

Pretreatment and Cooking of Forest Residues

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The aim of this work was to investigate the possibility of processing forest residues by chemical delignification preceded by mild steam explosion. The focus was on using soda pulping, due to its simplicity. Kraft cooking was used for comparison to improve the understanding of the separation of the complex yet promising resource. The raw material consisted of chipped branches, bark, and twigs of mixed hardwood and softwood. Analysis of the raw material proved to be challenging due to the presence of a substantial fraction of extractives. Analysis of the pulps showed that the forest residue delignification was faster than that of wood. The effects of steam explosion were evaluated with the help of composition analysis, gel permeation chromatography (GPC) for the molecular weight of lignin, and NMR for the changes in its structure. The impact of steam explosion was found to be limited, possibly due to the relatively small size of the material.

Keywords: Forest residues; Steam explosion; Pretreatment; Kraft cooking; Soda cooking

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INTRODUCTION

In the light of global climate change, there is an urgency to find replacements for fossil-based materials, chemicals, and fuels. While fuel-related applications (e.g. transportation and heat pumps) will most likely be replaced over time by alternatives based on electric power, the only solution for materials and chemicals is to produce replacement products from various types of biomass. Among the different types of biomass available, wood is the most abundant on land. It is already used for a variety of products. Sawn timber and various paper products are the dominating material applications, although wood is also currently used as fuel. Biomass is renewable, is a virtually zero net generator of carbon dioxide, has a relatively low raw material cost (particularly if biomass residue is used), and has a promising perspective of being able to use, at least partially, existing technologies and infrastructure.

Wood can be characterized as a complex bio-composite with structural elements on different size-scales. Wood fibers are a structural element that are used on a large industrial scale. These are various types of cells in the wood that have a length on a millimetre scale and a diameter on a micron scale. The cell walls are built up of nanostructures of cellulose embedded in a matrix of lignin and hemicelluloses, bound together by the middle lamella, which consists mainly of lignin. The fibers are extracted from wood by a chemical pulping process and are used mainly to produce different paper products. The part of the tree used for this purpose is the stem, since it is where the best fibers are found and the morphology

is reasonably homogeneous.

Replacing many of the fossil-based products used today means that the smaller structural elements are of great interest. For chemicals and fuels, it is the monomers, for textiles (*e.g.*, viscose), it is the cellulose polymers, and for many materials, it is a combination of polymers and nanostructure elements. Therefore, for these applications it is unnecessary to use the stem wood. Branches and other residual materials will, in most cases, provide the same type of components. Branches and non-stem wood are often considered to be residue and are thus priced much lower than stem wood.

Although the forest residues, *e.g.*, bark, tops, and branches, resulting from harvesting trees are quite a diverse mixture of different tissues, they are comprised mostly of wood and bark. The outer bark of a tree serves for protection, so its composition and structure are therefore quite different compared to the xylem. Firstly, the content of extractives is considerably higher due to the greater amount of various resin acids. In Scots pine (*Pinus sylvestris*), extractives form 25.2 wt% in the bark compared to 5 wt% in the xylem. In Norway spruce (*Picea abies*), extractives form 32.1 wt% in the bark and 2.0% in the xylem. In silver birch (*Betula pendula*), extractives form 25.6 wt% in the bark and 3.8 wt% in the xylem (Räisänen and Athanassiadis 2013). Bark also contains more lignin, which generally has a similar structure to xylem lignin. However, the ratio of the different units and structures may vary. In pine bark, lignin has more condensed structures compared to stem wood, a higher molecular weight, and a high polydispersity (Huang *et al.* 2011). Secondly, bark contains lower amounts of polysaccharides than stem wood. Cellulose is reported to have shorter fibers and a lower degree of crystallinity (Fengel and Wegener 1984), the composition of the hemicelluloses is different, and there are higher amounts of pectins (Krogell *et al.* 2012; Le Normand *et al.* 2012). Finally, bark contains structures such as polyphenols (tannins in softwood) and suberin (in birch) that are not present in other parts of the tree.

Using forest residues as a resource is promising but poses some challenges. First, forest residue is comprised of a mixture of materials originating from various sections of the tree as well as from different species, which results in morphologically and chemically inhomogeneous material. Moreover, assigning the composition accurately is extremely difficult, as traditional methods are designed for purposes important to the pulp and paper industry and not for extractive rich materials. There are several consequences to these challenges. The mass balance may be poor, the lignin content may be overestimated due to the extractives precipitating with the Klason lignin, and the carbohydrate analysis may be distorted (Huang *et al.* 2011; Kempainen *et al.* 2012; Krogell *et al.* 2012; Burkhardt *et al.* 2013). Moreover, bark and wood tissues have a different morphology and chemistry, so the mass transport of chemicals and reaction products as well as the chemical reactions will be influenced. This implies that the bark and the wood tissues will be influenced differently (*e.g.* the yield of the various components will differ).

Despite the difficulties mentioned above, several ideas for using forest residues can be found in the literature, such as pyrolysis for bio-oil and biogas (Janzon *et al.* 2014), separation of tannins from bark (Kempainen *et al.* 2014), producing cellulose nanocrystals (Le Normand *et al.* 2014; Moriana *et al.* 2016), or cellulose based nanocomposites and polymeric materials (Moriana *et al.* 2015; Li *et al.* 2016).

It is worth noting that when the target products are of nanoscale or smaller constituents, the freedom of choosing the type of process and conditions is much more extensive compared to traditional pulp processes, since the fiber properties are not important. Today, the dominating process for recovering cellulose from wood is the kraft

pulping process, whereby fibers are liberated by dissolving the lignin by the active chemicals, which are the hydroxide and hydrogen sulphide ions. The kraft process also results in the degradation of a large part of the hemicelluloses and the disintegration of some of the cellulose. Another method, called soda cooking, uses only hydroxide ions as the active chemical. It is less efficient and requires a prolonged time to achieve the same extent of delignification, resulting in lower yields of both hemicelluloses and cellulose. However, the soda cooking process is robust, requires a less expensive chemical recovery system, and generates sulphur-free lignin (which is currently in demand).

