

Hemicelluloses Prior to Aspen Chemithermomechanical Pulping: Pre-Extraction, Separation, and Characterization

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ABSTRACT: A portion of hemicelluloses and acetic acid can be pre-extracted with dilute sulfuric acid prior to the aspen chemithermomechanical pulp process. The streams collected from the second press-impregnation stage after acid pre-extraction contain a significant amount of acid pre-extracted hemicelluloses. Most of the total sugars obtained from the pressate were xylan, in which xylan was further hydrolyzed to sugar monomers under the acid pre-extraction condition. To fully understand the characteristics of hemicelluloses yielded prior to pulping, the pre-extracted hemicelluloses were separated and characterized by FT-IR, ¹H NMR, and thermogravimetric analysis in this study. Most of the FT-IR bonds from the hemicelluloses agreed well with the other two spectra of birch xylan and CA0050 xylan, except a new absorption at 1734 cm⁻¹ contributed to acetyl groups. The hemicelluloses obtained from acid pre-extraction began to decompose significantly at about 225 °C, slightly lower in comparison with organosolv and alkaline hemicelluloses reported in the literature.

KEYWORDS: acid pre-extraction, hemicelluloses, chemithermomechanical pulp (CTMP), xylan, characterization

■ INTRODUCTION

The concept of value prior to pulping (VPP) has been proposed where the hemicelluloses are either partially or completely extracted for value-added products.^{1,2} The remaining solids (mainly cellulose and lignin) can be further delignified for wood pulp or fiber production.³ The VPP concept has been mainly studied for the kraft pulping process.^{4–6} Hardwood is one typical wood species for making chemithermomechanical pulp (CTMP), one kind of main high-yield pulp mainly used in printing and writing paper,^{7–11} and contains an average of 22% hemicelluloses.¹² The extracted streams from hardwood CTMP mills would be rich in hemicelluloses and acetic acid depending on the type and extent of chemical treatments. Therefore, there are opportunities to produce value-added byproducts such as acetic acid and hemicelluloses before pulp is made.

Recently, the potential applications of hemicelluloses have been attracting attention because of unique characteristics such as high hydrolytic stability and biodegradability. The hemicelluloses can be used as food additives, thickeners, emulsifiers, gelling agents, adhesives, paper chemicals, and adsorbents.¹³ A variety of effective extraction methods can be used to obtain hemicelluloses from lignocellulosic materials, such as dilute acid extraction, alkaline extraction, autohydrolysis, steam explosion-based extraction, and dilute acid-steam explosion.^{14–16} The hemicelluloses extracted with each method have their characteristics, which plays a crucial role in processing and application.

In our previous work, the potential of pre-extracting hemicelluloses prior to a CTMP process was investigated.¹⁷ It was found that (1) a portion of the hemicelluloses and acetic acid can be pre-extracted with sulfuric acid prior to CTMP pulping, and the resultant chips can still be used to produce mechanical pulps under proper conditions, (2) acid pre-extraction significantly reduced refining energy consumption to

a given freeness, and (3) acid pre-extraction was found to have a very significant effect on pulp properties: at the specific refining energy, CTMPs produced with acid pre-extraction had a somewhat lower zero-span tensile strength, lower bulk, higher fines content and lower brightness, but much higher tensile index and Scott bond.

In the present study, the pre-extracted hemicelluloses were separated, purified, and further characterized by FT-IR and ¹H NMR to identify the structural characteristics, as well as by thermogravimetric analysis (TGA) to measure the thermal properties. The present work fits into the VPP concept, in particular the mechanical pulping sector, which has received relatively less attention.

■ MATERIALS AND METHODS

Materials. Aspen chips from an eastern Canadian mill were screened before the process. The main chemical compositions of the aspen chips were as follows: glucan 47.07%, xylan 16.50%, acid-soluble lignin 3.54%, acid-insoluble lignin (Klason lignin) 17.93%, and acetone extractives 1.07%.¹⁷ The rest of the components adding up to around 15% were mainly mannan, arabinan, acetyl groups, pectin, and ash. Acetone and H₂SO₄ used in this experiment were of analytical grade.

