Author(s): Lehto, Joni; Louhelainen, Jarmo; Huttunen, Marko; Alén, Raimo

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Spectroscopic analysis of hot-water- and dilute-acid-extracted hardwood and softwood chips

Joni Lehto[a,]*, Jarmo Louhelainen[a], Marko Huttunen[a], and Raimo Alén[a]
[a]Laboratory of Applied Chemistry, Department of Chemistry,
University of Jyväskylä, P.O. Box 35, FI-40014 University of Jyväskylä, Finland
*Corresponding author, email: joni.t.lehto@jyu.fi

Abstract: Hot-water and dilute sulfuric acid pretreatments were performed prior to chemical pulping for silver/white birch (*Betula pendula/B. pubescens*) and Scots pine (*Pinus sylvestris*) chips to determine if varying pretreatment conditions on the original wood material were detectable via attenuated total reflectance (ATR) infrared spectroscopy. Pretreatment conditions varied with respect to temperature (130 °C and 150 °C) and treatment time (from 30 min to 120 min). The effects of the pretreatments on the composition of wood chips were determined by ATR infrared spectroscopy. The spectral data were compared to those determined by common wood chemistry analyses to evaluate the suitability of ATR spectroscopy method for rapid detection of changes in the wood chemical composition caused by different pretreatment conditions. In addition to determining wood species-dependent differences in the wood chemical composition, analytical results indicated that most essential lignin- and carbohydrates-related phenomena taking place during hot-water and acidic pretreatments could be described by applying this simple spectral method requiring only a small sample amount and sample preparation. Such information included, for example, the cleavage of essential lignin bonds (*i.e.*, mainly β-*O*-4 linkages in guaiacyl and syringyl lignin) and formation of newly condensed lignin structures under different pretreatment conditions. Carbohydrate analyses indicated significant removal of hemicelluloses (especially hardwood xylan) and hemicelluloses-derived acetyl groups during the pretreatments, but they also confirmed the highly resistant nature of cellulose towards mild pretreatments.

Keywords: ATR spectroscopy, autohydrolysis, dilute acid, infrared, pretreatment, wood

1. Introduction

The manufacture of novel, high-value products from lignocellulosics has been considered as a solution to facilitate an evolutionary shift within the conventional forest industry towards a more competitive business model and more efficient utilization of raw materials [1,2]. This viewpoint has led to a transformation that includes implementing different biorefinery units into existing pulp and paper mills and evolution of integrated forest biorefineries (IFBRs) [3]. In modern IFBRs, the target is to extract carbohydrates, extractives, lignin, and other materials from biomass and convert them into value-added products, simultaneously minimizing the production of waste. Within this context, biomass pretreatment technologies (physical, chemical, or biochemical methods) mainly applied to recover hemicelluloses-derived carbohydrates from wood prior to pulping have been considered a crucial step [4].

The most common chemical pretreatments utilized for recovering particularly hemicelluloses-derived carbohydrates are performed either with pressurized hot water or diluted mineral acid [4-8]. By hot-water extraction, the main aim is usually to produce hydrolysates, especially containing oligo- and polysaccharides, whereas the pretreatments conducted with diluted acid typically result in the intensive formation of monosaccharides [9]. However, in addition to carbohydrates, other wood components (*i.e.*, lignin and

extractives) as well as all their degradation products (*e.g.*, aliphatic acids and furanoic compounds) are also incorporated to hydrolysates.

The pretreatment processes have a profound effect on the chemical composition of wood and the subsequent delignification behavior of the pretreated feedstocks [10,11]. In order to maintain the quality of the produced chemical pulp, the detailed effects of conducted pretreatments on wood composition must be understood. Within this framework, reliable and rapid methods for measuring the residual, structural, chemical components constituting cell walls of the pretreated wood material are highly appreciated. Conventional wet chemical analyses are accurate, but they have limitations, especially with regard to the amount of material required to confirm the analysis and overall time-consuming processes [12]. However, several spectroscopic analysis methods, such as Fourier transform infrared (FTIR) [13-16], near infrared (NIR) [17-19], and attenuated total reflectance (ATR) [21-23] infrared spectroscopy, have been proposed for providing a solution to the above mentioned problems; they comprise low-cost instrumentation and generally require very little sample preparation.

In this study, hot-water- and dilute-acid-extracted silver/white birch (*Betula pendula/B. pubescens*) and Scots pine (*Pinus sylvestris*) wood materials were investigated by ATR spectroscopy, especially keeping in mind their potential utilization for biorefineries. The main aim was to clarify if essential effects of varying pretreatments conditions on the original wood materials could be easily detected by this method.

2. Experimental

2.1. Raw materials

Industrial silver/white birch (*Betula pendula/B. pubescens*) and Scots pine (*Pinus sylvestris*) chips were used in the laboratory-scale pretreatments with hot-water and diluted sulfuric acid. The used chips were laboratory-screened according to SCAN-CM 40:94 [24], and chips having knots, bark residues, and other visible impurities were manually removed. The maximum thickness of the used chips was 7 mm, maximum width 13 mm, and minimum width 7 mm.

2.2. Pretreatments

Laboratory-scale pretreatment experiments of screened birch and pine chips were conducted in 1.25 L rotating stainless steel autoclaves heated in an oil bath (CRS Autoclave System 420, CRS Reactor Engineering AB, Stenkullen, Sweden). Chips were treated at two treatment temperatures (130 °C and 150 °C) and with four treatment times (30, 60, 90, and 120 min), thus corresponding to the P-factor [25] range of 10 to 238. In each case, a 30 minute heating period was added to the treatment times. The liquid-to-wood ratio was 5 L/kg. The chosen cooking liquors were ultra-high quality (UHQ) water (internal resistance ≥18.2 MΩcm at 25 °C) obtained from a Milli-Q Plus water system (Millipore, Bedford, MA, USA) and aqueous sulfuric acid having a pH value of 3. Pretreated wood chips were separated from the hydrolysates by using filtration bags. Chips were then washed with tap water, and each treatment yield was calculated based on the dry solids (DS) content of untreated and pretreated chips.

