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ENGINEERING

**Mild Steam Explosion of Wood and Forest
Residues in the Perspective of a Materials
Biorefinery**

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Cover:

From left: Wood chips of native wood, steam exploded for 15 and 30 min, hot water extracted for 15, 30 and 60 min.

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Abstract

The main objective of this work was to explore the prospects of using mild steam explosion as a pretreatment step in a forest based material biorefinery. During the steam explosion saturated steam is applied to the biomass at elevated pressure leading to an autohydrolysis of the lignocellulosic tissue, which is followed by a rapid pressure discharge, disintegrating and opening up the structure. As a consequence, the pretreatment enables the extraction of the most sensitive hemicelluloses and facilitates further processing, e.g. enzymatic treatment and chemical pulping. To investigate the effects rendered by the pretreatment, it was performed on two different types of forest biomass: Norway spruce wood chips and forest residues of mixed origin. The focus was on investigating the effects on the chemical structure of the material. In order to gain improved understanding of the fundamental mechanisms behind the pretreatment, the local effects on the composition of the wood tissue pretreated using steam explosion were investigated and compared with those accomplished by hot water extraction. Furthermore, cooking experiments were performed on pretreated forest residues to evaluate how the changes rendered by the pretreatment affect further processing of the material. The effects of the steam explosion were evaluated in terms of compositional analysis, molecular weight distribution and structural changes of extracted material (lignin and hemicelluloses). The results show that, due to the advective mass transport during the explosion step, steam explosion accomplishes a more even removal of hemicelluloses from the pretreated wood chips compared to the hot water extraction. Moreover, the impact of the steam explosion was found to be limited when material of a smaller size, namely refined forest residues, was pretreated.

Preface

This thesis is based on the following papers:

I. **Hydrothermal pretreatment of wood by mild steam explosion and hot water extraction**

Joanna Wojtasz-Mucha, Merima Hasani & Hans Theliander
Bioresource Technology, Vol. 241, 2017, pp.120-126.

II. **Pretreatment and pulping of forest residues**

Joanna Wojtasz-Mucha, Cecilia Mattsson, Merima Hasani & Hans Theliander
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Chemical pretreatment of wood chips: a comparative study of mild steam explosion and hot water extraction

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27 – 30 June 2016, *Grenoble, France*

Chemical pretreatment of wood chips: a comparative study of mild steam explosion and hot water

Presented by Merima Hasani

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1

Introduction

Wood was an important resource to humans even before civilization existed. It was first used for tools, weapons and fuels and, in time, as raw material for the production of furniture, paper, etc.. Today it is still of great economic importance. Moreover, as a renewable resource, it can become a key factor in the circular economy by being a raw material for biorefineries. There are many aspects of wood that have been studied in the context of its mechanical properties, as fuel and in pulp and paper applications. Now, focus is shifting and a different perspective for research is opening. There is an urgency for finding a new, more sustainable replacement for fossil-based materials and chemicals, and wood components are potential sources of building blocks for these materials and chemicals. Advantages of using biomass include there being virtually zero net generation of carbon dioxide, it is renewable and relatively low in cost (as in some cases may be considered being a residue) and the promising perspective of using existent technologies and infrastructure at least partially.

In general, wood can be characterized as a complex bio-composite with high recalcitrance towards the separation of its structural elements (i.e. cellulose, lignin and various hemicelluloses). The main structural element that is currently recovered for use in various products is cellulose: this is usually done using a chemical pulping process, most commonly via kraft pulping. In this process, hydroxide and hydrogen sulphide ions are employed for the fairly efficient separation of cellulose by fragmentation and dissolution of the lignin, while the hemicelluloses are depolymerized

and degraded to varying extents. Finally, the cooking liquor, which then contains the extracted sugars, sugar acids and lignin, is incinerated in order to recover heat and the process chemicals. The reactions involving hemicelluloses contribute to the consumption of cooking chemicals, thus adding to the operational costs. More importantly, these polysaccharides offer a variety of structures (monomers, oligomers and polymers) that constitute attractive building blocks for bio-based materials and chemicals. It is of great interest, therefore, that the hemicelluloses are recovered in a pretreatment step prior to the pulping process.

Apart of the stem wood, other fractions of the tree that are currently considered as being low value residues, can be used as raw materials in a biorefinery. Forest residues may be used e.g. in the production of nano materials and textile fibres [Le Normand *et al.*, 2014; Li *et al.*, 2016; Moriana *et al.*, 2016b]. If the target products are nano-scale sized constituents, the freedom of choosing the type of process and conditions is much greater when compared to traditional processes. In this context, the fibre properties do not need to be considered. This opens up the possibility of using other pulping methods, such as soda cooking, which is based solely on using hydroxide ions as the active chemical. It results in less efficient delignification and therefore longer time is required to accomplish the same extent of delignification and consequently the yields of hemicellulose and cellulose are lower. However the process is relatively robust, offers the benefits of a less expensive chemical recovery system and generates sulphur-free lignin, which is more suitable for further conversion into materials and chemicals. Hemicelluloses need to be pre-extracted from the material prior to cooking in order to achieve a good overall yield.

Along with the raw material and selected separation method, the choice of pretreatment is decisive for achieving efficient separation. Among the kinds of pretreatment available, mild steam explosion offers the recovery of hemicelluloses as well as enhanced accessibility of the remaining constituents in the material with minimal degradation of the native structure. It relies on so-called autohydrolysis (acidic conditions generated by the deprotonation and deacetylation of hemicelluloses lead to the hydrolysis of labile glycosidic bonds), whereby the dissolved hydrolysis products are transported out of the wood tissue by diffusive and advective transport. The latter is caused by the rapid, disintegrating, release of pressure (an “explosion”). It increases also the structure’s accessibility for further treatment.[Garrote *et al.*, 1999; Laser *et al.*, 2002; Lora and Wayman, 1978; Jedvert *et al.*, 2012]. The choice of process conditions determines the quality of the products: mild conditions favour recovery of the longer chain structures, whereas more severe conditions (e.g. high temperature and long treatment time) facilitate the formation of monomers and their degradation products, such as hydroxymethyl furfural, HMF (from hexoses) and furfural (from pentoses) [Abatzoglou *et al.*, 1990; Li *et al.*, 2005].

1.1 WWSC

The work presented in this thesis was performed within the realm of the Wallenberg Wood Science Center (WWSC). WWSC is a joint research centre at Chalmers University of Technology in Gothenburg and the Royal Institute of Technology in Stockholm (KTH), and was founded by the Knut and Alice Wallenberg Foundation. The research undertaken by the organisation is focused on developing new processes and material products based on the Swedish forests.

1.2 Objectives

The main objective of this work was to explore the prospects of pretreatment using mild steam explosion by investigating its effects on two different types of forest biomass: Norway spruce wood chips and forest residues of mixed origin. The local effects on the composition of wood tissue pretreated using steam explosion were investigated and compared with hot water extraction in order to understand the mechanism behind this pretreatment better. Furthermore, the cooking experiments were performed on forest residues to evaluate how the changes rendered by pretreatment effect further processing of the material.

1.3 Outline

This work is based on two papers, which are appended at the end. Those studies were based on different materials and different aspects of steam explosion.