Because the hemicelluloses are degraded (forming mostly different kinds of monomeric carboxylic acids) under alkaline conditions, they must be removed prior to the alkaline cooking if they are to be recovered. Therefore, pretreatment can be advantageous. Among the pretreatment methods available, mild steam explosion (STEX) allows for the recovery of hemicelluloses and enhances the accessibility of the remaining constituents in the wood with minimal degradation of the native structure. Mild steam explosion relies on autohydrolysis, a process by which the acidic conditions generated by the deacetylation of hemicelluloses lead to the hydrolysis of labile glycosidic bonds (Lora and Wayman 1978; Garrote *et al.* 1999; Laser *et al.* 2002). The dissolved hydrolysis products are transported out of the wood tissue by diffusion and by advective transport triggered by the pressure discharge. The explosion renders changes in the wood tissue, increasing accessibility for further treatment (Jedvert *et al.* 2012). More severe conditions (*i.e.* higher temperatures, the addition of acid) enable a more efficient extraction upon steam explosion. However, severe conditions also lead to the degradation and extraction of monomers, whereas mild pretreatment yields polymeric hemicelluloses (Abatzoglou *et al.* 1990; Jedvert *et al.* 2014). Some reports show that steam explosion can increase the enzymatic hydrolysability of bark (Kemppainen *et al.* 2012).

Given the previous research, there are a number of options for future material biorefineries. For large-scale bulk production, there are several different acid or alkaline-based treatments that are promising. The choice of process must take into consideration the fact that all the wood constituents will be affected, to some extent, in the acid or alkaline environments of the different treatment steps. In a strongly acidic environment, all carbohydrates will be depolymerized and the lignin will be heavily condensed. In a relatively strong alkaline environment, some of the lignin will be depolymerized. The influence on the structure of cellulose will be limited, while the hemicelluloses will be heavily degraded. Consequently, the process should be designed for the desired product.

In a material biorefinery, the main constituents of wood must be separated in such a way that losses and changes to the structure of the different constituents are minimized. One method for recovering at least some of the hemicelluloses in the polymeric or oligomeric form is to start with a mild weak acid extraction of the wood and then apply an alkaline method to separate the cellulose from the lignin. Soda pulping is a good option here, as it is simpler than the kraft process, and has a less complicated and more economical chemical recovery system. Moreover, other parts of the process, such as the pulp washing unit, can be constructed more cost-efficiently. However, the heart of the process is the separation of the cellulose and the lignin, and the overall kinetics of soda cooking is substantially slower than kraft cooking. On the other hand, it has been shown that the delignification kinetics increase when the wood material is pretreated with mild steam explosion, which is a relatively mild, weakly acidic method that may be used for the extraction of hemicelluloses (Jedvert *et al.* 2013).

In this study, forest residues were explored as a raw material for processing by soda

cooking preceded by mild steam explosion. The efficiency of soda delignification of this material both with and without steam explosion pretreatment was investigated and compared to kraft delignification in order to shed light on the decoupling possibilities of this complex, but attractive raw material.

EXPERIMENTAL

Materials

The forest residue samples (branches, bark, and twigs) were provided by Domsjö Fabriker (Örnsköldsvik, Sweden). The forest residue consisted of a mixture of softwood (mostly spruce and pine) and hardwood (mostly birch). The material was chipped into uniform size prior to shipping. All chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received.

Methods

Steam explosion

Fractions of the forest residue material were pretreated using bench-scale steam explosion equipment. For each pretreatment process, 500 g of forest residue was loaded into the top chamber and heated with saturated steam from the boiler until the pressure in the vessel reached either 4 or 7 bar. The material was kept under pressure for 15 min and then discharged rapidly into the lower chamber of the apparatus.

Refining

The forest residues were homogenised using a Sprout-Waldron 12-1CP 12-inch disc refiner (Muncy, USA). Prior to refining, the material was warmed up by steam at 125 °C for 15 min. The resulting samples were then stored at -20 °C.

Kraft cooking

The forest residue samples were cooked using 50 g of oven-dried material, a liquor-to-wood ratio of 9:1, an effective alkali of 29%, a sulphidity of 35%, and a carbonate concentration of 0.1 M. The high liquor to wood ratio was chosen in order to assure as constant as possible chemical conditions during entire cooking process.

The material and liquor were charged into a 1.2 L steel autoclave, which was placed in a polyethylene glycol bath. The cooker was preheated to 80 °C. After a 20 min heating up period, the temperature was increased to 170 °C at a rate of approximately 1 °C/min. Once the target temperature was reached, the material was cooked for either 30 min, 60 min, 90 min, 120 min, or 180 min. The pulp was separated by filtering it through a woven polypropylene mesh and washing with 10 L of water. The solid material obtained was defibrillated for 10 min in a L&W Noram pulp defibrillator (Lorentzen and Wettre, Kista, Sweden) at 3000 rpm, before the solids were re-filtered once and washed with 2 L of water.

Soda cooking

The soda pulping conditions were the same as the kraft cooking conditions, apart from the liquor composition. Sodium hydroxide was the only active chemical in the soda cooking, and its concentration was adjusted to reach the same concentration of hydroxide ions as used in the kraft cooking process (0.37 mol/kg liquor).

Dry content and yield

The dry content of the samples was determined by drying them in an oven at 105 °C overnight. The solids fraction yield was determined as a proportion of the dry mass and the initial mass of the material.

Precipitation of lignin

The spent liquors from both soda and kraft cooks were acidified to a pH 2.5 at room temperature to precipitate the lignin. Subsequently, the lignin was separated and washed with water and the pH was adjusted to 2.5. The lignin obtained was dried for 3 d at 40 °C.

Chemical characterisation

The wood and pulp samples were subjected to complete acid hydrolysis using 72% sulphuric acid. The residual solid material was termed Klason lignin, the amount of which was determined gravimetrically. The filtrate from the hydrolysis process was used to determine the contents of the acid soluble lignin (ASL) and the carbohydrates.

