FEASIBILITY OF INTEGRATING HOT WATER EXTRACTION INTO A DISSOLVING PULP PROCESS TO RECOVER HEMICELLULOSES FROM *PINUS RADIATA*

CHUNLIN XU, TOMÁS NUÑEZ, STEFAN WILLFÖR and ANNA SUNDBERG

Johan Gadolin Process Chemistry Centre, c/o Laboratory Wood and Paper Chemistry, Åbo Akademi University, 3, Porthansgatan, 20500, Åbo/Turku, Finland
✉ *Corresponding author: Chunlin Xu, cxu@abo.fi*

Hot water extractions using *Pinus radiata* sawdust as raw material were performed both at laboratory and pilot scales to investigate their feasibility with a view to scaling up the extractions to an industrial process. The laboratory scale extractions were performed at 160 °C, 170 °C and 180 °C, for up to 100 minutes without adjustment of pH. The pilot scale extractions were done at 160 °C and 170 °C for 40 min. Additionally, the pilot scale extractions were also performed at 150 °C, 160 °C and 170 °C with a P-factor of 600. The highest yield obtained in the pilot scale extractions was 112.6 mg/g at the extraction temperature of 170 °C with the P-factor of 600. It was proved that it is feasible to scale up the hot water extraction from laboratory to pilot scale, but the extraction parameters must be tuned to achieve a high extraction yield of carbohydrates.

Keywords: feasibility, galactoglucomannans, hot water extraction, *Pinus radiata*, pilot scale, sawdust

INTRODUCTION

Due to an emerging urge to find natural alternatives to petrolium-based chemicals and synthetic materials, it is of great significance to improve the sustainability of forest and forest-based industries, i.e. the concept of 'biorefinery', dealing with biomass-based energy, materials and chemicals. The novel forest biorefinery concept should allow the use of the three main biomass components in wood, i.e. hemicelluloses, lignin and cellulose, preferably in high-value end applications. In the traditional chemical processing of wood, most of the hemicellulose fractions are degraded and solubilized during the kraft cooking, ending up in the black liquor, which also contains lignin. The black liquor is finally burnt in the recovery boiler for energy production and recovery of chemicals.[1]The hemicellulose fractions are therefore poorly utilized due to the lower calorific value that hemicelluloses have in comparison with lignin, decreasing the specific heating value of the generated black liquor.[2] The incorporation of novel biorefinery concepts will revolutionize the use of biomass to allow the production of hemicelluloses as a value-added product from the pulping process.

Thus, numerous efforts have lately been made to extract and isolate hemicelluloses during the pretreatment of wood materials before processing.[3-7] Among the different extraction technologies, pressurized hot water extraction (PHWE) has been studied exclusively and has proved to be a promising technology to isolate hemicelluloses with controlled properties. The use of water as a solvent is beneficial from an environmental aspect. Moreover, sawdust is a residue of the pulp mills obtained from the initial classification of wood chips in the wood yard, as well as from sawmills. It is today mainly used as a combustible material in the power boiler of pulp mills. Total sawn wood production in EU countries was 103 million cubic meters in 2010.[8] Earlier, a flow-through PHWE process for birch and spruce sawdust was successfully upscaled with regard to hemicelluloses.[7] In this work, pine sawdust was used as the starting material to extract valuable hemicelluloses.

Hemicelluloses are common polysaccharides present in nature, representing about 20-35% of the total lignocellulosic biomass. According to their composition and structure, hemicelluloses

are suitable for the production of liquid fuels, such as ethanol or other bioproducts with a high added value like chemicals, polymers, adhesives, pharmaceuticals and dietary products.[9,10]They can also be used to enhance animal feedstock, clarification of juices, and even to improve the consistency of beers.[11] For example, galactoglucomannans (GGMs), the major hemicellulose in softwoods, are promising natural materials as such or after modification, which find a broad range of applications.[12-16] GGM is an emulsion stabilizer for hydrophobic beverage flavors.[17] GGM can be processed to films with the addition of a plasticizer, being rather weak by itself, but with chemical modifications and addition of other polysaccharides, the strength can be improved.[18] Spruce GGM has been studied in the formation of copolymer hydrogels that find application in heavy metal removal for water treatment.[19-21] More recently, composites of GGM and nanocellulose, as well as other compounds, have attracted increased interest and thus extended the application of GGM to higher valued endproducts, such as biomedical scaffolds and devices.[14] It is mostly GGMs isolated from spruce that have been studies; applications of GGMs from pine are still inadequate due to the limited availability of the material.

In this study, the isolation of hemicelluloses from the sawdust of *Pinus radiata* by hot water extraction was first carried out at laboratory scale. Based on the understanding of the hot water extraction processes, pilot scale hot water extraction was incorporated in the dissolving pulping process. Thus, the feasibility of scaling up the optimal hot water extraction process from laboratory to pilot scale was investigated.