Hemicellulose Pre-Extraction with Dilute Sulfuric Acid in a Pilot Plant. Two pilot trials were done with (CTMP2) and without (CTMP1) acid pre-extraction. The screened aspen chips were presteamed at 100 °C for 15 min. Then an Andritz-Bauer 6 in. MSD press impregnator was used for the impregnation of screened chips with 0.50% (w/v) sulfuric acid at 60 °C. The resulting sulfuric acid charge for CTMP2 was 1.0% on the basis of the oven-dried (od) chips. The impregnated chips were then cooked in a vapor-phase

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digester at 140 °C for 10 min, as shown in Table 1. After that, the cooked chips were fed into the press impregnator again to collect the

Table 1. Pulping Conditions for the Pilot Plant Trials

	CTMP1	CTMP2
H ₂ SO ₄ concn on od wood chips, % (w/w)		1.0
pre-extraction temp, °C		140
pre-extraction time, min		10
Na ₂ SO ₃ concn on od wood chips, % (w/w)	2.6	3.1
sulfonic group concn, mmol/kg	17.2	17.9
preheating time, s	180	180
refining pressure in TMP refiner, kPa	250	250

pressates. All the pressates (PL1, PL2, and PL3) were collected at different stages and analyzed further, as shown in Figure 1.

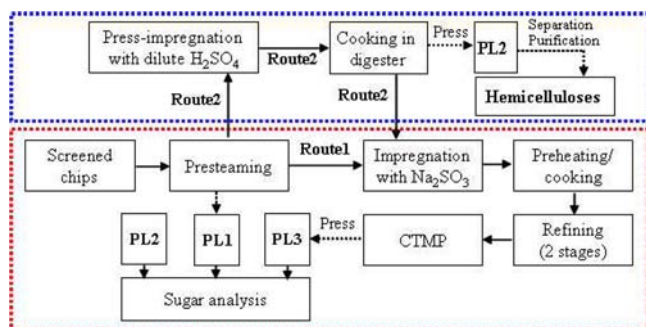


Figure 1. Experimental procedure.

To make CTMPs from the pressed chips, the press impregnator was used to impregnate sodium sulfite (Na₂SO₃) into the chips. Na₂SO₃ charges were adjusted to achieve similar sulfonation levels for CTMP1 and CTMP2 (17.2 and 17.9 mmol/kg, respectively). The impregnated chips were retained at 70 °C for 30 min and preheated at 100 °C for 3 min before refining. The chips were then refined in two stages with a 22 in. Andritz pressurized thermomechanical pulp (TMP) refiner and followed by a Bauer 400 36 in. atmospheric refiner, respectively.

Analysis of Pressates. The pressates obtained from the press impregnating process were neutralized with dilute NaOH (0.1 M) and stored in a cool room at 4 °C for later use. The pressates were analyzed for monosugar and oligomer content with acid hydrolysis in an autoclave at 121 °C for 1 h. The content of oligomer was calculated from the increase in monosugar anhydride content due to acid hydrolysis. Before the analysis, the precipitated solids in the liquor were removed by filtration. In acid hydrolysis, 25 mL of filtrated pressates and 1.04 mL of 72.0% H₂SO₄ were mixed in a COD test tube for each sample, and then the tubes were autoclaved at 121 °C for 60 min. The obtained samples were then filtrated through a 0.45 μm Millipore filter, and the clear liquor was collected for sugar analysis. The sugar analysis was performed by ion chromatography (IC) according to the method described by Zhang et al.¹⁸ The sugar monomers in the filtrate, including arabinose, galactose, glucose, xylose, and mannose, were separated by an anion exchange column (Dionex CarboPac PA1) in a Dionex DX-600 ion chromatography system (Dionex, Sunnyvale, CA) equipped with an AS50 autosampler and a GP50 gradient pump. The factors used to convert sugar monomers to anhydromonomers were 0.90 for glucose and 0.88 for xylose and arabinose.¹⁹ The standard curves of sugar measurement are shown in Figure 2.