The ASL content was calculated based on the absorbance measured with an ultraviolet (UV) spectrometer at a wavelength of 205 nm in a Specord 205 (Analytik Jena, Jena, Germany). The absorptivity constant was assumed to equal 110 dm³/g¹cm¹.

The composition of the carbohydrates was determined as the amount of monomeric sugars by using high performance anion exchange chromatography (HPAEC). A Dionex ICS-5000⁺ system (Sunnyvale, USA) equipped with a CarboPacTM PA1 column and an electrochemical detector was used for the HPAEC determination, and NaOH and NaOH + NaAc were used as eluents. The software used was the Chromeleon 7, Chromatography Data System, Version 7.1.0.898 (Thermo Fischer Scientific, Waltham, MA, USA). The amounts detected were corrected to the hydrolysis yield. The hydrolysis yield was calculated from experimental data, established by performing acid hydrolysis on pure monosugar standards, as the ratio of the amount detected to the mass of the sample used. Arabinose was found to be 93.1% ± 1.9%, galactose was 92.9% ± 1.7%, glucose was 91.8% ± 2.0%, xylose was 78.6% ± 1.6%, and mannose was 90.2% ± 0.6%.

Extractives

The amount of solvent-soluble, non-volatile material in the raw material was quantified using the TAPPI T204 cm-07 (2007) standard method with acetone as the solvent. The final extractive content was then calculated as a fraction of the original sample of dry forest residue.

Gel permeation chromatography (GPC)

The molecular weight of the precipitated lignin fraction was determined by size-exclusion chromatography using a PL-GPC 50 Plus (Varian, Church Stretton, UK) integrated system connected to refractive index (RI) and ultraviolet (280 nm) detectors. The system was equipped with two columns, a PolarGel-M and a PolarGel-M Guard (300 mm × 7.5 mm and 50 mm × 7.5 mm) (Agilent, Santa Clara, USA) with 8 µm mixed size pores. The mobile phase consisted of dimethyl sulphoxide (DMSO)/LiBr (10 mM) with a flow rate of 0.5 mL/min. Samples with a concentration of 250 mg/L were dissolved in mobile phase DMSO/LiBr (0.01 mol dm³), and filtered through a GHP Acrodisc syringe filter (Pall Corporation, Port Washington, NY, USA) (d = 13 mm, 0.2 µm GHP membrane).

Gas chromatography-mass spectrometry (GC-MS) and flame ionized detection (FID)

An Agilent 7890A gas chromatographic system equipped with parallel FID and mass spectrometer (MS) detection (Agilent, Santa Clara, CA, USA) operating in an electron ionisation mode was used to analyze the volatile compounds in the evaporated crude extractive residues. The derivatives were protected by trimethylsilyl (TMS) and were semi-quantified using the internal standard of heptadecanoic acid methyl ester. A 10 mg residue sample was dissolved using 0.6 mL of ethyl acetate and 15 mg to 25 mg of the internal standard, *i.e.* heptadecanoic acid methyl ester (15 mg to 20 mg/0.9 g to 1.1 g ethyl acetate), was added to the sample. The solution was then derivatized with 0.1 mL of 99:1; N, O-bis(trimethylsilyl)trifluoroacetamide: chlorotrimethylsilane) (BSTFA) and TMS reagent. After 30 min, 1 μ L of the solution was injected *via* an autosampler into the gas chromatographic system. Once injected, the analytes were split up and separated into two chromatographic columns (HP-5MS, Agilent, Santa Clara, CA, USA). The columns were 30 m long, had a 0.25 mm internal diameter, and were 0.25 μ m thick at the stationary phase. Helium was used as the carrier gas with a flow rate of 1 mL/min for the MS column and 0.6 mL/min for the FID column. The temperatures for the system were set to 300 °C for the injector, 250 °C for the FID detector, and 50 °C for the GC oven for 2.25 min before being raised to 300 °C at a rate of 2 °C/min. Thereafter, the temperature of the GC oven was set at 300 °C for 30 min. The temperature of the MS source and the quadrupole were set to 250 °C and 150 °C, respectively. The NIST MS search program (Version 2.0) operating on the NIST/EPA/NIH Mass Spectral Database 2011 (NIST 11) was used for the spectral interpretations.

NMR

The $^1\text{H}^{13}\text{C}$ HSQC NMR spectra of precipitated lignin were recorded (*ca.* 100 mg in 0.75 mL of DMSO- d_6). The phase-sensitive qualitative $^1\text{H}^{13}\text{C}$ HSQC NMR spectra were all recorded at 25 °C on a Bruker AVANCE III HD 18.8 T NMR spectrometer (Rheinstetten, Germany) equipped with a 5 mm TCI Cryoprobe (cold ^1H and ^{13}C channels) operating at a frequency of 800 MHz for ^1H and 201 MHz for ^{13}C . The ^1H spectra were recorded at a 30° pulse angle, a 6 s pulse delay, 1024 scans, and 2.04 s acquisition time. The phase-sensitive qualitative HSQC spectra were recorded at a standard Bruker pulse sequence “hsqcetgpcisp 2.3” with a 0.25 s ^1H acquisition time, a 5.3 μ s ^{13}C acquisition time, a 3 s interscan delay, and a $^1\text{J}_{\text{C-H}}$ coupling constant of 145 Hz. Eight scans were conducted, and each spectrum was recorded for 4 h.

The NMR spectra were processed and analyzed by means of the default processing template of MestReNova version 10.0.0 software (Mestrelab, Santiago de Compostela, Spain), along with automatic phase and baseline correction.

RESULTS AND DISCUSSION

The forest residues used in this study were a mixture of xylem and bark tissue taken from various parts of the tree and from different tree species. Figure 1 shows images of the mixture as well as the wood chips (possibly originating from stem wood and bigger branches), small branches, and bark handpicked from the starting material. In order to learn more about the composition of the different main fractions, these were considered separately when the mixture was analysed, as can be seen in Table 1.



Fig. 1. The material analyzed: untreated, steam exploded, and refined forest residues and the separated fractions: wood chips, bark, and branches.

