgum	17,058	-	-	104
Commercial Xylan	55,000			335
Sugar beet pulp hemicellulose (Sun and Hughes 1998)				
10% KOH, 15 °C, 16h	91,330	6,920	13.05	556
24%KOH, 15 °C, 2h	21,990	6,320	3.48	134
8% NaOH, 15 °C, 16h	88,850	10,650	8.34	541
18%NaOH, 15 °C, 2h	21,620	6,490	3.33	131

The observed release of large-molecular weight hemicelluloses was due to the disruption of the macrostructure of holocellulose during the alkaline treatment at low concentrations. Samples extracted at 50% NaOH had lower molecular weight and DP (degree of polymerization) and high PD (polydispersity), indicating that a significant

amount of degradation occurred during the extraction. Some studies using sawdust (Ayoub *et al.* 2013) have demonstrated that the optimum concentration of NaOH to obtain high molecular weight is 10%. In this study and based on the molecular weights, the 10% NaOH extraction method is preferred over using 50% NaOH. Similar to other studies (Schild *et al.* 2010; Sun and Hughes 1998), the hemicelluloses extracted from the lignified residue of sugar beet pulp with 8% NaOH or KOH at 15 °C for 16 h had a much higher degree of polymerization (about 4 x higher) than at 18% NaOH or KOH.

To further confirm the GPC findings, the intrinsic viscosity of commercial xylan and extracted xylans were determined at 25 °C with an Ubbelohde-type viscometer (Koshijima *et al.* 1965), with results reported in Table 6. The degree of polymerization of the xylan extracted at high concentration (50% NaOH) was about 50% lower than the xylan extracted at 10% NaOH, in agreement with trends from GPC. TGA analysis showed that the degradation temperature under a nitrogen atmosphere (50% weight loss) was significantly higher for the 10% than the 50% extracted materials.

Oligoglucans (cellulose) are more difficult to degrade than oligoxylose (hemicellulose). Materials extracted with 10% NaOH had more oligoglucan content than material extracted with 50% NaOH. This is also in agreement with the theory that the 50% material was more degraded during extraction (Fig. 3).