2.3. Chemical analyses

For the chemical analyses, wood samples were ground in a Retsch SM100 (Retsch GmbH, Haan, Germany) cutting laboratory mill equipped with a bottom sieve with trapezoid holes (perforation size of <1.0 mm) and stored in sealable plastic bags. Prior to analysis, the moisture content of the samples was determined. All analyses were carried out with two parallel samples, and the results reported were calculated as percentages of the original dry wood.

The extractives content of the ground samples was determined by extracting the sample with acetone for 4 h (6-10 percolations per hour) in a Soxhlet apparatus according to TAPPI Test Method T280 pm-99 [26]. The extract obtained was first concentrated by vacuum evaporation with a rotary evaporator (Heidolph VV2000, Gemini BV Laboratory, Apeldoorn, the Netherlands), and drying was finally accomplished before weighing by means of a gentle nitrogen gas stream.

The lignin content of the extractives-free sawdust samples (each about 200 mg) was determined as the sum of "acid-insoluble Klason lignin" and "acid-soluble lignin" according to TAPPI Test Methods T222 om-98 [27], T249 cm-00 [28], and T250 [29]). In this determination, sawdust was first treated with H_2SO_4, and the precipitated lignin was filtered off, washed, dried, and weighed. The content of acid-soluble lignin was determined using a Beckman DU 640 UV/Vis-spectrophotometer (Beckman Instruments Inc., Fullerton, CA, USA) at 205 nm after dilution of one portion of the hydrolysate with H_2SO_4 until the absorbance (A) was in the range 0.3 to 0.8. The concentration of dissolved lignin (c, g/L) was calculated according to the equation:

$$c = \frac{A}{a*b}$$

where a is absorptivity (110 L/(gcm) for hardwoods and 120 L/(gcm) for softwoods [30]) and b is the light path (cm).

Monosaccharide content (*i.e.*, arabinose, galactose, glucose, mannose, and xylose) in the Klason hydrolysates was determined by means of a Dionex high performance liquid chromatography-pulse amperometric detection (HPLC-PAD, from Dionex Corp., Sunnyvale, CA, USA) equipped with an AS50 autosampler, an LC25 chromatography oven, a GS50 gradient pump, a CarboPac PA-1 column, and an ED50 detector with carbohydrate pulsing. Samples were eluted (with a NaOH gradient in UHQ water) at a flow rate of 0.3 mL/min. The UHQ water employed for mobile phase preparation was degassed via ultrasonic treatment for approximately 15 min prior to use. Post-column alkali (NaOH) addition was performed at a flow rate of 0.1 mL/min with an IC25 isocratic pump to enhance the performance of PAD. Data were stored and processed using a Dionex Chromeleon (6.50) data system. The peak identification and the mass-based response factors between the internal standard (fucose) and each monosaccharide were based on separate runs with model monosaccharides.

2.4. ATR analyses

The samples for the ATR analyses were ground to fine powder using a Fritsch Pulverisette analytical grinder (Fritsch GmbH, Idar-Oberstein, Germany) equipped with a 0.5 mm sieve.

The ATR measurements were made from pellets pressed from the ground samples with a Bruker Alpha FTIR spectroscopic device (Bruker Optics, Billerica, MA, USA) fitted with a Platinum ATR single reflection diamond ATR module that measured the spectra in the 400-4000 cm^{-1} wavenumber range. In each measurement, 64 scans were obtained at a spectral resolution of 2 cm^{-1}. The assignment of the spectra bands was performed by utilizing the data presented previously elsewhere [13,15,23,31-33].

3. Results and discussion

3.1. Raw materials for pretreatment experiments

Chemical composition of the feedstock materials used for the hot-water and acidic pretreatment experiments is presented in Table 1. As expected, the two wood species differed from each other, especially in the contents of hemicellulose moieties and lignin, showing characteristic differences commonly described in the literature [34]; birch contains more xylose but less galactose, mannose, and lignin than pine.

Table 1
Chemical composition of raw materials used in hot-water and acidic pretreatments (% of the DS)

Component	Birch	Pine
Monosaccharides*	**61.9**	**58.8**
Arabinose	0.6	1.9
Galactose	0.7	2.9
Glucose	38.2	37.7
Mannose	1.5	10.7
Xylose	20.9	5.6
Lignin	**24.2**	**31.6**
Klason	18.4	31.2
Acid-soluble	5.8	0.4
Extractives	**2.7**	**3.3**
Unidentified materials**	**11.2**	**6.3**

*Monosaccharide moieties are presented as anhydrosugars.
**Mainly consisting of uronic acids, acetyl groups, proteins, and inorganic components.

3.2. Pretreatments

Yields of wood residues after pretreatments are presented in Table 2. In general, with mild pretreatments (*i.e.*, low temperature and short treatment time), more material was dissolved from pine chips when compared to that from birch chips. However, as the pretreatment conditions became harsher, clearly more material was also dissolved from birch samples. By adjusting the pH of the pretreatment liquor to a value of about 3, the yield of solid residue decreased only very slightly.

Table 2
Yield of the wood residue after pretreatment experiments (% of the original DS)

Material	Birch				Pine			
Treatment	**Hot water**		**Dilute acid**		**Hot water**		**Dilute acid**	
Temperature, °C/ Time, min	**130**	**150**	**130**	**150**	**130**	**150**	**130**	**150**
30	98.8	93.8	99.3	92.6	97.8	93.1	96.4	92.7
60	98.7	90.6	98.5	89.0	97.4	92.6	95.2	91.7
90	98.0	83.1	98.7	84.7	97.2	90.9	96.2	85.6
120	97.6	83.2	97.4	81.2	96.7	85.4	93.5	86.5

The main pretreatment effects included the degradation and dissolution of hemicelluloses accompanied with the small removal of lignin. For birch chips, the dissolved carbohydrates accounted for 0.5-14.7% of the wood DS, whereas the removed lignin contributed for 0.6-2.7% of the wood DS. For pine chips, the values were 1.5-12.1% and 0.6-1.1% of wood DS for carbohydrates and lignin, respectively.