The “other fraction,” corresponding to the undetected compounds, is substantial and especially so for the bark and branches. As mentioned above, this is a result of the high percentage of extractives and other organic compounds (ash was determined to constitute 0.8 wt% of the sample (Martinsson, 2017)) present in these sections of the tree. Extractives can form up to 20% of spruce, 30% of pine, and 40% of birch bark in weight (Räisänen and Athanassiadis 2013). Moreover, extractives contribute to high contents of Klason lignin in these fractions when compared to wood (xylem), as some extractives co-precipitate with lignin during acid hydrolysis. The arabinose content is relatively low in the wood material but higher in the bark and branches due to the arabinans and pectins present in the bark. The fraction of galactose in the branches is also substantial, possibly due to the presence of reaction wood.

Table 1. The Composition of the Corresponding Samples [^]

Sample	Ara (%)	Gal (%)	Glu (%)	Xyl (%)	Man (%)	Klason (%)	ASL (%)	Other (%)
Bark Fraction	3.9	1.9	18.1	5.7	1.7	47.0	0.9	21.7
Branches Fraction	2.3	3.8	26.3	10.1	4.4	36.4	0.3	16.8
Wood Fraction	0.5	0.9	37.8	22.4	3.5	22.4	0.7	12.6
Refined Material	1.2	1.6	36.7	14.2	5.5	30.4	0.2	10.3
*	(0.1)	(0.1)	(1.3)	(1.6)	(0.3)	(1.1)	(0.0)	(1.7)

*The deviation found from 3 samples

[^] Amounts of anhydrosugars sugars and klason lignin present are expressed as a weight fraction.

Obtaining an estimate of the overall composition of the material was made possible by refined residues which were milled to increase their homogeneity further, and three samples were analysed. The deviation obtained is in a similar range as obtained previously for stem wood, although measurement was only possible after taking two homogenization steps (refining and milling).

Analysis of the extractives content in the refined residues revealed that it is 4.2% of the material (16.9% of the total extractives was characterized and is presented in Table 2). The procedure was performed on refined samples, which means that the content of extractives in the original material could be even higher, as some of the extractives can be vaporised during steaming and refining. The presence of extractives typical of softwoods (such as isopimaric acid, dehydroabietic acid, and abietic acid), as well as those more commonly found in hardwood (such as β -sitosterol and betulin) (Fengel and Wegener 1984), indicate that the material is a mixture of softwood and hardwood (Table 2). However, the relatively low contents of lignin (30.4%) and mannose (5.5%), together with a high xylose content (14.2%), suggests a high fraction of hardwood (Table 1) (Räisänen and Athanassiadis 2013; Teleman 2016). Moreover, comparison of the detected xylan fraction in the wood fraction to the composition of softwood and hardwood reported in the literature (7.6% xylose in softwood and 24.6% in hardwood) allowed estimating the hardwood fraction to be approximately 87% (Rydholm 1965).

Table 2. Extractives Content in Forest Residues, Expressed as Fraction of the Obtain Extract

Extractive	Amount (%)
Linoleic Acid	2.8
Octadecanoic Acid	2.9
Isopimaric Acid	1.3
Dehydroabietic Acid	3.7
Abietic Acid	2.0
β -Sitostero	1.6
Betulin	2.6

Steam explosion

Steam explosion caused changes in the macrostructure (physical defragmentation was obvious) as well as the chemistry (change in color and chemical composition) of the material. The results of the chemical analysis are presented in the Table 3, where the amounts of the components are presented as the weight percent of the sample and not of the original material. An obvious change is the decrease of the “other fraction.” One plausible explanation for this is that some of the extractives were dissolved or solubilized and/or evaporated during steam pretreatment. On the other hand, some of the extractives may have also condensed with the lignin during the treatment or precipitated with it during the acid treatment in the Klason analysis (Burkhardt *et al.* 2013). Both of these changes in extractives, *i.e.* the removal through solubilisation/evaporation and condensation/co-precipitation with lignin, could account for the small increase in the Klason lignin fraction observed in material that underwent STEX treatment performed at 7 bar. The decrease of the “other fraction” is probably the reason for the apparent increase of glucose. The overall mass of the material decreased as some fractions were extracted. In the meantime, the amount of cellulose (the main source of glucose) remained stable and thus formed a larger fraction of the material, resulting in a relative increase in the glucose content. Keeping this in mind, the relatively stable content of sugars originating from hemicelluloses suggests that small fractions of hemicelluloses were removed. If it were completely stable, a relative increase in the content of hemicelluloses would otherwise have been observed. The removal of hemicelluloses was limited and, in general, seemed to have very limited effects on xylan, whereas the mannan content decreased with treatment at 7 bar. The steam

explosion experiments in this study were performed on refined material. Previous studies have shown that the size of the treated wood influences the effect of the treatment, showing a higher impact for larger chips (Ballesteros *et al.* 2000; Jedvert *et al.* 2012; DeMartini *et al.* 2015). Since both the type and the size of the material differ, there may be several reasons for the difference, *e.g.* the high content of extractives or that the pressure difference in the refined solid material, as used here (the explosion effect), has very small or no influence when the whole sample is subjected to the sudden drop in pressure. Interestingly, despite rather modest compositional changes, steam explosion rendered more profound effects on the further delignification of the forest residues, as will be discussed later in the paper.

Delignification of forest residues

Forest residues were subjected to the kraft and soda pulping processes. The hydroxide ion concentration was 0.37 mol/kg liquor in both types of treatment. In the kraft cook, 0.19 mol/kg liquor hydrogen sulphide ions and 0.1 mol/kg solution carbonate ions were added. The cooking times ranged from 30 min to 180 min, and the pulps and precipitated lignin obtained from the black liquors were analysed for composition. The results are presented in Table 4. Some of the extractives were probably volatilized during refining and were thus not detected in the analysis. The “other fraction” is much smaller for the pulps than for the steam exploded material shown in Table 3, most likely indicating the dissolution of the extractives during the cooks. Consequently, the mass balance was improved. The yields obtained were relatively diverse but notably higher for the soda pulps (reflecting the higher lignin content). The cooking process appeared to follow the typical wood cooking process. The rapid removal of lignin and carbohydrates in the beginning was followed by a slower process, although there were several differences in the cooking efficiency. As expected, the kraft cooking process accomplished a more efficient delignification rate. Compared to previous studies, the pulps obtained here from forest residues contained less lignin than the corresponding kraft (Jedvert *et al.* 2013) and soda cooks of wood (Wigell *et al.* 2007). This may be because the forest residues that were studied had a different structure.