Separation and Purification of Hemicelluloses. The pressates collected from the CTMP process were evaporated at about 45 °C in a rotavapor (BUCHI Rotavapor R-114, Brinkmann Instruments Inc., Westbury, NY), and then most of the lignin in the pressates was precipitated by adding 0.1 N H₂SO₄ to pH 2.5 at room temperature. The precipitated lignin was removed by centrifuging at a speed of 4400

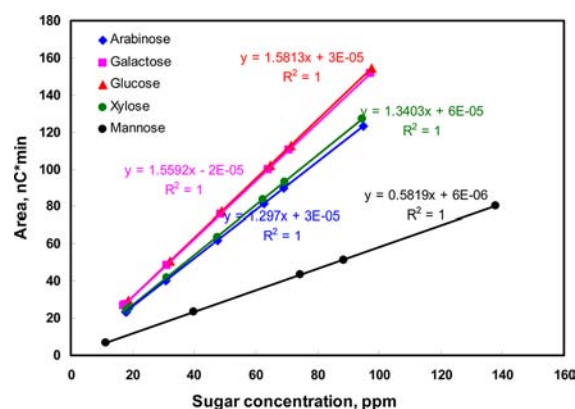


Figure 2. Standard curves of sugar measurement.

rpm for 8 min in a centrifuge (IEC centra-8, International Equipment Co., Chattanooga, TN), followed by filtration through a 0.22 μm Millipore filter. After filtration, 95% ethanol was added to the filtrate in a volumetric ratio of 3:1 with stirring at room temperature. The precipitated materials, i.e., hemicelluloses, were separated by centrifugation at a speed of 4400 rpm for 8 min followed by filtration and washed with 95% ethanol until the supernatant became colorless.^{20,21} The separated hemicelluloses were further purified with a dialysis tube (Spectrum Laboratories Inc., Rancho Dominguez, CA) in deionized water until the conductivity was lower than 10 μs/cm. The molecular weight cutoff (MWCO) of the dialysis tube used in the study was 1000 Daltons. The hemicelluloses after treatment in the dialysis tube were then dried in a vacuum oven at 50 °C for 24 h.

FT-IR Analysis. The hemicellulosic sample was characterized by FT-IR spectrometry (Nicolet 6700, Thermo Scientific, Waltham, MA). The spectra were recorded in transmittance band mode in the range of 4000–600 cm⁻¹ with 100 scans at a nominal resolution of 4 cm⁻¹. The spectra were monitored with Nicolet OMNIC 4.1 software. The baselines of the spectra were adjusted and normalized by the software. Two samples (birch xylan and CA0050 xylan) were chosen from the infrared spectrum library supplied by Thermo Scientific for comparison with the hemicellulosic sample.

NMR Analysis. A 15 mg hemicellulosic sample was dissolved in 1 mL of D₂O,²² and ¹H NMR spectra were obtained by using a Varian 300 NMR spectrometer with an Oxford magnet operating at 299.84 MHz at 25 °C. The chemical shifts were calibrated relative to the signals from D₂O, and the acquisition time was 3.74 s.

TGA. Thermal stability determination of the hemicellulosic sample was performed by using a thermogravimetric analyzer (Q-500, TA Instruments, New Castle, DE). Before the thermal stability measurement, all samples were dried in a vacuum oven at 50 °C for 24 h. About 18 mg of the dried hemicellulosic sample was detected in the range from room temperature to 650 °C under a nitrogen flow.

RESULTS AND DISCUSSION

Hemicellulose Pre-Extraction with Dilute Sulfuric Acid in a Pilot Plant. The analysis of pressates from the first press impregnation (PL1), second press impregnation (PL2), and refined pulps (PL3) collected from the pilot plant trials was reported in our previous paper.¹⁷ The results showed that (1) more xylans than glucans were extracted from aspen chips, (2) the concentrations of hemicelluloses (sum of arabinose, galactose, xylose, and mannose) in the pressates from CTMP2 were much higher than those from CTMP1 without acid pre-extraction, and (3) acetic acid was also detected in the pressates.