- *Paper I* Mild steam explosion was compared to hot water extraction. The effects of pretreatment on the local composition of Norway spruce wood chips were investigated.
- *Paper II* Forest residues were used as the study material. The effects of the pretreatment on its composition and subsequent soda and Kraft cooking were evaluated.

This thesis is organised as follows: Chapter 2 recounts the theoretical background, i.e. the basics of wood structure, along with the pulping and pretreatment processes. The experimental methods and materials used are described in Chapter 3, whilst a discussion of the results is presented in Chapter 4. Finally, the conclusion and suggestions for future work are presented in Chapter 5.

2

Theory

2.1 Wood and pulping

There is a large variety of tree species, but most of them can be categorized as being either softwood (conifers) or hardwood (broad-leaf). In general, trees are higher order plants with a complicated hierarchical structure in both the longitudinal and radial directions. The main parts of a tree can be distinguished easily: top, stem, branches, leaves or needles and root. Furthermore, various sections of a tree contain different tissues. Traditionally, attention is focused on the stem, which is comprised of:

- outer bark: dead tissue that, provides mechanical barrier and chemical protection;
- phloem (inner bark): living cells for the transport of nutrients and for storage;
- vascular cambium: a layer of living cells, produces cells toward the inside and outside;
- secondary xylem: mostly dead cells that, serves as mechanical support to the tree and conducts water and minerals upwards. This can be divided into two parts: sapwood (both living and dead cells; tissue responsible for the transport

of water and minerals, producing extractives and providing storage for nutrition) and heartwood (dead cells, rich with extractives). It is the xylem that shows the annual growth rings visible in the cross-section of the stem [Fengel and Wegener, 1984; Henriksson *et al.*, 2016].

The structure and composition of xylem and bark are described in details below.

2.1.1 The structure of wood

The xylem is the part of the tree that is often considered as being “wood”, and is used for construction purposes, making furniture and producing pulp and paper. It is the most uniform part of the tree. Around 90-95% of the softwood xylem consists of tracheids, which are elongated, slender cells with flattened edges. Their length, on average, is 3 mm and they are arranged in radial files. Two other types of cells present in softwood, namely parenchyma and epithelial cells. Hardwood, on the contrary, has a more complicated structure and is built up of a number of more specialized types of cell: it has different fibre (librifrom fibres, fibre tracheids) and parenchyma cells (ray and longitudinal), as well as tracheids and conducting vessels. Measuring around 1mm, hardwood fibres are much shorter than softwood tracheids.

Wood cells have a rigid cell wall, comprised of a cellulose matrix scaffold encrusted with hemicelluloses and lignin. The cell wall is built up of two main layers:

- *primary cell wall*: an outer layer with randomly orientated cellulose microfibrils
- *secondary cell wall*: 2-3 layers (S1-S3) in which the cellulose microfibrils have different orientation (which is very important for physical strength).

Moreover, the space between adjacent cells is filled with a lignin-rich, thin layer called the *middle lamella* [Daniels, 2016].

In general, wood can be considered as being a biocomposite where cellulose is a reinforcing agent and lignin, hemicelluloses and extractives provide barrier/stiffness, interaction possibilities and protection, respectively. However, the proportions between the polymers, as well as some of their characteristics vary between species and different parts of the tree. The general compositions of softwood and hardwood are shown in Table 2.1 [Henriksson *et al.*, 2016].

Cellulose

Cellulose is the most abundant polymer present on Earth, constituting at least 30% of the mass of advanced plants [Kamide, 2005] and 40-45% of wood. It is built up by glucose units and is organized in a hierarchical structure.

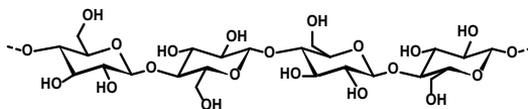


Figure 2.1: *Molecular structure of cellulose*

The **primary structure** is a linear, unbranched chain of D-glucopyranosyl units connected by $\beta(1-4)$ glycosidic bonds (Figure 2.1). The degree of polymerization is usually high, with a maximum of 15 000 glucose units. The monomers are rotated 180° towards each other so that the repeating unit, called cellobiose, contains two glucose residues. The chains are stabilized by intramolecular (intrachain) hydrogen bonding between the C6 and C2 hydroxyl, as well as the C5 oxygen and the C3 hydroxyl of adjacent units.

Chains are organized into semi-crystalline microfibrils, the neighbouring chains in the crystalline regions are arranged in a **sheet** formation (stabilized by C2-C6 and C3-C6 interchain hydrogen bonds). The cellulose sheets are piled up, probably via van der Waals interactions and hydrogen bonds, into long and relatively narrow sheet stocks, with at least partially overlapping chains (**crystalline structure**).

The semi-crystalline microfibrils are organised further into very long **fibrils** (at least $40 \mu\text{m}$, compared to the $5-7 \mu\text{m}$ of cellulose chains). The size of the fibrils differs not only between species of trees but also between the types of tissue found in them [Henriksson and Lennholm, 2016]. Cellulose fibrils are deposited in the layers of the cell wall mentioned above. The organisation of fibrils is different in each layer, being random in the primary wall and having different, but consistent, directions in the S1-S3 layers in secondary cell wall.

Table 2.1: *Composition of softwood and hardwood [Henriksson et al., 2016].*

| Wood type | Wood composition | | |
|-----------|------------------|-------------------|------------|
| | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
| Softwood | 40-45 | 25-30 | 25-30 |
| Hardwood | 40-45 | 30-35 | 20-25 |

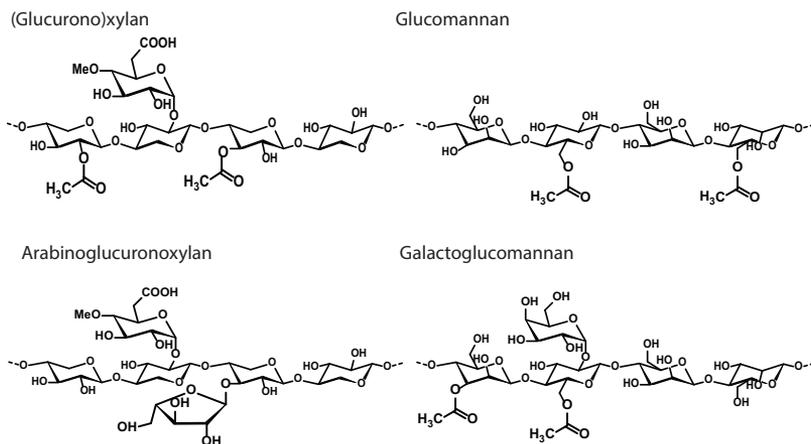
Table 2.2: Hemicelluloses in softwood and hardwood and their average content in the xylem.

| Wood type | Hemicellulose | Content (%) |
|-----------|-------------------------|-------------|
| Softwood | (galacto)glucomannan | 5-8 |
| | glucomannan | 10-15 |
| | (arabino)glucuronoxylan | 7-15 |
| Hardwood | glucuronoxylan | 15-35 |
| | glucomannan | 2-5 |

Hemicelluloses

Hemicelluloses are heteropolysaccharides and have a relatively low degree of polymerization compared to cellulose. They contribute to the mechanical properties of the cell wall and regulation of its porosity and flexibility. The composition and quantity of hemicelluloses in the cell wall vary between plant species: in trees the most abundant are glucomannans and xylans (see Table 2.2). The content and composition of hemicelluloses can vary for different tissues in the tree [Teleman, 2016].