Table 3. Compositions of the Refined, Untreated, and Steam-Exploded Material, Given in wt% of the Refined Wood Residues

STEX (bar)	Ara (%)	Rha (%)	Gal (%)	Glu (%)	Xyl (%)	Man (%)	Klason (%)	ASL (%)	Other (%)
-	1.2	1.6	1.1	36.7	14.2	5.5	30.4	0.2	10.5
4	1.0	1.6	1.1	38.0	15.7	5.7	29.1	0.1	8.7
7	0.7	1.6	1.1	39.6	15.6	5.3	31.1	0.1	6.1

A comparison between the steam-exploded and untreated material cooked for 60 min shows that the pulps had similar contents of Klason lignin. This is in contrast to the behavior observed previously for wood, where the pretreatments enhanced the delignification (Jedvert *et al.* 2013). The difference can be related to the effect of the size of the material being treated. While the Klason lignin content was the same in the pulps, it was higher in the precipitates obtained from the black liquor of the pretreated samples. This discrepancy can be a result of the generation of pseudo-lignin (lignin condensed with degradation products from hemicellulose) during steam explosion (Heitz *et al.* 1991).

Table 4. Composition of the Pulps and Precipitate from Acidified Black Liquor

Pretreatment	STEX (bar)	-	-	-	-	4	7	-	-	-	-	4	7	7
Cooking Conditions	Type	-	kraft	kraft	kraft	kraft	kraft	soda	soda	soda	soda	soda	soda	soda
	Time (min)	-	30	60	120	60	60	30	60	120	180	60	60	180
	Yield (wt%)	-	42.2	44.7	39.8	39.0	45.7	46.6	48.8	50.1	42.2	51.2	49.5	49.5
Pulp Composition (wt% on Initial Material)	Ara	1.16	0.16	0.13	0.08	0.09	0.10	0.28	0.25	0.15	0.10	0.21	0.14	0.10
	Gal	1.60	0.22	0.16	0.08	0.11	0.11	0.33	0.31	0.23	0.15	0.29	0.19	0.14
	Glu	36.69	32.66	33.85	29.69	29.17	35.47	27.47	29.49	34.69	27.02	29.11	25.42	35.08
	Xyl	14.17	6.32	7.24	6.52	7.17	6.25	6.57	6.81	7.93	6.56	7.31	6.49	6.48
	Man	5.50	1.33	1.41	1.18	1.08	1.18	1.24	1.35	1.48	1.47	1.64	1.18	1.31
	Klason	30.37	3.64	2.53	1.53	2.53	2.43	8.65	8.97	5.81	4.29	8.48	8.87	5.69
	ASL	0.12	0.41	0.31	0.39	0.38	0.27	0.66	0.63	0.56	0.00	0.54	0.50	0.25
	Other	10.27	-2.52	-0.93	0.31	-1.49	0.17	1.46	1.02	-0.70	2.59	3.60	6.75	0.70
Precipitate (wt% on Lignin)	Ara	-	0.6	0.6	0.4	0.5	0.2	0.7	0.7	0.5	0.4	0.5	0.3	0.1
	Gal	-	0.4	0.6	0.4	0.5	0.2	0.4	0.5	0.5	0.5	0.4	0.2	0.1
	Xyl	-	7.3	6.3	2.3	5.0	1.2	13.8	10.2	5.3	3.3	8.8	2.6	0.2
	Klason	-	71.2	71.9	66.1	73.5	78.7	70.8	72.9	76.1	76	73.2	82.3	77

Changes in the carbohydrate composition for the different pulping times show interesting trends (Fig. 2, Table 4). In general, kraft cooking of wood causes the degradation of about 75% of the galactoglucomannan (GGM) and 40% of the arabinoglucuronoxylan (AGX) in softwood (Sjostrom 1977). Hemicelluloses face rapid dissolution and peeling during the heating-up (GGM) and in the beginning of the cooking (both GGM and AGX) phases, followed by the alkaline hydrolysis of glycosidic bonds and secondary peeling later in the cook. When cooking forest residues, the arabinose, galactose, and mannose seem to follow this behavior. However, as the cook progresses, the amount of xylan decreased roughly by half and the remaining amount was relatively stable, albeit showing a minimal increase with time (Fig. 4).