The chemical compositions of the pretreated wood residues showing the main wood components are reported in Table 3. The degradation of the main wood components during the pretreatments proceeds *via* hydronium-catalyzed reactions, during which water autoionization initiates the formation of hydronium ions capable for separating the acetyl groups from wood hemicelluloses with the simultaneous formation of acetic acid. Under the acidic conditions, lignin depolymerization proceeds via homolytic cleavage of α-*O*-4 and β-*O*-4 bonds linking the phenylpropane subunits together. The most important degradation reactions responsible for the loss of wood dry matter during these pretreatments included dissolution of non-degraded and degraded polysaccharides (*i.e.*, mainly hemicelluloses-derived mono-, oligo-, and polysaccharides), deacetylation of acetyl groups in hemicelluloses, and dissolution and/or degradation of lignin from the feedstock. On the other

Table 3
Chemical composition of birch (top) and pine (bottom) wood residues after hot-water (HW) and acidic (A) pretreatments

Pretreatment temperature, °C	**130**								**150**							
Pretreatment time, min	**30 (HW)**	**30 (A)**	**60 (HW)**	**60 (A)**	**90 (HW)**	**90(A)**	**120 (HW)**	**120(A)**	**30 (HW)**	**30 (A)**	**60 (HW)**	**60 (A)**	**90 (HW)**	**90 (A)**	**120 (HW)**	**120 (A)**
Carbohydrates	**62.8**	**63.4**	**63.8**	**63.6**	**61.9**	**63.0**	**63.3**	**63.4**	**63.9**	**63.0**	**64.4**	**64.8**	**65.7**	**65.9**	**66.2**	**66.2**
Arabinose	0.6	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.3	0.3	0.2	0.2	0.1	0.1	0.1	0.1
Galactose	0.7	0.7	0.6	0.7	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.4	0.3	0.3	0.2	0.2
Glucose	38.8	39.4	39.6	39.7	38.3	39.4	39.5	39.7	40.9	40.3	43.8	44.2	47.0	47.0	48.4	49.1
Mannose	1.6	1.6	1.7	1.7	1.6	1.6	1.5	1.6	1.4	1.7	1.5	1.5	1.5	1.5	1.6	1.5
Xylose	21.1	21.2	21.4	21.0	20.9	20.9	21.3	21.1	20.7	20.2	18.4	18.5	16.8	17.0	15.9	15.3
Lignin	**24.3**	**23.6**	**23.8**	**22.9**	**22.8**	**22.9**	**22.1**	**21.7**	**22.4**	**22.4**	**21.3**	**23.1**	**23.3**	**23.5**	**23.6**	**23.8**
Klason	18.8	18.2	18.6	17.8	17.3	17.7	17.0	16.8	17.4	17.9	17.3	19.0	19.2	19.5	19.8	19.9
Acid soluble	5.5	5.4	5.2	5.1	5.5	5.2	5.1	4.9	5.0	4.5	4.0	4.1	4.1	4.0	3.8	3.9
Acetone soluble materials*	**2.5**	**2.5**	**2.4**	**4.0**	**2.5**	**2.7**	**3.4**	**3.0**	**3.2**	**3.4**	**4.5**	**5.6**	**6.3**	**7.4**	**7.2**	**7.3**
Others**	**10.4**	**10.5**	**10.0**	**9.5**	**12.8**	**11.4**	**11.2**	**11.9**	**10.5**	**11.2**	**9.8**	**6.5**	**4.7**	**3.2**	**3.0**	**2.7**
Total	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

Pretreatment temperature, °C	**130**								**150**							
Pretreatment time, min	**30 (HW)**	**30 (A)**	**60 (HW)**	**60 (A)**	**90 (HW)**	**90(A)**	**120 (HW)**	**120 (A)**	**30 (HW)**	**30 (A)**	**60 (HW)**	**60 (A)**	**90 (HW)**	**90 (A)**	**120 (HW)**	**120(A)**
Carbohydrates	**60.0**	**60.0**	**61.3**	**59.8**	**59.4**	**58.7**	**60.3**	**60.0**	**61.5**	**60.7**	**60.0**	**59.8**	**60.1**	**59.4**	**60.2**	**59.5**
Arabinose	1.0	0.9	0.8	0.7	0.6	0.5	0.5	0.5	0.4	0.4	0.2	0.2	0.2	0.2	0.1	0.1
Galactose	2.5	2.2	2.1	1.9	2.5	1.9	2.0	1.9	1.9	2.0	1.8	1.5	1.4	1.6	1.3	1.2
Glucose	40.0	40.6	41.4	40.6	40.1	40.0	41.1	41.3	43.0	42.5	43.8	43.9	44.8	44.3	45.9	45.9
Mannose	11.2	11.2	11.5	11.2	10.9	11.2	11.4	11.2	10.9	10.6	9.3	9.5	9.1	8.7	8.4	8.0
Xylose	5.3	5.1	5.5	5.4	5.3	5.1	5.3	5.1	5.3	5.2	4.9	4.7	4.6	4.6	4.5	4.3
Lignin	**32.4**	**28.9**	**28.3**	**29.3**	**30.0**	**32.2**	**31.1**	**30.2**	**32.3**	**31.4**	**30.4**	**32.5**	**31.6**	**32.2**	**32.5**	**31.2**
Klason	31.9	28.5	27.9	28.9	29.6	31.8	30.7	29.8	32.0	31.1	30.1	32.2	31.3	31.9	32.2	30.9
Acid soluble	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Acetone soluble materials*	**3.5**	**3.5**	**3.5**	**3.3**	**3.6**	**4.3**	**4.2**	**3.6**	**4.7**	**4.3**	**4.6**	**5.1**	**4.5**	**4.9**	**4.7**	**5.3**
Others**	**4.1**	**7.6**	**6.9**	**7.6**	**7.0**	**4.8**	**4.4**	**6.2**	**1.5**	**3.6**	**5.0**	**2.6**	**3.8**	**3.5**	**2.6**	**4.0**
Total	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

*Containing extractives, “activated” lignin, and furanoic components.
**Mainly consisting of uronic acids, acetyl groups, proteins, and inorganic components.

hand, the relative content of cellulose was increased during the pretreatments, due to its more resistant nature against these kinds of mild treatment conditions.