Glucomannan has a linear backbone of β -(1 \rightarrow 4)-D-mannopyranosyl and β -D-glucopyranosyl units (Table 2.2 and Figure 2.2). The proportions between glucose and mannose vary between tree species and, in the native state, glucoman-

**Figure 2.2:** Molecular structure of hemicelluloses.

nan is partially O-acetylated on mannosyl units. Softwood contains also galactoglucomannan, which tends to have longer chains than hardwood glucomannan (90-102 vs. 60-70 monomers); moreover, some of its glucopyranosyl units are connected to a single D-galactopyranosyl group attached by α -(1 \rightarrow 6). Irregular acetylation and substitution with galactosyl groups prevent organisation over longer distances: if deacetylated softwood hemicelluloses may crystallize.

Deacetylation occurs easily. The α -glycosidic linkage connecting the galactosyl unit to the chain is relatively sensitive and can therefore be cleaved in both alkaline and acidic conditions. Glucomannan is particularly sensitive to alkaline conditions due to its high solubility and lack of side groups that could prevent rearrangement leading to end-wise degradation, and they therefore undergo severe peeling during alkaline pulping processes. The β -D-mannopyranosidic linkage is relatively sensitive to acid conditions and even more so than β -D-glucopyranosidic. Glucomannan can therefore be depolymerized selectively in mild acidic conditions and the partially fragmented chains can be extracted [Teleman, 2016].

Xylan has a β -(1 \rightarrow 4)-D-xylopyranosyl backbone, however there are significant differences between its structure in softwood and hardwood. Softwood generally contains arabinoglucuronoxylan, i.e. xylan with α -L-arabinofuranose side groups; its chains have a DP of 90-120 units and are non-acetylated. Hardwood, on the other hand, contains O-acetyl-(4-O-methylglucuronoxylan with longer chains (100-220 units) (Table 2.2 and Figure 2.2).

Xylans are easily deacetylated in both acidic and alkaline conditions. In alkaline conditions xylan undergoes peeling, albeit less extensively than glucomannan, thanks to the side-groups preventing reengagements. Moreover, 4-O-Me glucuronic acid side groups can be converted into hexanuronic acid: this consumes bleaching chemicals and causes, in turn, discolouration of the pulp. Compared to glucomannan, xylan is more sensitive to degradation in acidic conditions [Teleman, 2016].

Lignin

Lignin is the most complex of the naturally occurring biopolymers. It is a hydrophobic, amorphous polymer comprised of monomers of coniferyl alcohol, p-coumaryl alcohol and sinapyl alcohol. Unlike other biomolecules, however, it does not have an ordered structure and forms a three-dimensional web of randomly cross-linked and branched polymers. Lignin synthesis via radical polymerisation is one of the last steps in cell wall formation, hence lignin fills up the spaces between the cellulose and hemicelluloses and thereby fixate these components together. It also makes the cell wall hydrophobic, protects it from degradation and contributes to stiffness.

The most common bond in lignin structural units, and the most important with

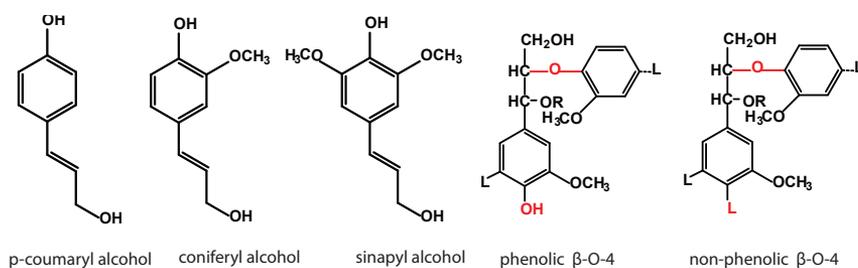


Figure 2.3: Molecular structure of lignin monomers and the β -O-4 bond.

regard to processing/fragmentation in alkaline conditions, is the β -O-4 ether bond (Figure 2.3). Another important bonds, for instance, are the beta-5' or 5—5' between the carbons in two aromatic rings. Softwood lignin is mostly built up of coniferyl alcohol, with small amounts of p-coumaryl alcohol, whereas hardwood lignin is comprised of coniferyl and sinapyl alcohols in different proportions. The proportion of the different monomers units and inter-unit linkages determine the properties and reactivity of the lignin (Figure 2.3).

Extractives

The extractives are compounds of low molecular mass that are extractable from wood. Comprised of terpenes, fats, fatty acids and phenolic compounds, they serve as protection from parasites, damage, UV radiation, oxidative degradation, etc. Although their amount in wood is relatively low, they constitute a significant fraction of the bark and branches.

Table 2.3: Content of extractives in bark and wood [Raisanen and Athanassiadis, 2013].

| Tree species | Bark (%) | Wood (%) |
|---------------|----------|----------|
| Scots pine | 25.2 | 5.0 |
| Norway spruce | 32.1 | 2.0 |
| Silver birch | 25.6 | 3.8 |

2.1.2 Bark

Bark is an outer layer of a tree and constitute 10-20% of the stem and 20-38% of the branches [Fengel and Wegener, 1984]. It is an inhomogeneous tissue, consisting of two layers with different properties and functions: the inner (phloem, for liquid transport purposes) and the outer (often coarse, for protection). These layers are built up of different tissues and cells. Compared to stem wood, bark contains more lignin and extractives (e.g. a fraction of polyphenols (tannins) and suberin that are not present in the stem wood tissue, see Table 2.3) and fewer polysaccharides [Ek *et al.*, 2016]. Bark lignin is composed of similar basic units as wood lignin, although the ratio of these can vary. For instance, it was shown that despite a similar basic structure, pine bark lignin has more condensed structures and more p-hydroxyphenyl than stem wood (which contains predominantly guaiacyl units). It also has a higher molecular weight and polydispersity than stem wood lignin [Huang *et al.*, 2011]. Bark cellulose is reported to be organized in shorter chains (lower DP) and shorter fibres [Fengel and Wegener, 1984]. Moreover, the composition of the hemicelluloses is different in this section of the tree and there are more pectins [Raisanen and Athanassiadis, 2013; Krogell *et al.*, 2012; Le Normand *et al.*, 2012].

Determining the exact composition of bark is difficult, as the traditional methods designed to evaluate xylem and pulp for papermaking purposes give a poor mass balance when the amounts of extractives are high. One reason for this, among others, is that extractives precipitate with lignin and result in the values of Klason lignin being overestimated [Kemppainen *et al.*, 2014; Krogell *et al.*, 2012; Burkhardt *et al.*, 2013; Huang *et al.*, 2011]. Describing bark is made even more difficult not only because its composition shows seasonal variation but also that it is affected by the debarking and storage methods used [Kemppainen *et al.*, 2014; Bajpai, 2013] (i.e. Kemppainen *et al.* [2014] showed, for example, that industrial bark is formed of up to 21% of wood tissue).