EXPERIMENTAL

Materials

P. radiata sawdust was collected in a sawmill in the VIII region of BioBio, Chile, and stored in a cold chamber (-5 °C) in sealed polyethylene bags prior to use. The sawdust sample used in the laboratory scale extractions was sieved and characterized according to the particle sizes in the ranges of smaller than 0.5, 0.5-1.0, 1.0-2.0, 2.0-2.8 and larger than 2.8 mm without any prior grinding processes. Sawdust of sizes ranging between 0.5 to 2.8 mm was used.

Pre-extraction with acetone

Pre-extraction to remove the extractives was performed with a mixture of acetone/water (95:5 volume ratio) using an ASE-300 equipment (Dionex, Sunnyvale, CA, USA). The wood sample was dried in a freeze-dryer. The extraction was performed at 100 °C for 1 h. The pressure in the extraction cell was 100 bar. The obtained extract was then dried and weighed to calculate the gravimetric content of extractives in the wood. All wood samples used in the laboratory scale extractions were pre-extracted in order to avoid any interference of extractives in the subsequent analysis. The sawdust used in the pilot scale experiments was not pre-extracted.

Laboratory scale PHWE

The first step was to study the impact of process conditions, such as temperature and time, on the resulting liquid extracts and solid residues. The investigation was performed at small scale in the laboratory. The total number of extractions performed and the conditions used are shown in Table 1. A total of nine hot water extractions were performed using the ASE-300 Equipment.

About 5 g of sample was placed in each cell. About 80 mL of water was injected for each extraction. The pressure in the cell was about 100 bar (10^6 Pascal). After each extraction, the extract was purged out with nitrogen gas and the cell was rinsed with 50 mL of distilled water.

Pilot scale PHWE

The pilot scale experiments consisted of five hot water extractions. The extractions were performed in a high-pressure reactor autoclaved with recirculation liquor capability and a total volume of 50 L.

A total of 5 kg dried sawdust was used in each experiment. A liquor-to-wood ratio of 7:1 was used in order to avoid any problems in the circulation due to the small particle size of sawdust material. A vaporization time of 10 min was used in order to homogenize the diffusion of water into the particles followed by an impregnation time of 15 min. The working pressure was 8 bar. After each experiment, the liquid extracts were recovered and cooled down for storage at -5 °C and the solid residues were washed and weighed.

In order to study the upscaling of the process from laboratory to pilot scale, two of the extractions had the same conditions, 160 °C and 40 min and 170 °C and 40 min. The condition of 160 °C with a P-factor of 600 for the pilot scale was also comparable with that of 160 °C and 100 min in the laboratory scale extraction, because the total operating time to reach the desired P-factor was very close to 100 min. The reason to study the extraction conditions with a P-factor of 600 lies in the fact that this parameter is used in the industrial process for the production of dissolving pulp, and the recovery of the hemicelluloses found in the prehydrolysis liquors is of particular interest in the industry in order to increase the economic feasibility of the process.

Table 1
Extraction parameters for laboratory and pilot scale systems

Parameter	Laboratory scale 0.08 L			Pilot scale 35 L				
Temperature (°C)	160	170	180	150	160	160	170	170
Pressure (bar)	100	100	100	8	8	8	8	8
Pre-extraction	Yes	Yes	Yes	No	No	No	No	No
Loading (go.d.)	5	5	5	5000	5000	5000	5000	5000
Wood to water ratio	1:13	1:13	1:13	1:7	1:7	1:7	1:7	1:7
Extraction time (min)	20, 40, 100	20, 40, 100	20, 40, 100	245*	40	100*	40	53*

*P-factor of 600 was set as the end of the targeted reaction

Total dissolved solids (TDS)

TDS content was determined gravimetrically. An exact 2 mL aliquot of the water extract was taken and dried in an oven at 105 °C overnight. The sample was weighed after it was completely dried.

Total non-cellulosic carbohydrates in water extracts

Total non-cellulosic carbohydrates were analyzed by gas chromatography (GC) after acid methanolysis, which cleaves non-cellulosic polysaccharides to monomer sugars by forming methyl glycosides and methyl ester methyl glycosides.[22]

The extract of a known weight (about 0.5-1 mg) was dried and subjected to an acid methanolysis reagent (1 M HCl in methanol) in an oven (100 °C) for 3 h. Next, the samples were silylated with pyridine, hexamethyldisilazane (HMDS) and trimethyl-chlorosilane (TMCS) reagents. Afterwards, the supernatants were transferred to GC vials for analysis. A known amount of a carbohydrate solution was used for calibration and sorbitol was used as an internal standard. The GC column temperature program was100 °C – 1 min, 4 °C/min– 170 °C, followed by 170 °C – 12 °C/min– 300 °C for 10 min. The detector (FID) temperature was 310 °C. Hydrogen was used as carrier gas.