In addition to the analysis of the pretreated wood samples, analyses of the chemical composition of the produced aqueous hydrolysates (analytical results presented previously elsewhere [9]) revealed that significant amount of other organic compounds formed during the pretreatments and they were incorporated to hydrolysates. Such compounds included furanoic compounds (*i.e.*, 2-furfural and 5-(hydroxymethyl)furfural), uronic acids (glucuronic and galacturonic acids), and volatile acids (formic and acetic acids).

3.3. ATR analysis and peak assignment of the reference materials

Fig. 1 shows the ATR infrared spectra recorded for the untreated (*i.e.*, without pretreatment) birch and pine samples, which revealed that only small shifts could be observed between these wood species. High absorbance values could be observed with absorption maxima at 1730, 1369, 1154, 1018, and 895 cm^{-1} (birch) and at 1726, 1368, 1154, 1022, and 895 cm^{-1} (pine), which are characteristic for polysaccharides (hemicelluloses and cellulose). Bands resulting from the presence of lignin could be assigned as those with maxima at 1263 and 1229 cm^{-1} (birch) and 1261 and 1232 cm^{-1} (pine) (CO groups in lignin) and those with maxima at 1603, 1507, and 1417 cm^{-1} (birch) and 1603, 1508, and 1422 cm^{-1} (pine) (caused by aromatic skeletal vibrations). Detailed peak positions and assignments of the reference wood samples are listed in Table 4.

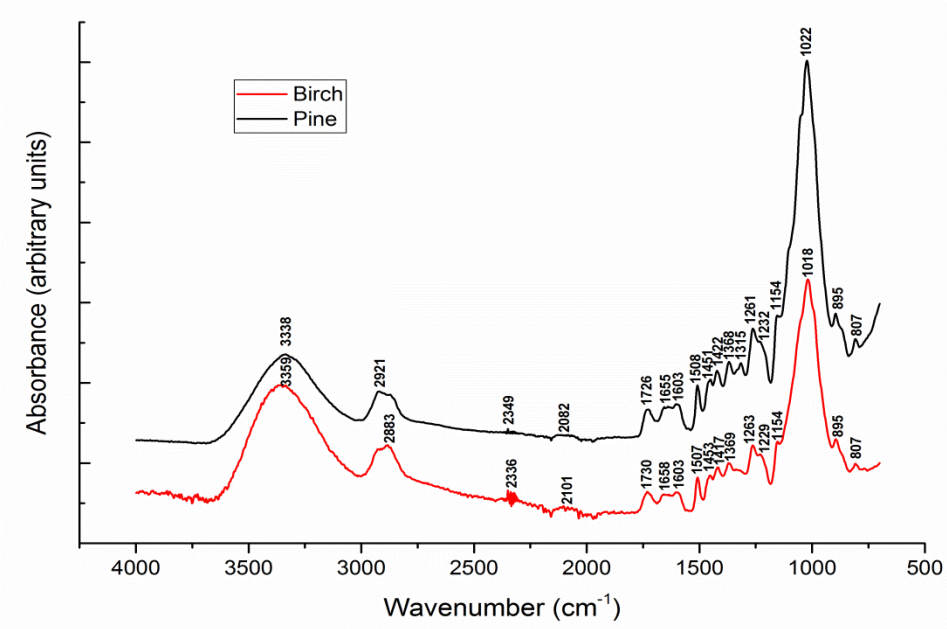

Fig. 1. ATR infrared spectra of untreated birch (red) and pine (black) wood.

Table 4
ATR infrared bands and related molecular bonds assigned

Wavenumber, cm^{-1}		Band assignment	References
Birch	**Pine**		
3359	3338	OH stretching in hydroxyl groups; intramolecular hydrogen bonds in cellulose	[13,15,21,23,36]
2883	2921	CH stretching in methyl and methylene groups; CH symmetrical stretching	[13,15,21]
1730	1726	C=O stretching in unconjugated ketone, carbonyl, and aliphatic groups (xylan); C=O vibration of esters (in lignin), ketones, and aldehydes in hemicelluloses	[13,15,23,35,36]
1658	1655	Absorbed OH and conjugated CO lignin or cellulose; HOH; OH bending of absorbed water; conjugated C-O in quinines coupled with C=O stretching of various groups	[15,23,35,36]
1603	1603	C=C aromatic cycle; aromatic skeletal vibrations typical for syringyl units and C=O stretching	[15,23]
1507	1508	Aromatic skeletal stretching; C=C aromatic cycle; aromatic skeletal vibrations in guaiacyl rings	[13,15,23,35,36]
1453	1451	CH_2 deformation stretching in lignin and xylan; CH deformation asymmetric in plane for lignin and hemicelluloses; HCH and OCH in plane bending vibration	[13,23,35,36]
1417	1422	Aromatic skeletal vibrations combined with CH in plane deformation for lignin and cellulose and stretching	[13,23,35]
1369	1368	Aliphatic CH stretching in methyl and phenol OH; CH deformation in cellulose and hemicelluloses; in plane CH bending	[13,23,35,36]
1263	1261	Stretching of OCO and guaiacyl ring; guaiacyl ring, CO stretching in lignin, and CO linkage in guaiacyl aromatic methoxyl groups	[13,23]
1229	1232	COC stretching in phenol-ether bonds of lignin; CO stretching in syringyl rings; COC symmetric stretching and OH plane deformation	[13,23,35]
1154	1154	COC stretching in pyranose rings and CO stretching in aliphatic groups; COC asymmetrical stretching	[13,35]
1018	1022	CO stretching in cellulose and lignin; CC, COH, and CH ring and side group vibrations	[13,23,35]
895	895	CH out of plane glucose ring in cellulose and hemicelluloses and for guaiacyl rings in lignin; COC, CCO, and CCH deformation and stretching	[13,23,35]