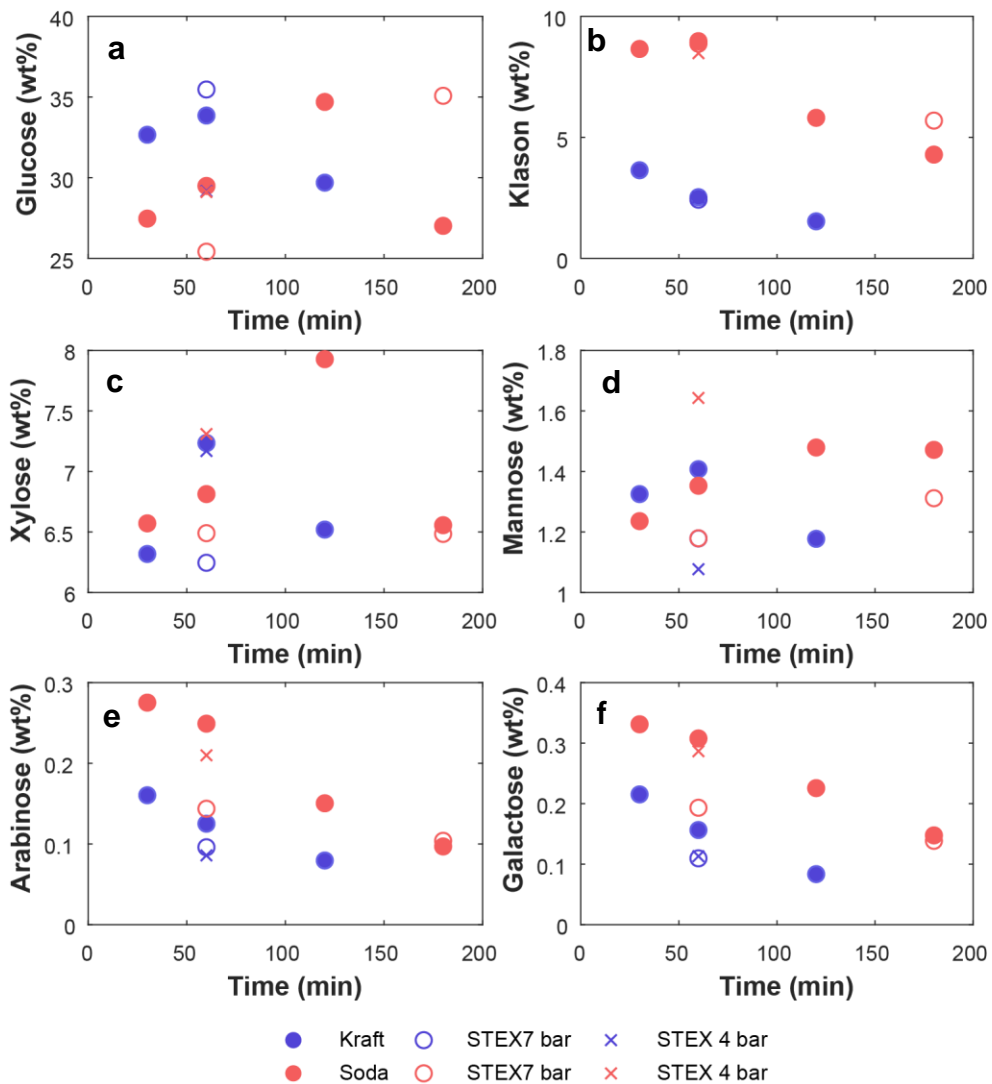


Fig. 2. Changes in the sugar and lignin composition upon cooking for 30 min to 180 min (as wt% of the initial material). The solid circles represent material with no pretreated prior cooking, solid circles material steam exploded at 7 bar prior to cooking and crosses material steam exploded at 4 bar prior to cooking. (a) glucose, (b) Klason, (c) xylose, (d) mannose, (e) arabinose, and (f) galactose

This trend follows the changes in the content of the Klason lignin in the precipitate from the black liquor, although the decrease in the Klason fraction in the precipitate can be also caused by the degradation of xylose molecules attached or coprecipitated with lignin. Moreover, there is no correlation between the contents of xylan and lignin in the pulp. Rather, a co-extraction, shown as a linear relationship between the contents of lignin and xylan attached or coprecipitated with lignin in the pulp, is commonly observed (Fig. 3) for both soda (Wigell *et al.* 2007) and kraft cooking of wood (Matthews 1974).

A possible explanation of the behavior of xylan may be its re-adsorption onto cellulose fibers during delignification, a phenomenon commonly associated with the chemical pulping of wood (Meller 1965; Hansson and Hartler 1969; Hansson 1970), dependent on both the cooking conditions and the concentration of xylan in the liquor. However, the structure and surface properties of the cellulose in forest residues may be different to those in wood, thereby promoting this process and resulting in higher resorption. Another explanation could be that the structure of the hemicelluloses in wood, bark, and forest residues may vary, and the different types/structures of xylan may therefore have different stability and/or different re-adsorption properties.

The soda pulps analysed had a higher fraction of xylan compared to the kraft pulps, which may be due to more lignin carbohydrate complexes being removed in the kraft cooking process or the different structure of xylan itself. It is interesting that steam explosion resulted in a lower content of xylan after 60 min of cooking, independent of the cooking method. Moreover, the material pretreated at 7 bar gave a lower content of xylan in the lignin precipitated from black liquor than in the corresponding untreated material. This can be related to the partial extraction of xylose, and its degradation into furfural, in acidic conditions during steam pretreatment (Abatzoglou *et al.* 1990; Li *et al.* 2005; Janzon *et al.* 2014). The degraded sugars tend to precipitate with the Klason lignin fraction, and for these liquor samples, it was indeed found to be higher.

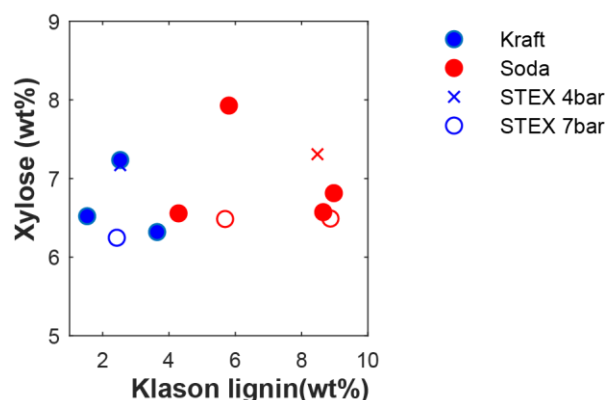


Fig. 3. The xylose and lignin content in the pulp

The glucose content was quite stable and, when compared with uncooked refined material, decreased only slightly. A likely reason for this decrement is the degradation of hemicelluloses, starch, and possibly small fractions of cellulose. It can be related to the cellulose in various elements of the tree having different structures. The cellulose in bark is commonly characterized by a lower crystallinity, a lower degree of polymerization, and higher polydispersity than that in the stem (Fengel and Wegener 1984). The variations in the content of cellulose can be also related to the inhomogeneity of the material. The kraft

cooking process seemed to yield higher contents of glucose than the soda process. If preceded by steam explosion, the cook resulted in pulps with decreased contents of glucose, which is possibly indicative of the changes rendered to the structures during the pretreatment.