The pressates were analyzed for sugar content with post acid hydrolysis in an autoclave at 121 °C for 1 h. As for CTMP1, all the hemicellulose (i.e., the sum of arabinose, galactose, xylose, and mannose) content in the pressates collected from PL1 and

PL3 was 10.84 kg/t of oven-dried chips, and that could reach 14.00 kg/t of oven-dried pulp if all the liquor could be totally pressed out from the refined pulp. As for CTMP2, the hemicellulose content increased greatly due to the acid pre-extraction, the hemicellulose content in the pressate collected from PL1, PL2, and PL3 was 31.32 kg/t of oven-dried chips, and that could reach 39.05 kg/t of oven-dried chips if all the liquor could be totally taken out, as shown in Table 2.

Table 2. Hemicellulose Contents from Pressates by Calculation^a

sugar analysis of the pressates		CTMP1		CTMP2		
		PL1	PL3	PL1	PL2	PL3
xylose	concn, g/L	1.07	0.47	1.07	6.05	1.22
	actual value, kg/t of od chips	1.89	1.56	1.89	12.71	3.53
	max, kg/t of od chips	2.50	1.93	2.50	15.61	4.29
	sum of stages, kg/t of od chips	3.45 ^a /4.43 ^b		18.13 ^a /22.40 ^b		
hemicelluloses	concn, g/L	4.04	1.11	4.04	9.19	1.68
	actual value, kg/t of od chips	7.16	3.68	7.16	19.30	4.86
	max, kg/t of od chips	9.44	4.56	9.44	23.71	5.90
	sum of stages, kg/t of od chips	10.84 ^a /14.00 ^b		31.32 ^a /39.05 ^b		

^aKey: PL1 and PL2, liquor from the first and second press impregnations, respectively; PL3, liquor from the refined pulps; a, based on the pressate that was actually pressed out; b, based on the liquor that could be totally pressed out.

Table 3 indicates that (1) most of the sugars were xylose, e.g., 66% of the total sugars were xylose in the pressates collected from the CTMP2 PL2, and (2) the xylan was mainly present in polymeric form in the pressates collected from CTMP1. However, most of the xylan was further hydrolyzed to sugar

Table 3. Sugar Analysis of the Pressates^a

sugar		concn (g/L) after the first and second presses		concn (g/L) after refining	
		CTMP PL1	CTMP2 PL2	CTMP1 PL3	CTMP2 PL3
arabinose	M	0.60	2.18	0.14	0.14
	O	0.59	1.13	0.13	0.10
galactose	M	0.44	0.59	0.15	0.10
	O	0.43	0.14	0.14	0.09
glucose	M	1.18	0.57	0.23	0.13
	O	1.12	0.24	0.20	0.12
xylose	M	1.07	6.05	0.47	1.22
	O	1.03	2.08	0.45	1.15
mannose	M	0.75	0.93	0.11	0.09
	O	0.74	0.69	0.10	0.08
total sugar	M	4.04	9.19	1.11	1.68
	O	3.92	2.02	1.04	1.55
acetate		0.18	2.59	0.41	0.43

^aKey: M, monomers; O, oligomers; PL1, PL2, and PL3, the same as in Table 2.

monomers under the condition of acid pre-extraction (CTMP2). As for all these sugars (i.e., arabinose, galactose, xylose, and mannose), the percentage of oligomers decreased after acid pre-extraction, which was caused by acid hydrolysis. The dehydration reactions of hydrolyzed sugars take place during thermal treatment and under acid hydrolysis conditions.²³ Dilute acid hydrolysis has been modeled as a homogeneous reaction in which cellulose and hemicelluloses can convert into glucose and xylose, respectively, and subsequently further into degradation products such as hydroxymethylfurfural (HMF) and furfural (F), respectively.²⁴ If the hydrolysis temperature is further increased, HMF will be converted into levulinic acid and formic acid.²³