2.1.3 Forest residues

Traditionally, focus is placed on processing the stem of the tree, while the branches (foliage) and tops are considered as residues. Whilst the availability of these residues together with their relatively low cost make them a promising raw material for a biorefinery, they also present some challenges.

Forest residues are comprised of a mix of wood and bark tissue from various sections and species of trees, and are consequently highly inhomogeneous in both physical and chemical properties. The composition and structure of different forest residue tissues vary between different sections which, in general result in higher contents of extractives, lignin and ash than in the stem wood. Assigning the composition

accurately is extremely difficult, mainly due to the complexity and variation of the composition but also because the methods, which were designed primarily for the pulp and paper industry, are not suitable for material rich in extractives [Burkhardt *et al.*, 2013].

Moreover, the different morphology and chemistry of the components affect the chemical reactions and diffusion of chemicals during the treatments to which they are subjected, resulting in different changes being made to different samples under the same treatment.

2.1.4 Pulping

Wood has to be delignified in order to make the cellulose fibres available. This is accomplished by different pulping processes based on chemical, mechanical or thermomechanical treatments. Choosing the most suitable process is important for obtaining the desired quality of the pulp. The dominating process for separating the constituents of wood is the kraft process, whereby fibres are liberated by the fragmentation and solubilization of lignin. Another widely-used process is sulphite pulping, based on the dissolution of lignin through sulphonation. A less used process, that might be important in the biorefinery perspective is soda pulping; it relies on the same principle as kraft cooking but has simpler chemistry and lower efficiency.

The active chemicals in the kraft process are sodium hydroxide and sodium sulphite. The hydroxide ion cleaves the non-phenolic β -O-4 bonds in a nucleophilic attack while phenolic β -O-4 cleavage occurs efficiently in the presence of hydro-sulphite ions. Although this separation is fairly effective, strong alkaline conditions cause the degradation of hemicelluloses and a small fraction of the cellulose, which decreases the yield. The black liquor containing spent chemicals and degradation products is burned to recover energy and chemicals.

Soda cooking relies on a simpler chemistry, as it involves using only sodium hydroxide as the active chemical. Delignification relies on the cleavage of the non-phenolic β -O-4, while the phenolic β -O-4 bonds remain mostly unaffected. The lignin fragments are thus bigger and need more time to diffuse out of the wood tissue, making this method less efficient when compared to kraft pulping: it requires a prolonged time frame to accomplish the same degree of delignification and this turn, results in lower yields of both hemicellulose and cellulose. In the context of a forest biorefinery this can, however, be useful: the mechanical performance of the fibres is not the main target and the process is more robust, allows simpler chemical recovery and generates sulphur-free lignin. Also, pretreatment is preferable prior to pulping to avoid degradation of the hemicelluloses.

2.2 Biorefinery

A biorefinery is a sustainable concept for transforming biomass into a spectrum of commercial products: bioenergy, biofuels, various biochemicals and biomaterials. This concept has great potential, as there is a wide diversity of bioresources that can be converted into range of various products. However, this potential is currently not exploited to the full because only very limited feedstocks are used, resulting in a narrow range of products [Aresta *et al.*, 2012].

2.2.1 General aspects

The objective of a biorefinery concept is to separate the chemical components or building blocks and convert them into a range of products. The feedstock consists of different compounds with varying characteristics, such as cellulose, hemicellulose, lignin and fats/oils [Aresta *et al.*, 2012]. Designing a suitable process is crucial to keeping the production sustainable and profitable. There are three important prerequisites for the process:

- low environmental impact (sustainable technology: low CO₂ footprint)
- low energy demand
- high material efficiency

The key to building an efficient biorefinery is adopting an interdisciplinary approach involving biochemical, chemical and thermochemical conversion.

2.2.2 Forest based biorefinery

The beginning of forest biorefineries can be seen in the early days of the sulphite pulp mills, as they used to work as rudimentary biorefineries. For instance, Domsjö Fabriker (Domsjö, Sweden) started on the path towards being a biorefinery as early as in the 1940s: apart from producing dissolving pulp, they started fermenting ethanol as a platform chemical for the chemical industry and producing cattle fodder [Domsjö, 2016]. Nowadays, they use cellulose from the sulphite process for production of viscose, the sugar stream is used for the fermentation to bioethanol and lignin is sold in the form of lignosulphonate. Another example of a sulphite-based, early biorefinery is Borregaard (Sarpsborg, Norway). This mill started producing chemicals alongside paper pulp as early as before the outbreak of World War II; today, it is a fully functioning biorefinery which, *using the different components of wood, [...] produces*

*lignin products, speciality cellulose, vanillin and bioethanol for a variety of applications in sectors such as agriculture and fisheries, construction, pharmaceuticals and cosmetics, foodstuffs, batteries and biofuels.*¹. The sulphite process, and biorefineries based on them, became less competitive after 1940 as kraft pulping became a more efficient process for producing pulp (efficient recovery, stronger pulp, etc.) and also due to the emergence of oil-based materials and chemicals that displaced other products from sulphite mills. However, kraft pulp mills can also be considered as being basic biorefineries, since the separated residue fractions in the form of bark, branches and black liquor (containing lignin, hemicelluloses and spent chemicals) are burned in the digester to recover energy and certain extractives fractions are recovered. Moreover, they should be considered as a platform for future forest-based biorefineries: this type of process offers the efficient separation of lignin and cellulose along with the possibility of improving material efficiency by recovering lignin and hemicellulose structures either prior to, or after, the main cellulose-lignin separation process.

As the concept of the biorefinery was introduced into the scientific discussion [Levy *et al.*, 1981; Rexen *et al.*, 1988; Wyman and Goodman, 1993], forest biorefineries became of interest due to the abundance of forest biomass and the advantage of using the existing infrastructure. For several reasons pulp mills, as traditional wood processors, offer a great platform for a modern biorefinery. Wood is a great bioresource: it is a highly abundant raw material, does not compete with the growing of food in large areas and, very importantly, is independent of season. Moreover, pulp mills allow a biorefinery to become integrated systems, as they have established wood collection, handling and processing technologies and infrastructure, as well as a skilled workforce [Bajpai, 2013; Lew *et al.*, 2012]. In an integrated system, forest residues (such as tops, branches and twigs) that nowadays are left behind in the forest or burned can be used for separating chemical building blocks and converted into value-added products. The literature already presents a number of ideas for using forest residues, such as the pyrolysis for bio-oil and biogas [Janzon *et al.*, 2014], the separation of tannins from bark [Kempainen *et al.*, 2014] and the production of cellulose nanocrystals [Le Normand *et al.*, 2014; Moriana *et al.*, 2015, 2016a] or nanocomposites [Li *et al.*, 2016].

In the case of the pulp and paper industry, creating a biorefinery would provide an opportunity to:

- increase productivity and profitability
- increase the usage efficiency of the raw material

¹Information from Borregaard [2018].

- continue already established production while opening up to new markets
- use side streams from conventional production[Bajpai, 2013; Lew *et al.*, 2012].

In this context, new processing steps must be added in order to separate the wood tissue more efficiently. A pretreatment step added prior to pulping could enable the recovery of useful chemical structures (primarily hemicelluloses, polymers and oligomers) that would otherwise be degraded, as well as lead to enhanced accessibility of the wood material and reduced consumption of cooking chemicals.