Total non-cellulosic carbohydrates in wood and residues after extraction

The non-cellulosic carbohydrates in the extracted ground wood samples were analyzed by GC after freeze-drying and acid methanolysis, as described above, with the difference in the initial amounts of samples used for analysis (about 10 mg) and methanolysis for 5 h.[22]

Cellulose content in wood and residues after extraction

The cellulose content was analyzed by acid hydrolysis of the wood material using 72% sulfuric acid at 20 °C for 2 h, followed by a dilution to 4% sulfuric acid and treatment at 100 °C and atmospheric pressure for a total of 4 h, filling with water when necessary to maintain the volume of reaction.[23]The resulting material was then neutralized with $BaCO_3$ using bromocresol green as an indicator. One milliliter of internal standard solution containing sorbitol was also added and the $BaCO_3$ precipitate was separated by centrifugation and the supernatant was mixed with a few mL of pure acetone and then evaporated with N_2 gas. Samples were then silylated and analyzed with GC. The GC column temperature program was100 °C – 1 min, 4 °C/min– 170 °C, followed by 170 °C – 12 °C/min– 300 °C for 10 min. The detector (FID) temperature was 310 °C. Hydrogen was used as carrier gas.

Monosaccharides in liquid extracts

Monosaccharides in water extracts were analyzed by GC of an aliquot of the extract solutions after freeze-drying and silylation.[24] A calibration standard also containing a solution of monosaccharides was used and xylitol was used as an internal standard. The methanol was evaporated under a stream of N_2 and the sample was silylated using pyridine, HMDS and TMCS reagents. The samples were left overnight and they were then transferred to GC vials for analysis. The GC column temperature program was100 °C – 8 min, 2 °C/min– 170 °C, followed by 12 °C/min– 300 °C for 10 min. The detector (FID) temperature was 310 °C and the injector was at 250 °C. Hydrogen was used as carrier gas.

Acid-insoluble lignin in wood and the residues after extraction

The procedure was modified from TAPPI T 222 om-02 “Acid-insoluble lignin in wood and pulp”. For this, 100 mg of wood material was weighed and then 1.5 mL of 72% sulfuric acid was added to the sample, macerating the material in order to ease the acid penetration. The material was kept at 20 °C ± 1 for 2 h. The acidic solution was diluted with water to a final concentration of 3%, and the sample was boiled for 4 h. The volume of liquid in the flask was maintained by frequent addition of hot water. The material was then filtered and the filtrate was dried and weighed in order to obtain the acid-insoluble lignin content.

Acid-soluble lignin in wood and the residues after extraction

This method was modified from UM 250 "Acid-soluble lignin in wood and pulp". The filtrates were obtained by the procedure for acid-insoluble lignin described above. This method was based on spectrometry using absorbance of ultraviolet radiation at a wavelength of 205 nm. To measure the absorption of the filtrate, a quartz cell was filled with the filtrate using a 3% H_2SO_4 as the reference. If the value of absorbance was higher than 0.7, the sample was diluted. A molar extinction coefficient of 128 was used for calculations.

Free acetic acid

Free acetic acid in the extract solution was analyzed using high performance liquid chromatography (HPLC) with a Synergi Hydro-RP 80R HPLC Column (250 mm x 4 mm, 4 mm, Phenomenex, Torrance, CA, USA) and a refractive index (RI) detector (Shimadzu, Tokyo, Japan). The pH was adjusted to 2.5-2.6 with 30% *ortho*-phosphoric acid. The eluent contained 20 mM KH_2PO_4 in distilled water and the pH was buffered to 2.5-2.6 with *ortho*-phosphoric acid. The eluent was then filtered through a 0.2 µm filter (Anodisc 47, Whatman International, Maidstone, UK). The injection volume was 100 µL.

Furfural and hydroxymethylfurfural (HMF)

Furfural and HMF were analyzed by HPLC (Agilent 1260 series, Waldbronn, Germany) with a Synergi Hydro-PR 80A HPLC column (250 mm x 4.6 mm, 4 µm, Phenomenex, CA, USA) and an RI detector (Agilent, Waldbronn, Germany). The hydrolysates were filtered through a 0.22 µm nylon filter. The eluent was 20 mM KH_2PO_4 buffer solution.

Molar mass (M_w)

The M_w was determined using size exclusion chromatography (SEC) with a multiangle laser light scattering (MALLS) detector and an RI detector. For this, a guard column (Ultrahydrogel 6 mm x 40 mm, Waters, Milford, MA, USA) and two columns (2 x Ultrahydrogel linear 7.8 mm x 300 mm, Waters, Milford, MA, USA) were connected in series. The water extracts were filtered through a 0.22 µm nylon syringe filter before injection. The eluent was 0.1 M sodium nitrate aqueous solution. The flow rate was 0.5 mL/min. The injection volume was 200 µL. Astra software (Wyatt Technology) was used to calculate average molar masses. A dn/dc value of 0.150 mL/g for GGMs was used for the calculations.[4,13]

RESULTS AND DISCUSSION

Chemical composition of the raw material

The contents of cellulose, hemicelluloses, lignin and extractives in *P. radiata* sawdust were analyzed and are presented in Table 2. The extractives were removed from the wood by acetone extraction using a mixture of acetone and water (95:5 volume ratio) prior to the laboratory scale extraction, while sawdust without pre-extraction was used in the pilot scale extraction.

Yields and pH of extracts

Plain water was used in both laboratory and pilot scale extractions. The temperature was thus the key parameter that affected the yield of the extraction and the composition of the extracts.