3.4. ATR analysis of pre-treated wood samples

ATR infrared spectra from the fingerprint regions (*i.e.*, at wavenumbers from 700 cm^{-1} to 1800 cm^{-1}) for the wood samples treated at varying temperatures and times are presented in Fig. 2. In general, slightly lower intensities were observed for birch samples than for corresponding pine samples throughout the spectra, excluding the wavenumber region ranging from 1700 cm^{-1} to 1780 cm^{-1} and in the wavenumber region ranging from 1150 cm^{-1} to 1300 cm^{-1} (circled in Fig. 2). Compositional differences between the two investigated wood species elucidated the differences in these wavenumber regions. In the region ranging from 1700 cm^{-1} to 1780 cm^{-1}, the peak having an absorption maximum at 1730 cm^{-1} was mainly caused by C=O transformations in unconjugated ketones, aldehydes, esters, carbonyls, and aliphatic groups commonly found in hemicelluloses, especially in the hardwood xylan. These transformations could include, for example, the cleavage of acetyl side chains commonly found from hardwood xylan [36]. However, this region can also indicate the formation of newly created carbonyl groups, possibly originating due to the increase of carbonyl or carboxyl groups in lignin degradation products.

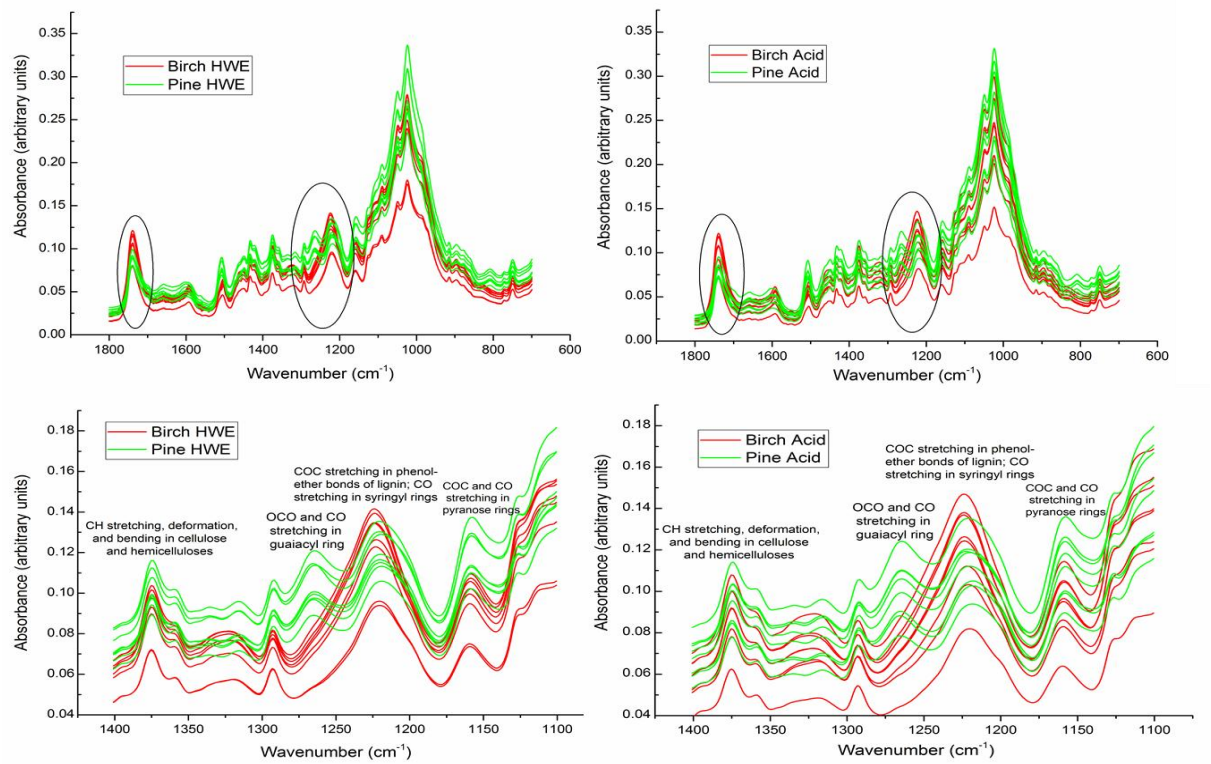

Fig. 2. ATR infrared spectra of the total fingerprint regions (top) and region ranging from 1100 cm^{-1} to 1400 cm^{-1} (bottom) for hot-water extracted (left) and acid-extracted (right) birch (red) and pine (green) wood samples treated at varying pretreatment temperatures and times.

Moreover, the differences in the content of various lignin precursors sheds light on the second main difference in the wavenumber region ranging from 1150 cm^{-1} to 1300 cm^{-1}. The ratio of the different precursors in wood lignin species-dependent [33,37-39]. In hardwoods, the guaiacyl-syringyl type predominates, being composed of *trans*-coniferyl and *trans*-sinapyl alcohols (in an approximate ratio of 50%:50%). In softwoods, guaiacyl type lignin is common, with its structural, biosynthetic precursors composed mainly of *trans*-coniferyl alcohol (90%) and the remainder consisting of *trans-p*-coumaryl alcohol. In the spectra, COC stretching in the phenol-ether bonds of lignin accounts for the peaks arising at wavenumbers in the vicinity of 1230 cm^{-1}, and such peaks were particularly denoted to syringyl rings (one of the main lignin precursors of hardwood lignin). On the other hand, clear peaks located at wavenumbers near 1260 cm^{-1} are commonly attributed to guaiacyl lignin (the main lignin precursor of softwood lignin).