2.2.3 Pretreatment

Among the pretreatment methods currently available, the mild methods that not only allow the recovery of hemicelluloses, but also enhance the accessibility of the remaining constituents in the wood, with minimal degradation of their native structure seem to be the most interesting options. Two examples of such pretreatments are mild steam explosion (STEX) and hot water extraction (HWE). Both of these pretreatment methods rely on recovering partially-degraded hemicelluloses from wood tissue by acid hydrolysis mediated dissolution that is known as autohydrolysis. At high temperature, the acidic conditions generated by the deprotonation of hemicellulose carboxylic acids are promoted further by the enhanced deacetylation of hemicelluloses, which leads to hydrolysis of the relatively labile back-bone glycosidic bonds. The hydrolysis products (hemicellulose side groups and chain fragments of varying lengths) dissolve and are transported out of the wood tissue [Garrote *et al.*, 1999; Laser *et al.*, 2002; Lora and Wayman, 1978]. Different products will be formed depending on the process conditions: mild conditions favour recovery of the longer chain structures, whereas more severe conditions (e.g. high temperature and long treatment time) facilitate the formation of monomers and their degradation products, such as hydroxymethyl furfural, HMF (from hexoses) and furfural (from pentoses) [Abatzoglou *et al.*, 1990; Li *et al.*, 2005].

HWE relies almost exclusively on autohydrolysis and the subsequent diffusive transport of the dissolved structures. In STEX, autohydrolysis is followed by a rapid, disintegrating, release of pressure (an "explosion"): apart from facilitating access to the structure, this also (through the pressure difference) gives rise to an advective mass transport of the liquid through the pore system [Jedvert *et al.*, 2012], rapidly pushing some of the hydrolysis products out of the wood tissue. The choice of the pre-treatment method employed is governed by the requirements of the subsequent processing steps (e.g. accessibility, contents of hemicellulose, etc.) as well as by the specific demands of the product (i.e. the properties of the hemicelluloses) and will be very dependent on a comprehensive understanding of both the methods and how they affect wood tissue.

The focus of this work has been placed on steam explosion in the context of different tissues, such as wood and bark. The local effects of this pretreatment have on wood have been investigated and compared to those of hot water extraction. The effect on the pulping behaviour of forest residues was also analysed.

3

Materials and Methods

3.1 Materials

The samples consisted of industrially-cut wood chips of Norway spruce (*Picea abies*). Chips were selected manually to provide the size fraction preferred (at least 6 mm in thickness, 3 cm in width and 4 cm in length) and reduce dirt, knots and bark.

The forest residues (branches, bark and twigs) were provided by Domsjö Fabriker (Örnsköldsvik) and consisted of a mixture of softwood (mostly spruce and pine) and hardwood (mostly birch); the material was chipped to uniform the size prior to shipping.

All chemicals were purchased from Sigma-Aldrich and used without further purification.

3.2 Methods

3.2.1 Steam explosion

Steam explosion applied to wood chips

One of the equipments used for mild steam explosion is a modified steel autoclave (approx. 1.2 L) fitted in an insulated container (Figure 3.1). The lid of the autoclave is equipped with an inlet and outlet for steam and a temperature sensor. The valve on the outlet allows for rapid release of the pressure into a collection vessel (approx. 15 L). The autoclave was filled with 50 g of o.d. wood chips and water corresponding to a water-to-wood ratio of 4:1 and the experimental conditions were chosen to be 150°C,

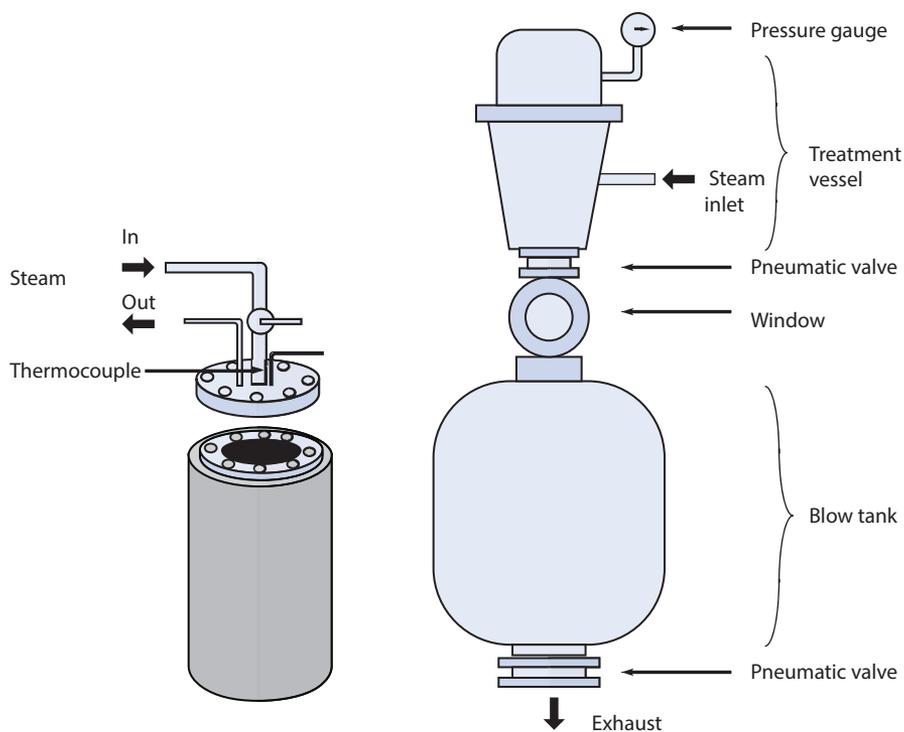


Figure 3.1: Steam explosion autoclave(left) and bench-scale steam explosion equipment (right)

and 15 and 30 min. Pretreated wood chips were washed first with approximately 5 L of warm water and subsequently with cold water for one week.

Steam explosion applied to forest residues

Batches of the material were pre-treated in bench-scale steam explosion equipment (Figure 3.1). Each run involved 500g of forest residues being loaded into the top chamber and heated with saturated steam from the boiler until the pressure in the vessel reached 4 and 7 bar, respectively. The material was kept under pressure for 15 min and then discharged rapidly into the lower chamber of the apparatus (atmospheric pressure).

3.2.2 Hot water extraction

Extraction with hot water is performed in a steel autoclave (approx. 1.2 L) placed in a pre-heated PEG bath with rotation. The amount of wood and wood-to-water ratio was the same as in the steam explosion treatment (4:1). The heating-up period was 15 minutes, and which the sample was kept at 150°C for treatment times of 15, 30, 60 and 90 min., respectively. The washing procedure was the same as for the STEX treatment.

3.2.3 Refining

A Sprout-Waldron 12-1CP 12 inch disc refiner was used to homogenize the samples of forest residues. Prior to refining, the material was heated by steaming at 125°C for 15 min. The samples were then stored at -20°C.

3.2.4 Cooking

Soda cooking

Liquor containing 0.37 mol NaOH/kg was charged into the autoclaves at a liquor-to-wood ratio of 9:1. The cooking was carried out in 1.2 L steel autoclaves placed in a polyethylene glycol bath. The cooker was preheated to 80°C and then the temperature was increased to 170°C at approximately 1°C/minute. Once the target temperature was reached, the material was cooked for 30, 60, 90, 120 or 180 min, respectively. The pulp was separated by filtering through a woven polypropylene mesh and washed with 10 L of water. The solid material thus obtained was defibrillated for 10 min in a pulp disintegrator and washed once more with 1 L of water.