FT-IR Analysis. Figure 3a shows the FT-IR spectra of the hemicellulosic sample from the pressates of the pilot trial with sulfuric acid pre-extraction (CTMP2 PL2) and the other two samples birch xylan and CA0050 xylan. Table 4 lists the infrared bands and corresponding assignments. Most of the FT-IR bands from the hemicellulosic sample in the present study agreed well with the other two spectra of xylan from birch and CA0050 xylan (~10% arabinose and ~15% glucose) except a new peak at 1734 cm⁻¹. This new peak agreed well with those reported by Liu et al.²¹ and Wen et al.,²⁵ which may be due to the carbonyl groups from 4-O-methyl-D-glucuronic acid or C=O stretching of acetyl groups in hemicelluloses. The existence of acetyl groups in the obtained sample has been further confirmed by the following ¹H NMR analysis. Acetyl groups have been found as side groups in hardwood xylan with a general ratio of 7 acetyl units for every 10 xylose units.²⁶ Part of the acetyl groups can be released from the dissolved acetylated xylan, while some others are still attached to the bone of xylan, so the absorbance strength is expected to be reduced due to the removal of acetyl groups. The absorbance at 2936 cm⁻¹ originates from C-H stretching of methyl and methylene groups.²² A signal at 1645 cm⁻¹ for CA0050 xylan in the carbonyl stretching region is mostly caused by the absorbed water in the samples. The signal did not show up in the other two samples, as shown in Figure 3a. As for the obtained sample, the spectrum shows that the absorption at 1421 and 1333 cm⁻¹ could be caused by -CH and -OH bonds and -CH bending, respectively. The absorption at 1249 cm⁻¹ is attributed to -C-O- in ester groups. The arabinose substitution at C-3 of the xylose residues would give a peak around 1164 cm⁻¹, compared with the absorption at 1173 cm⁻¹ reported by Subba and Muralikrishna,^{27,28} as shown in Figure 3b. The intensive absorbance at 1042 cm⁻¹ is assigned to the C-O-C stretching of glycosidic linkages, which is typical of xylans.²⁹

The peak multiplicity between the bands of 1120–1000 cm⁻¹ is a typical characteristic of highly substituted arabinoxylans. The absorption strength in the range of 990–900 cm⁻¹ of the obtained sample in the present study is much weaker than those of the other two samples. The absorbance at 895 cm⁻¹ is indicative of β-glycosidic linkages between the sugar units in hemicelluloses, which agrees with the absorbance at 900 cm⁻¹ reported by Zhang et al.²² However, the absorption strength of the obtained hemicelluloses in this study is much weaker than those of the other two samples.

¹H NMR Analysis. In this work, ¹H NMR was used to investigate the characteristics of polysaccharide structure. As seen in Figure 4, the anomeric region appeared in two regions, i.e., 5.6–4.9 ppm for α-anomers and 4.9–4.3 ppm for β-anomers, and the ring proton region occurred in the region of 4.5–3.0 ppm.²² The strongest signal appearing at 4.7 ppm was