Three temperatures, 160 °C, 170 °C and 180 °C, were used in the laboratory scale extractions (Table 3). Higher temperature yielded a larger TDS content. In the extraction at 160 °C, the TDS content increased with time from 124 mg/g at 20 min to 192 mg/g at 100 min.

When the temperature was increased to 170 °C, the TDS content increased from 188 mg/g at 20 min to 204 mg/g at 40 min, but decreased to 196 mg/g at 100 min. A temperature of 180 °C yielded a TDS content of 215 mg/g already at 20 min. Prolonging the extraction time did not increase the TDS content, but resulted in a lower content: 201 mg/g, at 100 min. The decrease in TDS yield with prolonged extraction time at higher temperature can be explained by the formation of degradation products, such as volatile acetic acid, furfural and HMF. This is also in accordance with other studies of hot water extraction of hemicelluloses at high temperatures.[5-7,25] Furthermore, the yields of carbohydrates in the TDS are also presented in Table 3. The details will be discussed in the next section, but the yield was apparently decreased when the extraction temperature of 180 °C was applied, down to only 20 wt% at an extraction time of 100 min.

The end-pH of the extract after 20 min extraction was about 4.0-4.1 for all temperatures. The pH was lower at a longer extraction time. At a higher temperature, the decrease of the end-pH was more pronounced. The decrease in pH value is mainly ascribed to the liberation of acetic acid from the naturally acetylated GGM.[26]

The extraction temperatures of 160 °C and 170 °C were chosen for the pilot-scale extractions. In addition, a milder condition at 150 °C was also tested. Moreover, the P-factor, which is generally used in industrial process control of the prehydrolysis step in the kraft process for the production of dissolving pulp, was used here to control the extraction process and was targeted at600. As a result, the reaction time at the P-factor

of 600 was 245 min at 150 °C, 100 min at 160 °C, and 53 min at 170 °C, respectively (Table 3). The TDS content of the extracts at the P-factor of 600 increased from 74.6 mg/g at 150 °C to 112.6 mg/g at 170 °C. The TDS contents of the extracts after 40 min extraction time at 160 °C and 170 °C were much smaller than those values in the laboratory scale extractions, which can be ascribed to the challenges in upscaling. The pressure of the extraction reactor, which was part of the equipment existing at the dissolving pulp mill, could not reach the high value of 100 bar, as it was the case of the ASE in the laboratory scale extractions. Moreover, considering economic feasibility, the wood-to-water ratio in the pilot scale extractions was kept to only 1:7 in comparison with 1:13 for the laboratory scale extractions. The end-Ph values in the extracts were higher in the pilot scale extractions than in the laboratory scale ones.

Table2
Chemical composition of the *Pinusradiata* sawdust

Composition	*Pinusradiata* sawdust (mg/g wood)
Cellulose	395
Hemicelluloses	258
Manose	76.5
Glucose	27.2
Galactose	48.3
Xylose	57.7
Arabinose	16.0
Others	31.9
Lignin	308
Extractives	28
Others	11

Non-cellulosic carbohydrates

The sugar unit composition and the contents of hemicelluloses in the hot water extracts as oligomeric and polymeric forms at laboratory scale, under different process conditions are shown in Figure 1a. Clearly, more carbohydrates were found in the extract after 40 min extraction time (116 mg/g) than after 20 min (83 mg/g) at an extraction temperature of 160 °C. However, the amount did not further increase when prolonging the extraction time to 100 min. At an extraction temperature of 170 °C, the amount of extracted carbohydrates was about 120 mg/g both after 20 and 40 min, although the TDS content was larger (Table 3). This means that under this condition more non-carbohydrate components such as lignin were released. With further prolonged extraction time to 100 min, the amount of extracted carbohydrates dropped significantly. Moreover, at an extraction temperature of 180 °C, the amount of extracted carbohydrates clearly dropped already at 40 min extraction time (Figure 1a). The decrease in the amount of extracted carbohydrates after 100 min at 170 °C and after 20 min in the case of 180 °C can be explained by the degradation of released sugars into monosaccharides and other degradation compounds, such as furfural.[26] Another possible explanation is the lower solubility of deacetylated GGMs, caused by the release of acetic acid groups,[5] resulting in re-precipitation onto fiber surfaces.

The sugar composition and contents of non-cellulosic oligomeric and polymeric carbohydrates in the hot water extracts of the pilot scale extractions are also presented in Figure 1a. At the same temperature and extraction time (160 °C, 40 min and 170 °C, 40 min), the amount of extracted carbohydrates was about half of that from the laboratory scale extraction. With prolonged extraction time to the P-factor of 600, the amount of extracted carbohydrates was increased. The largest amount was achieved at 170 °C with a P-factor of 600 and was about 71 mg/g. The extraction at 150 °C with a P-factor of 600 gave an amount of 41 mg/g. The yield of carbohydrates in the TDS was the highest at an extraction temperature of 170 °C (Table 3).