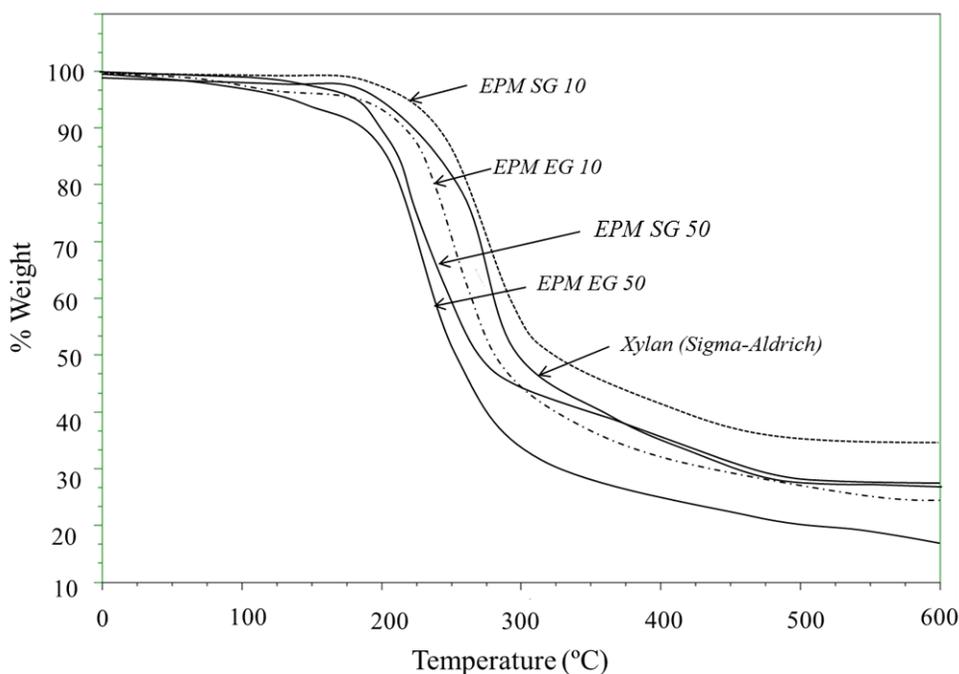


Fig. 3. TGA curves of different types of EPMs

The DSC traces showed that all of the EPM samples and the commercial xylan sample (xylan from birch wood - Sigma-Aldrich) had a T_g (computed as the midpoint temperature of the transition region) of about 132 °C (Fig. 4). Only the exotherm degradation around 180 °C was determined to be above the T_g . These results indicate that the hemicelluloses extracted from eucalyptus and sweetgum have similar properties to a commercial xylan from beechwood and may serve as a starting material for new biomaterials.

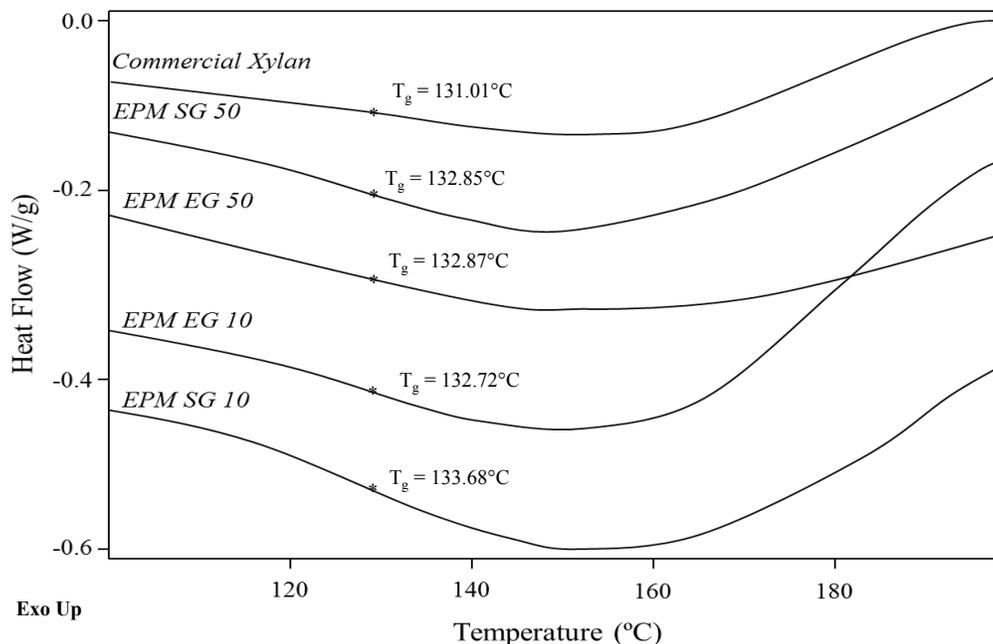


Fig. 4. DSC curves of different types of EPMS

CONCLUSIONS

1. In this study, an alkaline treatment with 50% NaOH showed better results when applied to sweetgum than when applied to *Eucalyptus globulus*, in spite of xylose removal.
2. An extraction at 100 °C recovered 4.3% of the ethanol precipitation material (EPM) as a predominantly hemicellulosic material with an average degree of polymerization of ~250 that could be used in various industrial applications.
3. FT-IR spectra show that all hemicellulose structures are identical to the commercial xylan.
4. EPM from sweetgum showed more thermal stability, mainly for high molecular weight (extraction with 10% NaOH), compared to EPM extracted from *Eucalyptus globulus*.
5. The results obtained indicate a promising combination between the effective extraction of hemicellulose from wood and a distillation process, which is a very attractive alternative to recovery liquor and ethanol after hemicellulose precipitation.

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