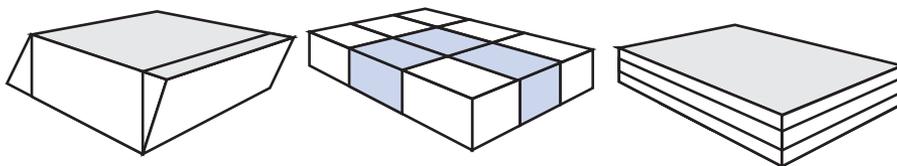


Figure 3.2: Illustration of how a wood chip was sectioned: (a) removal of damaged parts, (b) selection of sections from the corner, edge and middle areas, (c) division of the chosen fragments into layers.

Kraft cooking

The white liquor used for kraft cooking was charged at 9:1 liquor to wood ratio. The effective alkali was 29%, the sulphidity: 35% and the carbonate concentration 0.1 M (corresponding to 0.37 mol OH^- /kg liquor, 0.19 mol HS^- /kg liquor hydrogen sulphide ions and 0.1 mol CO_3^{2-} /kg solution). The cooking procedure was analogous to that for soda cooking.

3.2.5 Dry content and yield

The dry content of each sample was determined by drying it overnight at 105°C. The solid fraction yield was determined as a proportion of the dry mass and the initial dry mass of the material. The cooking yield was calculated by relating the dry content of the liquors to the initial mass of the sample.

3.2.6 Sectioning of wood samples

In order to investigate how different parts of the wood chip are affected during the treatments studied, different sections of the wood chips treated with STEX (15 and 30 min) and HWE (15, 30 and 60 min) were analysed separately. Prior to analysis, treated and washed wood chips were oven-dried and cut with a saw. The parts damaged during chipping were removed, and sections were collected from the corner, outer edge and middle of the wood chip. The fragments obtained were then sliced into layers using a microtome so that outer and inner layer could be analysed separately (see Figure 3.2).

3.2.7 Chemical characterization

All samples were subjected to complete acid hydrolysis using 72% sulphuric acid. The residual material was considered to be Klason lignin, the amount of which was determined gravimetrically. The filtrate from the hydrolysis was used to determine the contents of acid soluble lignin (ASL) and carbohydrates. The amount of ASL was calculated based on the absorbance measured with UV at a wavelength of 205 nm in a Specord 205, Analytic Jena, assuming the absorptivity constant equals $110 \text{ dm}^3 \text{ g}^{-1} \text{ cm}^{-1}$.

3.2.8 Chemical extraction

The amount of solvent-soluble, non-volatile material in the forest residues was quantified using the Tappi T204 cm-07 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.

3.2.9 Ion exchange chromatography

The carbohydrate composition was determined as the amounts of monomeric sugars by using high performance anion exchange chromatography (HPAEC). The system comprises a Dionex ICS-5000 equipped with a CarboPac™ PA1 column and an electrochemical detector; NaOH and NaOH + NaAc are used as eluents. The software used was Chromeleon 7, Chromatography Data System, Version 7.1.0.898. 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: for arabinose it was found to be $93.1 \pm 1.9\%$, galactose $92.9 \pm 1.7\%$, glucose $91.8\% \pm 2.0$, xylose $78.6 \pm 1.6\%$ and mannose $90.2 \pm 0.6\%$.

3.2.10 Gel permeation chromatography

The molecular weight was determined using size exclusion chromatography in a PL-GPX 50 plus integrated system connected with refractive index and ultraviolet (290 nm) detectors (Polymer Laboratories, Varian Inc.). The system was equipped with two columns PolarGel-M and PolarGel-M Guard ($300 \times 7.5 \text{ mm}$ and $50 \times 7.5 \text{ mm}$) with $8 \mu\text{m}$ mixed size pores and the mobile phase consisted of dimethyl sulphoxide (DMSO)/LiBr (10 mM) with a flow of 0.5 ml/min.

3.2.11 Gas chromatography

A gas chromatographic system of the model Agilent 7890A, Agilent 5975C, equipped with parallel flame ionized detection (FID) and mass spectrometer (MS) detection operating in an electron ionization mode was used to analyse the volatile compounds in the evaporated crude extractive residues.

The derivatives protected by trimethylsilyl (TMS) were semi-quantified using the internal standard of heptadecanoic acid methyl ester. A sample of 10 mg residue was dissolved using 0.6 ml ethyl acetate and 15-25 mg of the internal standard, heptadecanoic acid methyl ester (15-20 mg/0.9-1.1 g ethyl acetate), was added to the sample. The solution was then derivatized with 0.1 ml BSTFA (99:1; N, O-bis(trimethylsilyl)trifluoroacetamide: chlorotrimethylsilane) and TMS reagent. After a period of 30 minutes, 1 μ l of the solution was injected via an autosampler into the gas chromatographic system. Once injected, the analytes were split and separated into two chromatographic columns (HP-5MS, 30 m in length, 0.25 mm in internal diameter and 0.25 μ m in stationary phase thickness) using helium as carrier gas. 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 minutes before being raised to 300°C at a rate of 2°C/minute; the temperature of the GC oven was set thereafter at 300°C for 30 minutes. The MS source and the quadrupole temperature were set to 250 and 150°C respectively. The NIST MS search programme (Version 2.0) operating on the NIST/EPA/NIH Mass Spectral Database 2011 (NIST 11) was used to perform the spectral interpretations.

3.2.12 Severity factor

The effects of temperature and time of the pretreatment are often combined together into one value to give the so-called severity factor, which enables comparisons to be made between different processes. It is derived assuming first order kinetics and Arrhenius behaviour, so it should be used just as an arbitrary number representing experimental reaction conditions [Heitz *et al.*, 1991; Overend *et al.*, 1987]. The severity factor for multiple temperature stages may be determined as described in Equation 3.1:

$$\log(R_0) = \log \left[\sum_{i=1}^n t_i e^{(T_i - T_b)/\bar{\omega}} \right] \quad (3.1)$$

where:

t = time (min)

T_i = temperature of the treatment stage (°C)

T_b = base temperature (100°C) (°C)

ω = an empirical parameter $\omega = 14.75$ based on the activation energy [Chum *et al.*, 1990].

Here, the severity factor was calculated for the methods selected taking the heating-up period into consideration: this calculation took into account the differences in two procedures with very different heating-up times (2 vs. 15 min).

3.2.13 Nuclear magnetic resonance

$^1\text{H}^{13}\text{C}$ 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 13C channels) operating at a frequency of 800 MHz for 1H and 201 MHz for 13C. The 1H spectra were recorded at a 30° pulse angle, 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 “hsqcedetgpsisp 2.3” with a 0.25 s ^1H acquisition time, 5.3 μs ^{13}C acquisition time, 3 s interscan delay and 1JC–H coupling constant of 145 Hz, eight scans; each spectrum was recorded for 4 h.

The NMR spectra were processed and analyzed by means of the default processing template of MestReNova Vers.10.0.0 software, along with automatic phase and baseline correction.