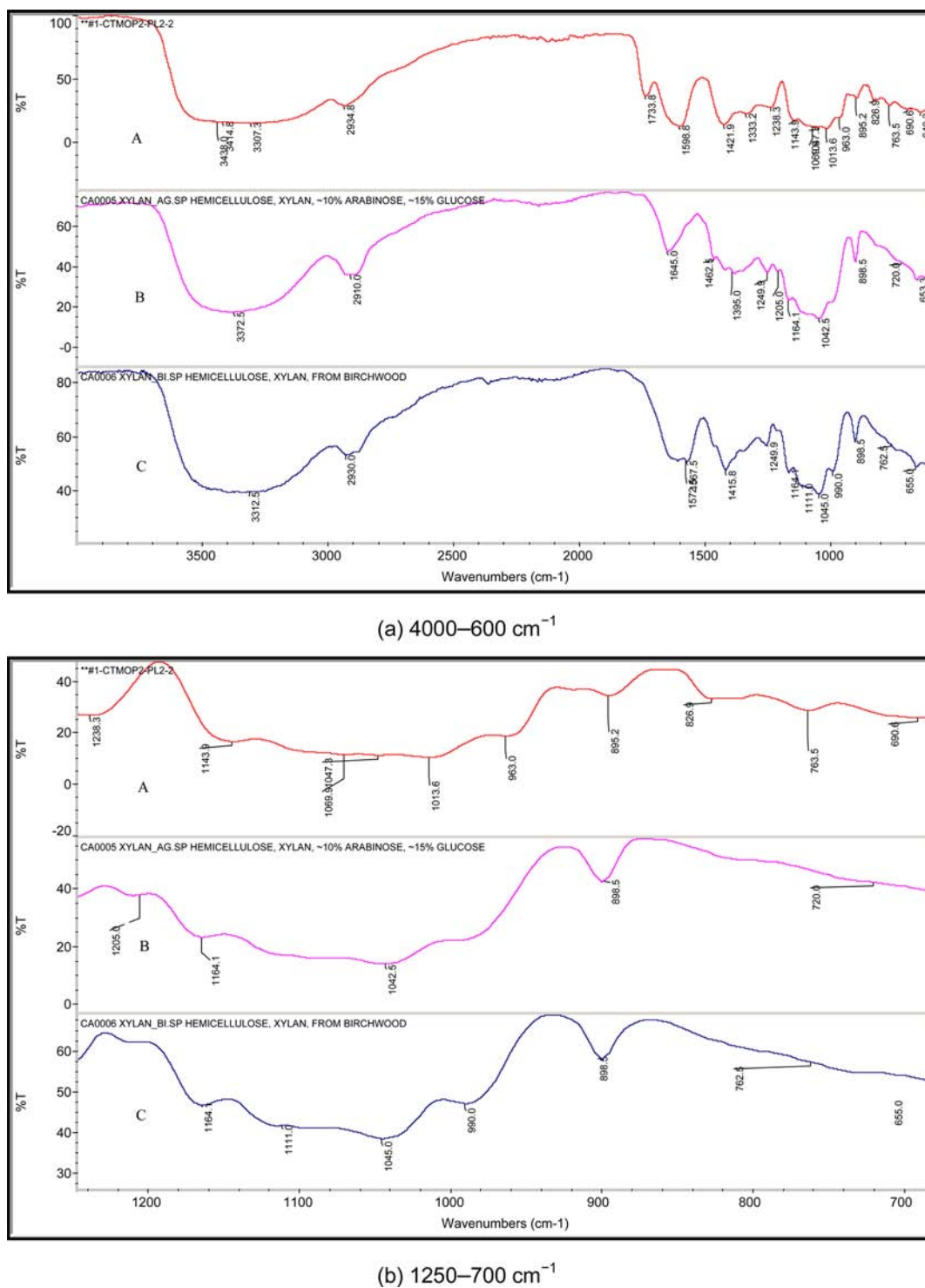


Figure 3. FT-IR analysis of hemicellulosic samples (A, hemicelluloses extracted with H_2SO_4 ; B, CA0050 xylan; C, birch xylan).

attributed to the residual D_2O .²² The distinct signals for the anomeric protons of β -glucose, β -xylose, and β -arabinose appeared at 4.63 ppm, 4.56 ppm,³⁰ and 4.51 ppm,³¹ respectively. Two signals at 4.4 and 5.2 ppm can be assigned to (1 \rightarrow 4)- β -D-Xylp and 4-O-Me- α -D-GlcpA, respectively, which agrees with the results reported by Zhang et al.²² The signals at 3.4 ($-\text{OCH}_3$) and 3.25 ppm may correspond to 4-O-methyl- α -D-glucuronic acid residues and β -D-xylopyranosyl residues. The signals at 3.2–4.8 ppm indicated the main β -glycosidic linkages between the sugar units. The signal at 3.4 ppm can be assigned

to 4-O-methyl- α -D-glucuronic acid residues. The resonance peaks in the region 2.0–2.1 ppm can be assigned to acetyl groups in the hemicelluloses,³² which is consistent with FT-IR analysis. The signals at 1.2 ppm may also be attributed to acetyl groups. Table 5 lists the summary of the signals from ^1H NMR analysis of the hemicellulosic sample.