3.5. Effects of the pretreatments

Infrared spectroscopy was a useful method for determining various changes taking place during autohydrolysis and slightly acidic pretreatments. The fingerprint region (*i.e.*, wavenumbers from 700 cm^{-1} to 1800 cm^{-1}) containing highly overlapped absorption bands of cellulose, hemicelluloses, and lignin is highlighted in this work, as the main phenomena taking place during the pretreatments are visible in this region. ATR infrared spectra of the fingerprint regions showed typical differences between the hot-water extracted and acid extracted birch and pine wood samples treated at varying pretreatment conditions (Fig. 3). In both wood species, intensities of the spectral main peaks were clearly increased when compared to reference materials. For both wood species, the intensity of the region ranging from 1700 cm^{-1} to 1780 cm^{-1} and especially the intensity of the peak with an absorption maximum near 1730 cm^{-1} (mainly caused by C=O transformations found in hemicelluloses) clearly increased after the pretreatments.

For birch, the second main difference was located in the wavenumber region ranging from 1150 cm^{-1} to 1300 cm^{-1} and more specifically at wavenumbers near 1230 cm^{-1} referred especially to syringyl lignin. During pretreatments, the minor part of lignin was removed, and lignin was enriched in the pretreated wood residues, which is the probable reason for the increased intensity of this peak. Moreover, the intensity of the other peaks typical for lignin structures between the wavenumbers 1263 cm^{-1} and 1658 cm^{-1} showed a clear increase caused by pretreatments, indicating the enrichment of lignin in pretreated wood residues. However, it is also known that during harsh pretreatments lignin can undergo various degradation and rearrangement reactions leading into formation of new chemical bonds and new free chemical groups which can also cause changes in the recorded spectra [40,41]. These kinds of newly formed structures can cause significant problems in the pretreatment processes, as they can form sticky and hardly removable lignin depositions into the process equipment.

In addition to the increased relative amount of lignin, the relative content of cellulose was increased during pretreatments. The reason for this was that cellulose, unlike its hemicellulose counterparts, showed a great resistance against mild pretreatments. The enrichment of cellulose could be clearly seen in the increased relative portion of glucose present in the pretreated wood residues (Table 3) and could also be seen *via* the intensification of the peak located at the 900 cm^{-1} to 1100 cm^{-1} wavenumber region, typically explained by evidence of cellulosic structures. These findings suggesting the non-destructible nature of cellulose were supported when the broad bands having maxima located at approximately 3350 cm^{-1} were investigated. As these bands were assigned mainly to the hydrogen-bonded O-H groups in intramolecular and intermolecular bonded cellulose, it could be concluded that cellulose was not significantly degraded and its relative content was actually increased.

Similar observations of the increased relative contents of lignin and cellulose could also be confirmed in the case of pine samples (Table 3) - a phenomenon could be verifiable by spectroscopic analyses. However, when compared to the corresponding birch samples, the changes in the yields and chemical compositions were smaller for the pine samples treated under the same pretreatment conditions, thus indicating a greater resistance of pine wood against mild pretreatments. In general, use of composition data or ATR spectroscopy analyses made observable only very small changes between the treatments conducted with hot-water or diluted acid.

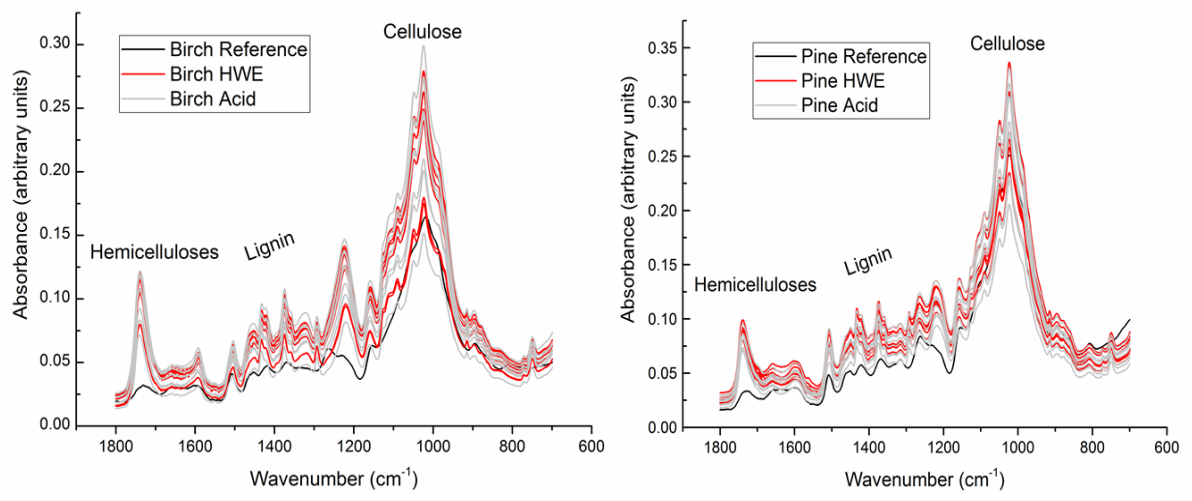

Fig. 3. ATR infrared spectra of the fingerprint regions for hot-water extracted (red) and acid extracted (grey) birch (left) and pine (right) wood samples treated at varying pretreatment temperatures and times.