An analysis of the molecular weight distribution (MWD) of the lignin precipitated from the black liquors obtained is presented in Fig. 4. The UV response reflects the molecules having an aromatic structure (in this case lignin), whereas the RI signal is more general and shows other structures as well. Consequently, the plots of the RI and UV signals overlap, as the precipitate from acidified black liquor is comprised mostly of lignin. However, at the long elution time, the RI response of all the samples shows a peak indicative of low molecular non-aromatic compounds, likely originating from the extractives and possibly the degradation products.

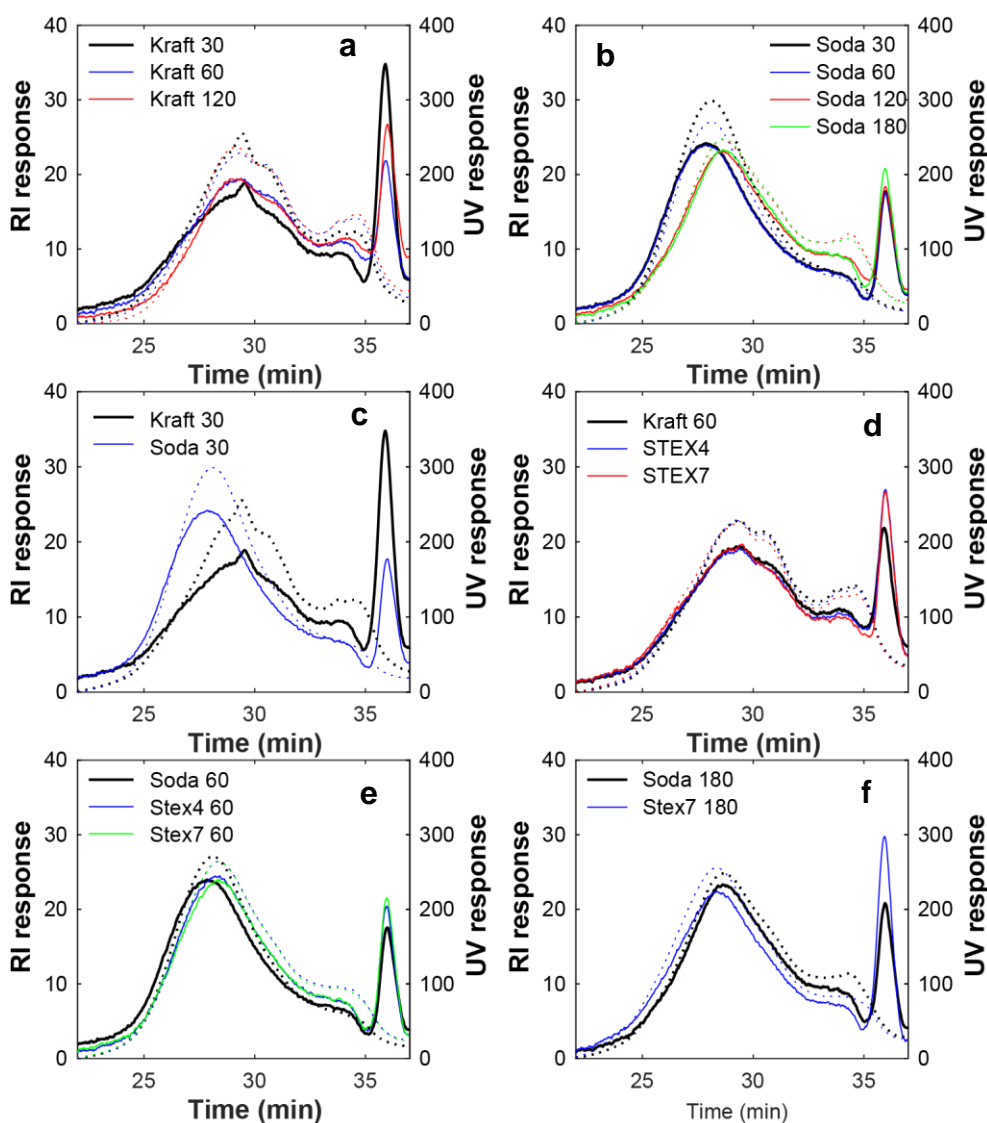


Fig. 4 The GPC results obtained. The RI response is depicted with the solid lines and the UV response is depicted with the dotted lines

Comparing the results of different pulping methods, the soda lignin generally had a higher molecular weight. The reason for this is not fully understood, but a possible explanation may be found in the higher xylan content in the lignin precipitate from the soda cook, indicating a possible higher frequency of lignin-carbohydrate complex (LCC) bonds, or in the lower the ionic strength in soda cooking.

The cooking time had no apparent effect on the GPC curves obtained for the kraft pulping, whereas some effect seems to have been apparent in the soda pulping. Plots obtained for the 30 min and 60 min cooks overlapped, and the prolonged cooking caused a shift toward lower molecular weights, suggesting degradation of the lignin in the liquor. The GPC results reflect the molecular weight distribution after pretreatment and cooking, making it difficult to evaluate the effect of steam explosion itself. The effect of pretreatment will not necessarily be detectable for all the pulping times. Steam explosion has an effect mostly on large lignin fragments (due to condensation) and its effects will therefore not be apparent until these fragments have been transported out from the material, *i.e.* only after long delignification times. In the case of kraft lignin, as Fig. 4 shows, the plots obtained for the untreated and STEX material fully overlapped. For the 60 min soda cook, STEX treatment caused a minimal shift towards longer elution times, suggesting a decrease of the molecular weight. However, when the cook was prolonged to 180 min, the MWD of the lignin in the pretreated sample was shifted towards the higher molecular mass region.