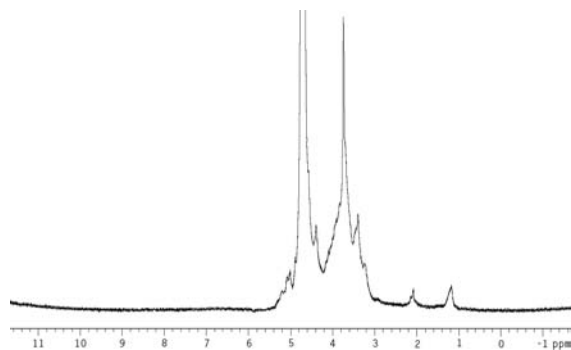
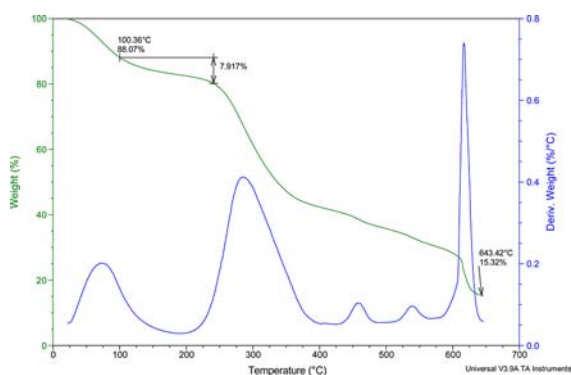
TGA. The hemicellulosic sample was investigated by using TGA, as shown in Figure 5. It can be seen that there were two stages in the pyrolysis process: a slow pyrolysis stage (150–225 $^\circ\text{C}$) and a fast pyrolysis stage (225–350 $^\circ\text{C}$). At the first stage,

Table 4. Summary of the FT-IR Bands of Hemicellulosic Samples in the Present Study

	band (cm ⁻¹)	assignment
1	3326	O–H stretching
2	2936	C–H stretching
3	1734	C=O stretching
4	1599	aromatic skeletal vibration
5	1422	C–H in-plane deformation with aromatic ring stretching
6	1333	C–O of the syringyl ring
7	1238	C–O of the guaiacyl ring
8	1042	C–O–C stretching of glycosidic linkages
9	895	β -glycosidic

Table 5. Summary of the Signals from ¹H NMR Analysis of the Hemicellulosic Sample

	signal (ppm)	assignment
1	5.3	proton of C1–C6 on glucose
2	4.75–4.93	mannose
3	4.5	proton of C1 on xylan
4	4.4	galactose
5	3.2–4.8	β -glycosidic linkages between the sugars
6	3.4	4-O-methyl- α -D-glucuronic acid residues
7	1.2, 2.2, and 2.1	acetyl group

**Figure 4.** ¹H NMR spectrum of the hemicellulosic sample.**Figure 5.** TGA of the hemicellulosic sample.

about 8% of the weight was lost in the range of 100–225 °C due to the pyrolysis of sugars with lower molecular weight. At the second stage, about 35% of the weight was lost. After 650 °C, about 15% of the weight remained due to the ash content. In the present study, the hemicelluloses obtained from acid pre-extraction began to decompose significantly at about 225 °C,

slightly lower in comparison to that of organosolv hemicelluloses (228 °C)²² and alkaline hemicelluloses (245 °C).³³

In summary, hemicelluloses can be pre-extracted with dilute sulfuric acid prior to the aspen CTMP process. Acid pre-extraction resulted in a release of hemicelluloses, especially at the second press-impregnation stage. The results indicate that the pre-extracted hemicelluloses had a structure similar to those of birch xylan and CA0050 xylan and significantly decomposed at about 225 °C.

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Notes

The authors declare no competing financial interest.

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