Table 3
Total dissolved solid (TDS) content, end pH, molar mass of polymeric carbohydrates (Mw), polydispersity (Mw/Mn) and total yield of non-cellulosic carbohydrates in the extracts from both laboratory and pilot-scale extractions

	Laboratory scale HWE									Pilot scale HWE				
	160 °C			170 °C			180 °C			150 °C	160 °C		170 °C	
	20 min	40 min	100 min	20 min	40 min	100 min	20 min	40 min	100 min	245 min*	40 min	100 min*	40 min	53 min*
TDS (mg/g)	124.0	175.4	192.0	188.0	204.7	196.2	214.9	214.3	201.3	74.6	69.2	90.2	77.3	112.6
End pH	4.1	4.1	3.9	4.1	3.9	3.7	4.0	3.6	3.4	4.6	4.4	4.3	4.2	4.0
Yield of carbohydrates (wt%)	66.7	66.3	59.4	64.0	59.9	54.6	61.6	50.6	20.2	55.6	50.2	61.4	63.9	63.0
Mw (g/mol)	8367	6136	2997	6204	3535	1074	3203	895	872	5726	5903	4684	5502	3302
Mw/Mn	2.73	3.20	2.90	1.74	2.21	1.22	3.49	1.24	3.22	1.98	1.95	2.22	1.77	1.41

* P-factor of 600 was set as the end of targeted reaction

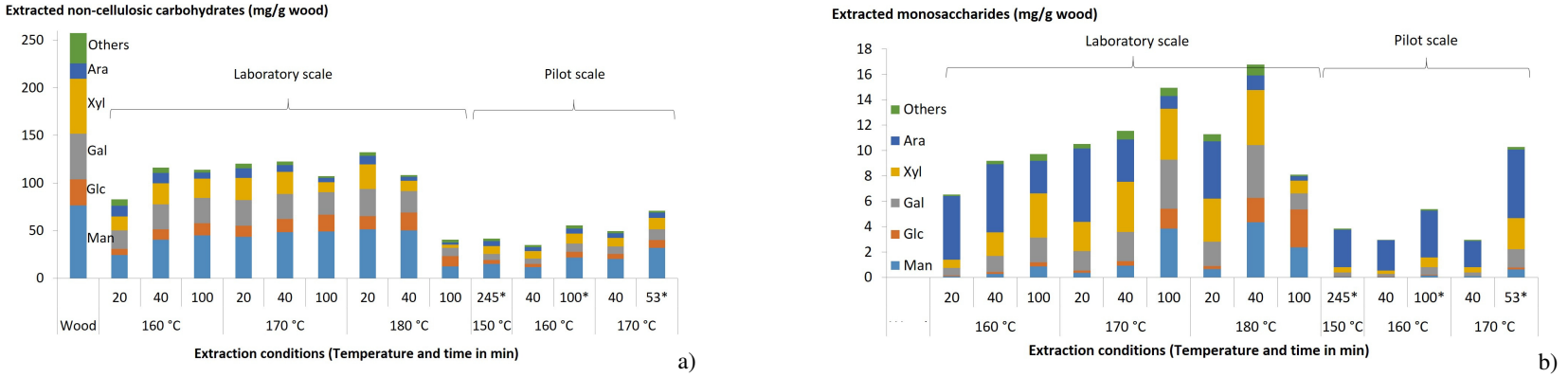

Figure 1: a) Total oligomeric and polymeric carbohydrates extracted at different temperatures and extraction time from both laboratory and pilot scale extractions; b) Total monosaccharides extracted at different temperatures and extraction time from both laboratory and pilot scale extractions (*P-factor of 600 was set as the end of targeted reaction)

In comparison with the total amount of non-cellulosic carbohydrates, about half in the form of oligomers and polymers, was extracted in the laboratory scale extractions and the conditions of 180 °C and 20 min gave the highest yield (Figure 1a). In the pilot scale extractions, the highest yield was achieved at an extraction temperature of 170 °C with P-factor of 600. In all extracts, galacto-glucomannan, which consisted of galactose, glucose and mannose, was dominant.

During hotwater extractions, the hemicelluloses are hydrolyzed to oligomers and further to monomers due to autohydrolysis caused by released acetic acid and high temperature.[5-7,27] As shown in Figure 2b, a larger amount of monosaccharides was found in the extracts at a higher extraction temperature, or at the same extraction temperature but at longer extraction time. In the extracts from the laboratory scale extractions, arabinose was dominant in the samples with short extraction time (20 min) and other sugars were gradually released with prolonged extraction time and higher temperature. Particularly, in the extracts from extractions at 170 °C and 100 min extraction time and 180 °C and 40 min extraction time, the sugar composition was quite similar to that of oligomeric and polymeric carbohydrates, which indicates that strong conditions caused the hydrolysis of all polysaccharides. The monosaccharide amount at 180 °C and 100 min extraction time was much smaller than that at 40 min extraction time, and proved the further degradation of monosaccharides. In the extracts of pilot scale extractions, arabinose was dominant in all samples. The easy release of arabinose has also been reported earlier,[3,27] and can be ascribed to the hydrolysis of the labile side chains in arabinogalactan.