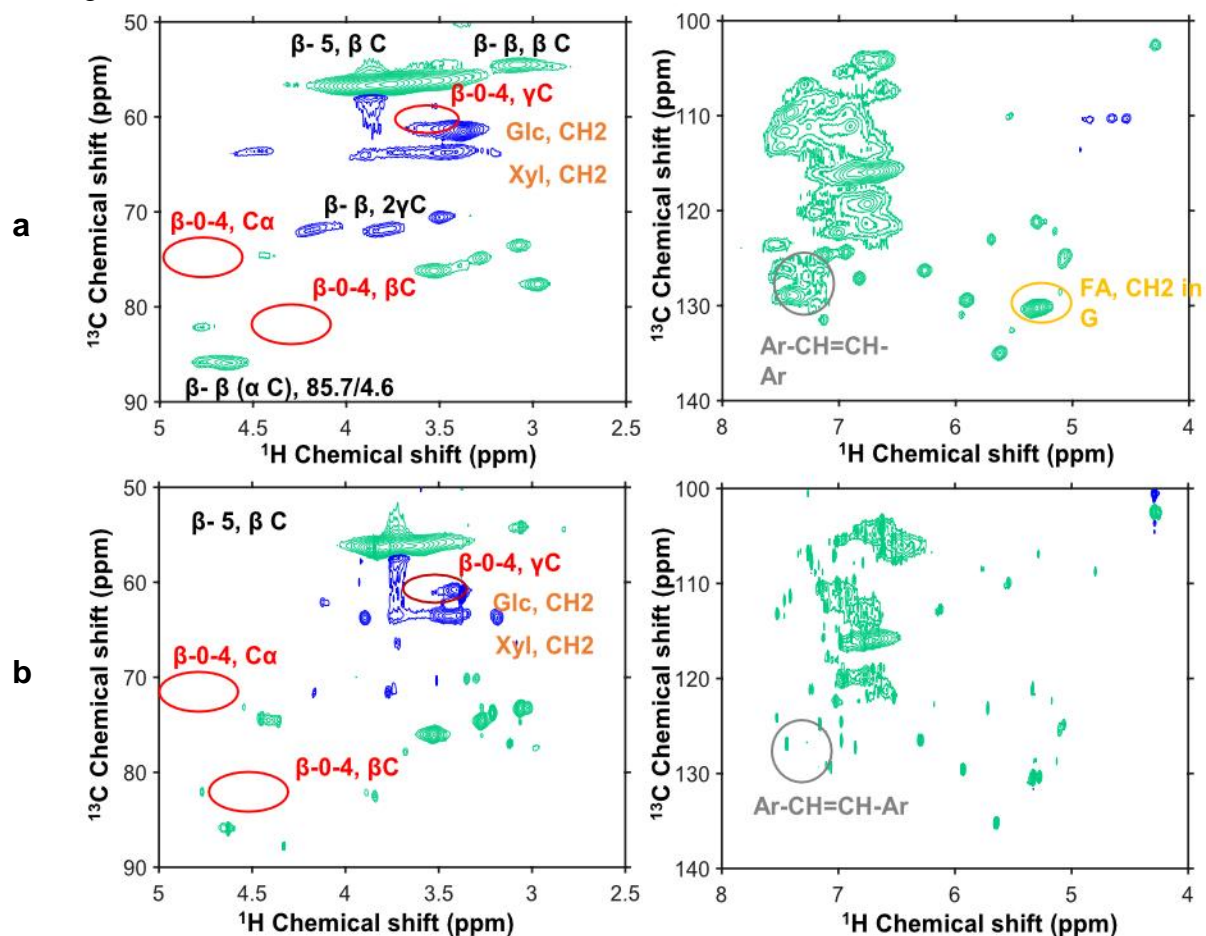


Fig. 5. The NMR-spectra of the lignin-rich fractions extracted in 180 min soda cook of (a) STEX and (b) non-pretreated forest residues

The $^1\text{H}^{13}\text{C}$ HSQC NMR-spectra of the lignin rich fractions extracted in the soda cooks of the forest residues reveal the presence of both S- and G-lignin (106.6/7.32 and 103.8/6.7 ppm) along with considerable amounts of extractives, mainly fatty acids such as $\text{CH}_2\text{-COOH}$ (34.2/2.2 ppm), CH_2 (25/1.5, 29.1/1.1, 31.8/1.2 ppm), and CH_3 (15/0.7 ppm) (Supplementary, Fig. S1). The latter concurs with the low molecular mass signal observed in the MWD chromatograms.

As observed in previous studies, no signals of $\beta\text{-O-4}$ could be found after the soda cooks were performed (Fig. 5a and 5b) (Mattsson *et al.* 2018). It may be noted that the lignin extracts from the soda cook preceded with the STEX treatment (7 bar) gave rise to signals that were absent or vague in the samples cooked without pretreatment, namely signals indicating:

- The increased presence of $\beta\text{-}\beta$ linkages: $\alpha\text{-C}$ (85.7/4.6), βC (54.1/3.1), and $2\gamma\text{C}$ (71.4/4.1 and 74.1-3.8).
- The presence of stilbene structures, ArCH=CHAr (126-129.7/7.0-7.4)
- The increased presence of xylane and hexose residues: Xyl (CH_2 , 62.1-64.3/3.3-3.8) and Glc (CH_2 60/3.-3.8)
- An increased presence of fatty acids such as CH=CH (128.2/5.3 130.1/5.3).

These findings disclose that the mass transport of material is improved during soda cooking upon STEX pretreatment (carbohydrates, extractives, and conjugated/condensed lignin structures). At the same time, they call attention to the possibility that lignin has been condensed during STEX treatment, which is indicated by the occurrence of $\beta\text{-}\beta$ linkage along with the shift to higher molecular weight in the GPC chromatograms.

It should be noted that these structures are also present in native lignin to varying extents. The relatively strong $\beta\text{-}\beta$ NMR signals observed can simply be a result of the enhanced extraction of these structures due to STEX combined with a relatively long delignification time (180 min), as seen in Fig. 5.

CONCLUDING REMARKS

1. The delignification of the forest residues seems to be more rapid than of wood.
2. The behavior of xylan during the delignification of forest residues is different compared to wood. A rapid initial extraction is followed by a rather stable content during the rest of the pulping. The commonly observed co-extraction of xylan-lignin is not observed, possibly indicating its enhanced re-adsorption onto celluloses and/or the occurrence of different types of xylan.
3. The impact of steam explosion was found to be limited when compared to wood, possibly due to particle size. However, there are some indications that pseudo-lignin is formed in pulps during STEX treatment of forest residues, which may be connected to the presence of extractives.

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