ATR infrared spectra of the fingerprint regions for the wood samples treated under varying pretreatment conditions are presented in Figs. 4 and 5 for birch and pine, respectively. In the birch samples, increasing the pretreatment severity caused a clear decrease of the relative intensities in ester structures at wavenumber 1730 cm^{-1} and conjugated carbonyl groups at 1658 cm^{-1}, suggesting the destruction of β-*O*-4 structures of lignin [31]. As the β-*O*-4 linkages are the most common structures bonding phenyl-propane units together (*i.e.*, accounting for 40-60 % of the total linkages) and as the cleavage of these bonds are evident also during the pretreatments, it was not unexpected that their degradation could also be seen in ATR spectra recorded from autohydrolyzed and acid-treated samples, especially as the pretreatment conditions became harsher (*i.e.*, when the temperature was increased and longer treatment times were applied). In addition, we viewed cleavage of the ether linkages in lignin by observing clear decrease in intensities of the bands at 1263 cm^{-1} and 1229 cm^{-1} (attributed to guaiacyl and syringyl lignin structures, respectively). Additionally, slight degradation of guaiacyl and syringyl lignins could be observed by absorption decreases near to wavenumbers 1600 cm^{-1} (syringyl) and 1500 cm^{-1} (guaiacyl) [36]. In general, syringyl lignin absorbing around 1600 cm^{-1}, showed less change indicating that syringyl lignin was more stable when compared to guaiacyl lignin. In HWE treatments, only the harshest treatments (*i.e.*, longest treatment time and the highest temperature) caused any significant degradation of syringyl lignin. However, also syringyl lignin started to show signs of degradation when a small amount of acid was added to the pretreatment liquor.

A decrease in the intensities of the peaks attributed to carbohydrate moieties (*i.e.*, mainly designated for hemicelluloses-derived structures) at wavenumbers 1369 cm^{-1} and 1730 cm^{-1} were clearly noticeable when the pretreatment conditions became harsher. In general, longer pretreatment times and higher treatment temperatures caused significant removal of hemicelluloses from the wood materials (Table 3), and this trend could also be seen in the decreasing intensities of hemicelluloses-derived peaks in the above mentioned wavenumber regions especially designated to hemicelluloses. On the other hand, the effect of adjusting the pretreatment liquor pH in the beginning to a value of 3 did not cause any significant effect on the dissolution efficiency. Absorption decrease in the conjugated carbonyl region near 1660 cm^{-1} could be assigned to conjugated C=O structures, indicating the previously mentioned cleavage of acetyl groups from hemicelluloses through deacetylation reaction [36]. The simultaneous formation of acetic acid further catalyzes the depolymerization reactions of hemicelluloses, together with various condensation and degradation reactions of lignin.

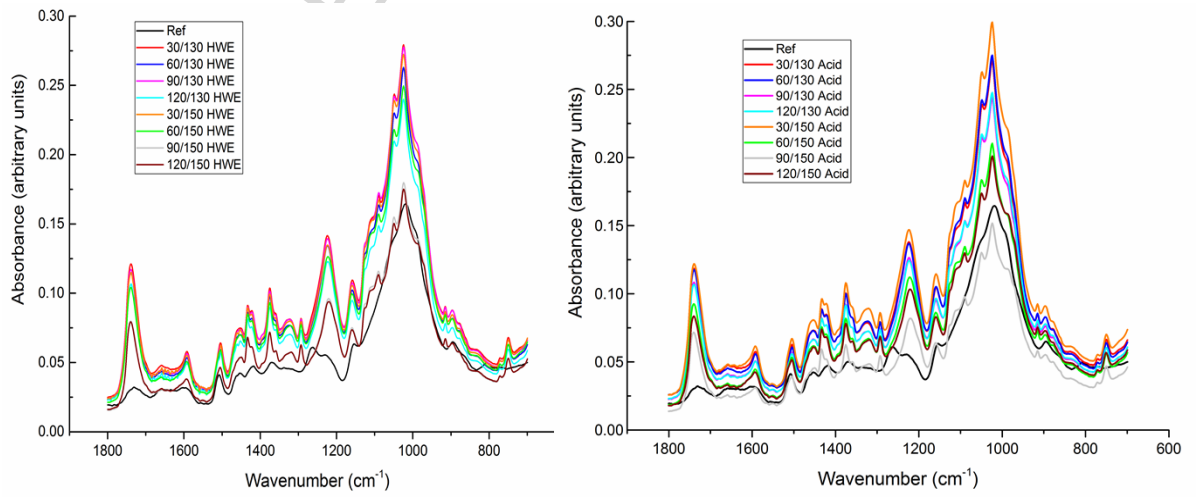

Fig. 4. ATR infrared spectra of the fingerprint regions for birch wood samples treated with hot-water (left) and diluted acid (right) at varying pretreatment temperatures and times.

Rather similarly, although minor effects of the pretreatments were determinable for the pine samples, the effects of an increase in treatment temperature and time did not lead to such significant effects as those detected for the birch samples. This observation was in agreement with the fact that pine wood generally was more resistant against these kinds of mild pretreatments.