4

Results and Discussion

This chapter describes the main results obtained in Papers 1 and 2.

4.1 Pretreatment of wood

The effects of mild hydrothermal pretreatments on wood tissue were investigated by subjecting wood chips to either hot water extraction or steam explosion before being analysed for composition. A series of treatments was performed for both methods at the same temperature but different residence times. The conditions, final pH, mass balances and composition of the native and treated wood as well as the extraction liquors are presented in Table 4.1.

4.1.1 Steam explosion and hot water extraction

A mass balance based on the weight of used wood chips of the recovered wood chips and dry content of the extraction liquors after pretreatment showed that 96-100% of the material was recovered after steam explosion. Based on the chemical analysis performed, 93 - 97% of the solid and 55 - 66% of the dissolved fraction were quantified and assigned to different wood components: the remaining 34-45% of the dissolved content may contain fatty acids and other organic compounds, such as

Table 4.1: Conditions, yields and compositional analysis of the treatments applied in the pretreatment of the wood chips

| | <i>Native</i> | <i>Hot water extraction</i> | | | <i>Steam explosion</i> | |
|--|---------------|-----------------------------|-------|------|------------------------|------|
| <i>Treatment conditions:</i> | | | | | | |
| Temperature (°C) | | 150 | | | 150 | |
| Heating-up time (min) | | 15 | | | 2 | |
| Treatment time (min) | | 15 | 30 | 60 | 15 | 30 |
| Severity factor | | 2.9 | 3.1 | 3.5 | 2.7 | 3.0 |
| <i>Extract pH</i> | | 3.6 | 3.5 | 3.3 | 4.3 | 4.1 |
| <i>Mass balance based on yield (%):</i> | | | | | | |
| Solid fraction yield | | 94.9 | 97.9 | 92.3 | 95.6 | 95.9 |
| Extraction yield | | 1.4 | 2.3 | 4.3 | 1.7 | 1.9 |
| Total solid yield | | 96.3 | 100.2 | 96.6 | 97.3 | 97.8 |
| <i>Mass balance based on compositional analysis (%):</i> | | | | | | |
| <i>A. On wood:</i> | | | | | | |
| Cellulose | 41.9 | 42.7 | 45.6 | 47.7 | 42.7 | 41.4 |
| GGM | 21.4 | 17.4 | 16.7 | 13.0 | 18.8 | 16.5 |
| AGX | 5.1 | 6.0 | 4.5 | 4.4 | 5.8 | 6.1 |
| Klason | 25.2 | 29.5 | 28.9 | 31.5 | 27.4 | 30.1 |
| Total in wood | 93.6 | 95.6 | 95.7 | 96.6 | 94.7 | 94.1 |
| <i>B. Based on extracts:</i> | | | | | | |
| Cellulose | | 0* | 0* | 0* | 0* | 0* |
| GGM | | 26.4 | 39.7 | 37.1 | 15.7 | 18.2 |
| AGX | | 12.3 | 15.2 | 13.8 | 12.6 | 13.9 |
| Klason | | 15.5 | 11.1 | 9.6 | 32.8 | 26.8 |
| ASL | | 0.2 | 0.2 | 0.1 | 0.1 | 0.2 |
| Total in extract | | 53.8 | 65.5 | 59.7 | 61.2 | 58.8 |

*acc. to the calculations all the glucose detected originates from galactoglucomannan

degradation products from sugar monomers [Jedvert *et al.*, 2014; Abatzoglou *et al.*, 1990]).

Figure 4.1 presents the wood chips that were subjected to STEX or HWE at different degrees of severity. It can easily be noticed from its appearance that the wood was affected differently by the various pretreatments. The change in the colour of the material may be related to the chemical changes in the hemicelluloses and lignin leading to the formation of new chromophoric groups [Zhang and Cai, 2006].

The main objective of performing a pretreatment is usually to recover hemicelluloses, and the extraction efficiency is highly related to the conditions of the pretreatment. This is visualised in Figure 4.2, where the yields obtained for both STEX and HWE are plotted against the severity factor (see also Table 4.1). The HWE treat-

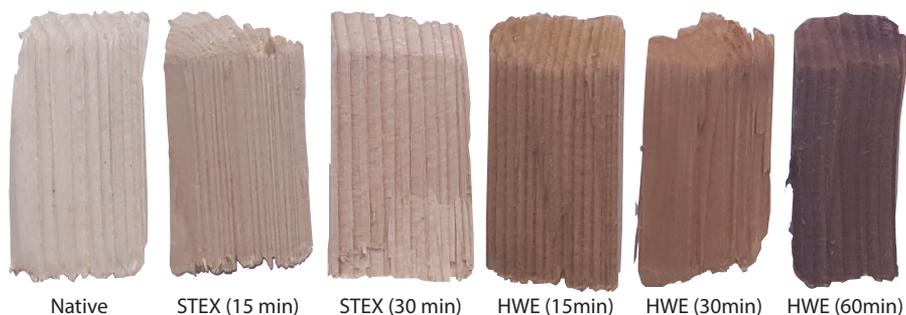


Figure 4.1: Morphological changes induced by the treatments. From left: native wood, STEX-treated and HWE-treated (residence times as stated).

ments had generally higher severity factors and higher yields (with the exception of that with the shortest treatment time); there is, moreover, a linear correlation between extraction yield and severity (see Figure 4.2).

The extraction of hemicelluloses is initiated by the generation of high local concentrations of hydrogen ions and acetates due to deprotonation, followed by the subsequent deacetylation and partial hydrolysis (glycosidic bond cleavage) of hemi-

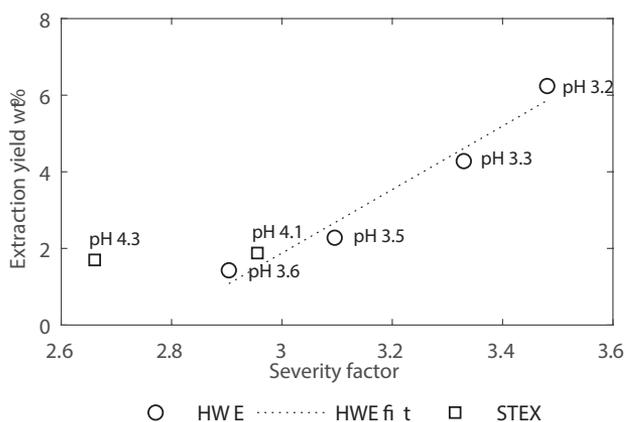


Figure 4.2: Extraction yield versus severity factor

celluloses, which leads to the hemicelluloses detaching from the wood tissue. The autohydrolysis is followed by the mass transport of the molecules generated: large hemicellulose molecules are transported rather slowly and are retarded in the wood tissue. This, in turn, leads to prolonged depolymerisation within the material prior to diffusion into the bulk liquid. Smaller ions, on the other hand, diffuse gradually out of the wood, lowering the pH of the bulk liquor and promoting the continued hydrolysis of the extracted hemicelluloses. The overall mass transport can be described by the three following steps: diffusive mass transport within the cell wall, diffusive transport in the pore system of the wood and mass transport from the wood surface to the bulk liquid. The rate-determining step is the diffusive mass transport in the cell wall and/or pore system; the overall rate has a strong dependence on the size of the hemicelluloses and the morphology of the wood [Rissanen *et al.*, 2014b].