Molar mass of extracted polymeric carbohydrates

The molar mass of all the extracts is presented in Table 3. The molar mass decreased at a higher temperature and prolonged extraction time. It is logical and in accordance with the results reported in previous studies.[5,6] In the laboratory scale extraction, the highest molar mass, about 8300 g/mol, was obtained for the extract at 160 °C and 20 min extraction time. The molar mass decreased to 6100 g/mol at 40 min and to 3000 g/mol at 100 min extraction time. The molar mass of the extract at 170 °C was about 6200 g/mol at 20 min and decreased to 3500 g/mol at 40 min, and was only about 1000 g/mol at 100 min. When the temperature was set to 180 °C for the extraction, the molar mass dropped to below 1000 g/mol already at 40 min.

The molar mass of the extracts at 160 °C and 40 min from the pilot scale extractions was about 5900 g/mol, which is close to 6100 g/mol, the value of the extract from the laboratory scale extraction at the same extraction temperature and time. However, at 100 min extraction time, the molar mass from the pilot scale extraction was still as high as about 4700 g/mol, which is much higher than 3000 g/mol achieved from the laboratory scale extraction. At 170 °C and 40 min, the molar mass of extract from the pilot scale extraction was 5500 g/mol, which is much higher than that from the laboratory scale extraction at the same temperature and extraction time. The pilot scale extraction at 150 °C gave a molar mass of 5700 g/mol even after 245 min, which was with the P-factor of 600. In general, the pilot scale extractions yielded mostly carbohydrates with higher molar mass than those of the laboratory scale extractions. That can also be clearly seen from the plot of the cumulative weight fraction in Figure 2. A tentative assumption is that less severe autohydrolysis driven by the lower hydrogen ion concentration in the pilot scale extractor also corresponded to the higher end-pH value of the extracts (Table 3).

Acetic acid, furfural and HMF of extracts in pilot scale extractions

The contents of released acetic acid, furfural and HMF as products of further degradation from monosaccharides from the pilot scale extractions are presented in Table 4.

The hydroxyl groups at C-2 and C-3 in the mannose units of GGM are partially acetylated. The presence of acetyl groups contributes to the water solubility of GGM.[28,29] Partial cleavage of *O*-acetyl groups can be seen by an increase in the amount of acetic acid with higher extraction temperature and longer extraction time. The highest amount of released acetic acid was 2.768 mg/g found for the extraction at 170 °C with the P-factor of 600. The value is relatively low in comparison with the laboratory scale hot water extraction at higher pressure, which could yield as high as 8.5 mg/g acetic acid.[3]

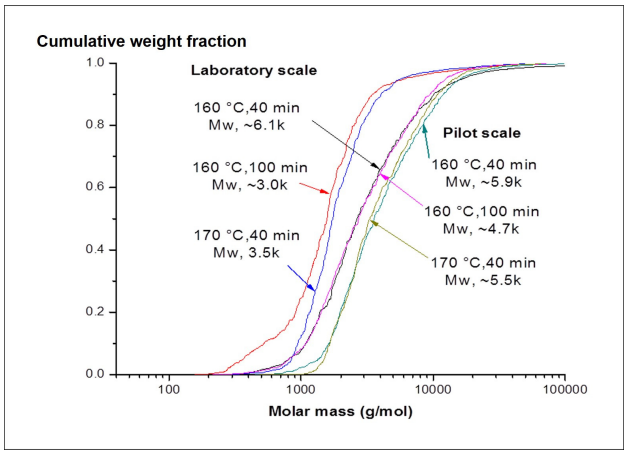

Figure 2: Cumulative molar mass distribution of extracted polymeric hemicelluloses

Table 4
Contents of HMF, furfural and acetic acid in the extracts of pilot scale extractions

Content based on dry wood	150 °C	160 °C		170 °C	
(mg/g)	245 min*	40 min	100 min*	40 min	53 min*
HMF	0.04	0.03	0.10	0.06	0.18
Furfural	0.01	0.15	0.52	0.31	0.66
Acetic acid	1.58	1.06	2.46	1.46	2.77

* P-factor of 600 was set as the end of targeted reaction; The extraction was controlled to the P-factor of 600

Furfural and HMF are further degradation products of pentoses and hexoses, respectively, and these were also determined. Their amounts were quite low, below 1 mg/g under all the conditions that were applied in the pilot scale extractions.

Chemical composition of extracted sawdust residues

The contents of cellulose, hemicelluloses and lignin of extracted sawdust residues were determined (Figure 3). In comparison with the starting sawdust, which had a hemicellulose content of 27% and cellulose content of 41%, all extracted sawdust residues had lower hemicellulose content and higher cellulose content. The cellulose content in the extracted residue increased with an increase in the extraction temperature and time. In all the extracted residues of the pilot scale extractions at a P-factor of 600, the cellulose content was about 50% or higher.

Feasibility of upscaling from laboratory to pilot scale extraction

To evaluate the feasibility of upscaling, laboratory and pilot scale extractions under three similar conditions were compared. The conditions of 160 °C and 40 min extraction time and 170 °C and 40 min extraction time were chosen for both processes, while 160 °C for 100 min in the laboratory scale process was compared with 160 °C and 600 P-factor due to the equal amount of time. The difference in the extraction is the higher wood-to-water weight ratio and lower pressure for the pilot scale than for the laboratory scale (Table 1).