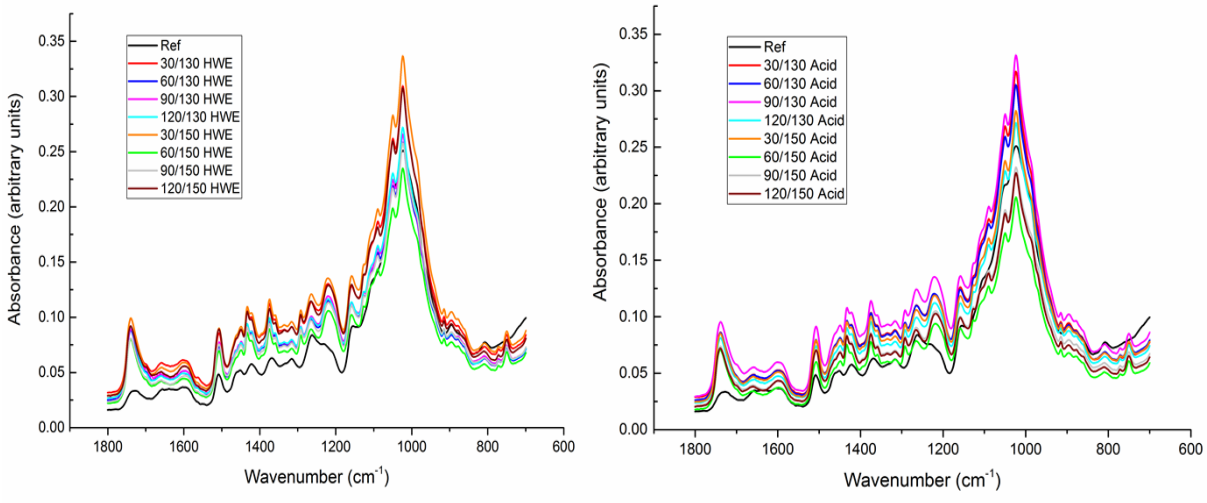

Fig. 5. ATR infrared spectra of the fingerprint regions for pine wood samples treated with hot-water (left) and diluted acid (right) at varying pretreatment temperatures and times.

4. Conclusions

Effects of hot-water and dilute acid pretreatments on chemical composition of hardwood and softwood were investigated by attenuated total reflectance (ATR) infrared spectroscopy. Spectral data were compared to the corresponding chemical composition data determined by conventional wood chemistry analyses for evaluating the suitability of ATR spectroscopy for describing the phenomena taking place during such pretreatments. Results clearly indicated that this rapid and simple spectral method could track and describe several fundamental changes caused by pretreatments. It was possible to describe by this technique, for example, differences between the two treated wood species in terms of chemical composition and behavior during pretreatments. In addition, chemical phenomena, such as degradation of lignin and carbohydrates, could be explained when the data obtained via different analytical routes were compared to each other.

Acknowledgement

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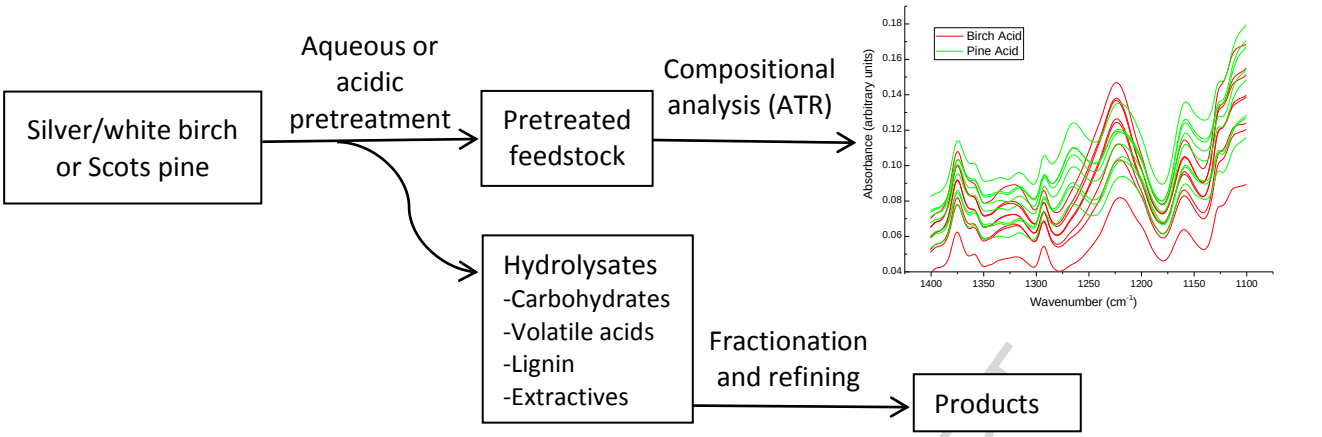

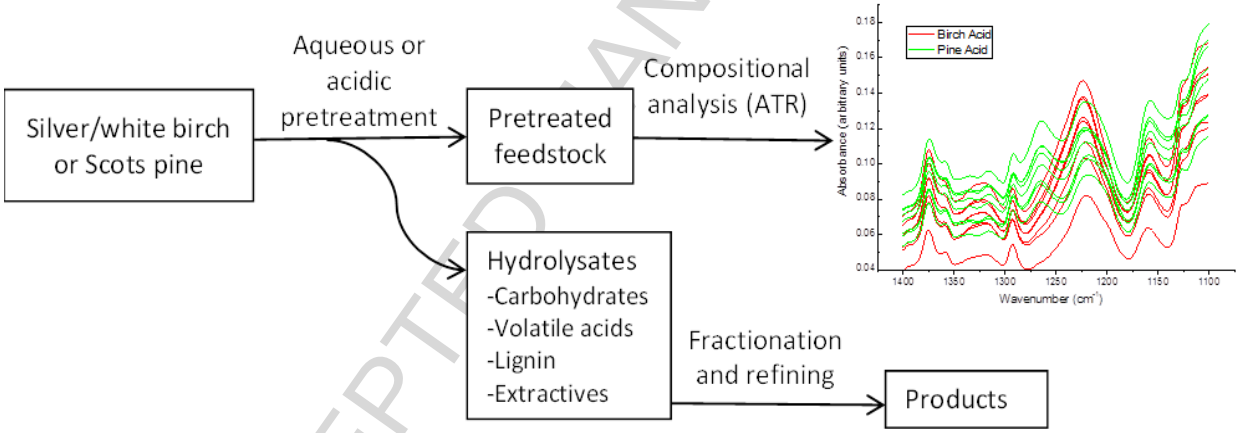

Graphical abstract

Highlights

- Characterization of hot-water- and dilute acid-extracted wood by ATR spectroscopy.
- ATR spectroscopy results were compared to those from wet chemistry analyses.
- Changes in the carbohydrate and lignin structure could be determined and explained.
- Changes between the pretreatments and wood species could be determined.
- The main phenomena of the pretreatments could be explained by ATR results.