The upscaling from laboratory to pilot scale extraction process faces some challenges, principally concerning the extraction yields, release of acetic acid, and further degradation in the hot water extracts. As discussed above, relatively lower extraction yields were obtained for the pilot scale extractions in comparison with those for the laboratory ones. Yet, the TDS contents calculated based on the total volume of the extracts were at about the same level for both scale extractions (Figure 4).

A higher working temperature is preferable when a required P-factor is applied to control the process. With higher temperatures, shorter extraction times are needed to preserve the structural features of the extracted hemicelluloses and less free acetic acid content is released to the water extracts.

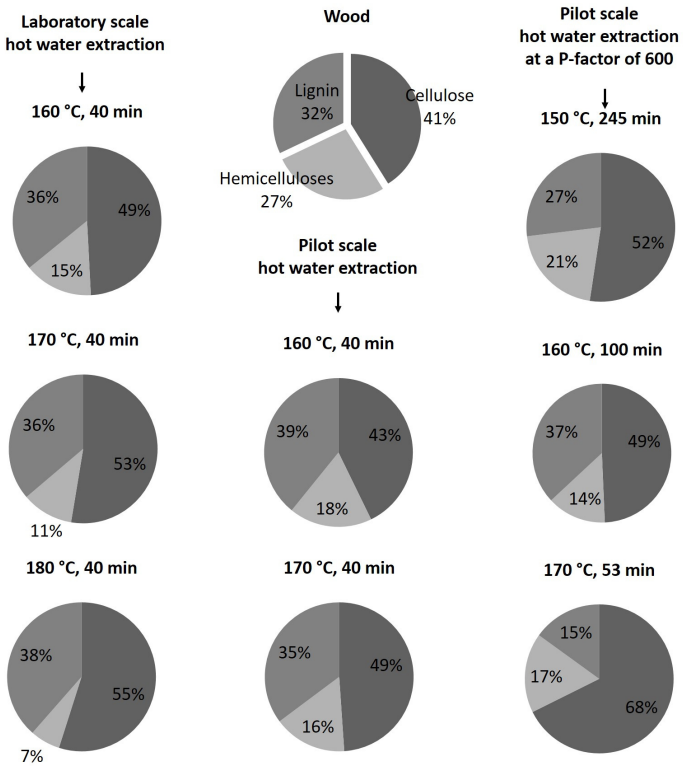

Figure 3: Chemical composition of extracted sawdust residues in comparison with that of starting sawdust

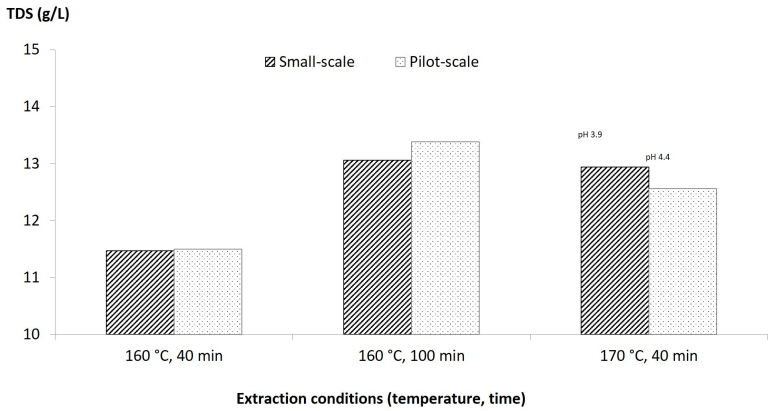

Figure 4: TDS content of extracts under comparable extraction conditions from both laboratory and pilot scale extractions

The latter will cause autohydrolysis of hemicelluloses and further degradation. The pilot scale extractions also require longer extraction time than the laboratory scale extractions to achieve similar concentrations of the extracts. In order to improve the process, other variables, such as the particle size, which affects the diffusion between solid-liquids and the pH at which the extraction takes place, need to be studied in the future in order to reduce the difference between the two scales.

CONCLUSION

The valorization of wood sawdust through hot water extraction towards the production of hemicelluloses as materials was first evaluated by laboratory scale extractions. The extraction temperature and time clearly affect the yield of extraction and the chemical composition of the extracts. Based on the results of the laboratory scale extractions, pilot scale extractions were carried out for the first time in a dissolving pulp mill, using the existing extraction reactor

in the pulping line. The pilot scale extractions were proved feasible, in spite of the challenges found in upscaling. The highest yield in the pilot scale extraction obtained was about 112.6 mg/g, using the extraction temperature of 170 °C with the P-factor of 600. Overall, the extraction yields of the pilot scale extractions were lower than those of the laboratory scale extractions at the same extraction temperature and time. In order to compensate the decrease in the extraction yield, longer reaction times are required for pilot scale extractions. This study provides important information for the development of industrial processes to produce hemicelluloses in a next generation biorefinery plant.

ACKNOWLEDGEMENTS: TomásNuñez would like to thank Arauco for financial support. This work was also part of the activities at the Johan Gadolin Process Chemistry Centre, Center of Excellence appointed by Åbo Akademi University.

REFERENCES

[1] J. Helmerius, V. Von Walter, U. Rova, A. Berglund and D. Hodge, *Bioresour. Technol.*, **101**, 5996 (2010).
[2] L. Kang, D. Cullinan and Y. Lee, *Procs. BioProExpo & Marketplace*, Atlanta, GA, March 14-16, 2011, p. 1.
[3] T. Song, A. Pranovich and B. Holmbom, *Bioresour. Technol.*, **102**, 10518 (2011).
[4] T. Song, A. Pranovich and B. Holmbom, *Bioresour. Technol.*, **130**, 198 (2013).
[5] T. Song, A. Pranovich, I. Sumerskiy and B. Holmbom, *Holzforschung*, **62**, 659 (2008).
[6] J. Rissanen, H. Grénman, C. Xu, S. Willför, D. Yu Murzin *et al.*, *ChemSusChem*, **7**, 2947 (2014).
[7] P. Kilpeläinen, S. Hautala, O. Byman, J. Tanner, R. Korpinen *et al.*, *Green Chem.*, **16**, 3186 (2014).
[8] Eurostat, <http://epp.eurostat.ec.europa.eu/portal/page/portal/forestry/introduction>, accessed in January, 2013.
[9] A. Mamman, J. Lee, Y. Kim, I. Hwang, N. Park *et al.*, *Biofuels Bioprod. Bioref.*, **2**, 438 (2008).
[10] F. Gírio, C. Fonseca, F. Carvalheiro, L. Duarte, S. Marques *et al.*, *Bioresour. Technol.*, **101**, 4775 (2010).
[11] J. Zeikus, Y. Lee and B. Saha, in "Enzymes in Biomass Conversion", Washington, USA, American Chemical Society, 1991, pp. 36-51.
[12] D. Dax, P. Eklund, J. Hemming, J. Sarfraz, P. Backman *et al.*, *BioResources*, **8**, 3771 (2013).
[13] C. Xu, C. Eckerman, A. Smeds, P. Eklund and S. Willför, *Nordic Pulp Pap. Res. J.*, **26**, 167 (2011).
[14] A. Leppänen, C. Xu, J. Liu, X. Wang, M. Pesonen *et al.*, *Macromol. Rapid Commun.*, **34**, 1056 (2013).
[15] C. Xu, A.-S. Leppänen, P. Eklund, R. Sjöholm, B. Holmlund *et al.*, *Carbohyd. Res.*, **345**, 810 (2010).
[16] C. Xu, S. Willför, K. Sundberg, C. Pettersson and B. Holmbom, *Cellulose Chem. Technol.*, **51**, 57(2007).
[17] K. Mikkonen, M. Tenkanen, P. Cooke, C. Xu, H. Rita *et al.*, *LWT – Food Sci. Technol.*, **42**, 849 (2009).
[18] K. Mikkonen, A. Mathew, K. Pirkkalainen, R. Serimaa, C. Xu *et al.*, *Cellulose*, **17**, 69 (2010).
[19] D. Dax, C. Xu, O. Langvik, J. Hemming, P. Backman *et al.*, *J. Polym. Sci. Part A*: *Polym. Chem.*, **51**, 5100 (2013).
[20] D. Dax, M. Chavez, C. Xu, S. Willför, R. Mendonca *et al.*, *Carbohyd. Polym.*, **111**, 797 (2014).
[21] M. Söderqvist-Lindblad, A.-C. Albertsson and E. Ranucci, in: "Hemicelluloses: Science and Technology", ACS Symposium Series, vol. 864, 2004, p. 347.
[22] A. Sundberg, K. Sundberg, C. Lillandt and B. Holmbom, *Nordic Pulp Pap. Res. J.*, **11**, 216 (1996).
[23] A. Sundberg, S. Willför, P. Rehn and B. Holmbom, in *Procs. 12th International Symposium on Wood and Pulping Chemistry*, Madison, 2003, vol. 2.
[24] S. Willför, A. Sundberg, J. Hemming and B. Holmbom, *Wood Sci. Technol.*, **39**, 245 (2005).
[25] J. Rissanen, H. Grénman, C. Xu, J. Krogell, S. Willför *et al.*, *Cellulose Chem. Technol.*, **49**, 449 (2015).
[26] Y. Lai, in "Wood and Cellulose Chemistry", New York, Mercel Dekker, 2001, p. 443.
[27] C. Xu, A. Pranovich, L. Vähäsalo, J. Hemming, J. Holmbom *et al.*, *J. Agr. Food Chem.*, **56**, 2429 (2008).
[28] C. Xu, A.-S. Leppänen, P. Eklund, R. Sjöholm, P. Holmlund *et al.*, *Carbohyd. Res.*, **345**, 810 (2010).
[29] T. Hannuksela, M. Tenkanen and B. Holmbom, *Cellulose*, **9**, 251 (2002).