The final pH is strongly correlated to the severity of the treatment (temperature and residence time) (Table 4.1). This was observed for both methods as a decrement in pH with treatment time: it was more pronounced for HWE, performed in a rotating autoclave with a longer heating-up period (and thus a longer autohydrolysis time [Rissanen *et al.*, 2016]) than for STEX, performed in a fixed autoclave with a relatively short heating-up time. For STEX, the residence time is shorter and thus allows very limited autohydrolysis, although relatively large amounts of material (i.e. hemicelluloses) may be transported out of the tissue due to forced advective mass transport during the explosion step.

The severity factor at the shortest HWE treatment time was close to that of STEX treatments ($\log R_0$ 2.9 and 3.0), which allows comparison to be made. At those conditions STEX gives slightly higher extraction. In both STEX and HWE, the polymers undergo autohydrolysis and reaction products diffuse out of the wood tissue. Additionally, the rapid pressure release in STEX creates a pressure gradient across the wood tissue, which pushes the liquid out through the pore system, thereby facilitating removal of the dissolved material. The combined effect of these phenomena determines both the amount and properties of the wood components extracted, and thus, at similar severity more material is extracted from steam exploded material.

A chemical analysis of the resulting solid materials and liquors was performed to understand the nature of the two pretreatments. It is a consequence of the steam explosion and hot water extraction treatments performed that the content of carbohydrates in the liquors increased; in the solid material, the content of (galacto)glucosmannan (GGM) decreased and a moderate decrease in the amount of arabinogluconoxylan (AGX) was observed for HWE. The results confirm the different effects of the two treatments as seen from visual inspection. The removal of acid-sensitive GGM increases with time in both treatments, while the AGX follows this trend only in HWE (at longer overall treatment times). A possible explanation here is that the

lower pH applied during HWE at long times provides conditions sufficient to accomplish the degradation and extraction of the relatively stable AGX. However, these trends were not fully found in the composition of the liquor. In fact, the relative amounts of GGM and AGX in the liquid fractions decreased at long treatment times (HWE 60 min), which is an indication that degradation of the monomer occurs during the more severe HWE treatments. These observations are consistent with previous studies showing monomer degradation at comparable severity: typically at the severity factor corresponding to HWE 60 min (3.5) and above [Garrote *et al.*, 2004; Li *et al.*, 2010].

Table 4.1 shows that, the content of hemicellulose in the wood samples decreased and the relative amounts of lignin and cellulose increased [DeMartini *et al.*, 2015]. This change was more pronounced for the HWE pretreated wood, and very clear upon longer treatment, which is in line with the findings presented above.

The molecular weight of the structures extracted was studied: chromatograms are presented in Figure 4.3. The UV signals reflect the molecules having aromatic structures (in this case lignin), while the RI signal is more general and includes both

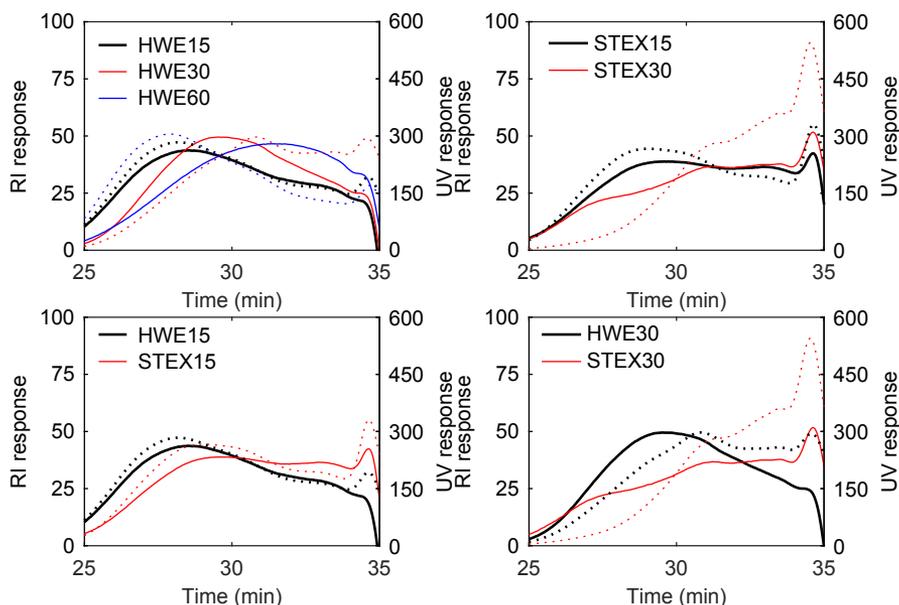


Figure 4.3: The GPC results obtained. RI response: solid lines; UV: dotted lines.

carbohydrates and lignin. The plots obtained for the material analysed show a considerable overlap of the UV and RI signals, which could indicate presence of lignin-carbohydrate complexes [Tunc *et al.*, 2010; Lawoko and van Heiningen, 2011].

As the HWE treatment time is prolonged, the onset of the RI response shifts towards a lower molecular weight, suggesting that the carbohydrates undergo a higher degree of hydrolysis. For STEX liquors, the response for both treatment times shows a substantial overlap and thus no time-related change. The higher molecular weight fractions observed for the STEX samples are in agreement with data in the literature on the extraction of hemicellulose from systems with a lower mass transport resistance (small-size wood chips, milled wood, etc.) [Rissanen *et al.*, 2014b; DeMartini *et al.*, 2015].

For both HWE and STEX treatments, the UV signals show a shift from a relatively high molecular weight fraction for liquors from the sample treated for 15 min towards a lower molecular weight after 30 min of treatment. This change can indicate either the degradation of the extracted lignin into smaller fragments or the disintegration of sugars in lignin-carbohydrate complexes upon prolonged treatment [Li *et al.*, 2005; Martin-Sampedro *et al.*, 2014]. It is interesting to note that the prolonged HWE treatment (60 min) results in an increased molecular weight, possibly because of either the partial condensation of lignin structures or the extraction of structures that require a longer time to diffuse out of the wood tissue.

4.1.2 Local effects of HWE and STEX on wood

In order to investigate local effects caused by the treatments studied, variations in the contents of carbohydrate and lignin in the individual sections of the treated wood chips were studied. The central section of each chip (the inner layer of the middle section, see 4.4) was used as a reference because its composition was assumed to be the least affected. Deviations from this reference were calculated by subtracting its contents of carbohydrate and lignin from the values determined for the individual sections.

All treated sections show variations in composition depending on their location in the wood chip. They are more pronounced in the HWE than in STEX samples, and mostly in the form of variations in the content of hemicellulose between the outer and inner layers: the edge, corner and outer layer fragments of the HWE treated chips contain less hemicelluloses than the middle fragment for all treatment times (Figure 4.4). A profile is visible in the local composition already after 15 min of HWE treatment and becomes more pronounced after 30 min as the autohydrolysis proceeds: these variations are most probably a consequence of mass transport within the treated wood chip [Krogell *et al.*, 2016; Rissanen *et al.*, 2016, 2014a,b]. The

reaction products accumulate partially in the inner fragments, while the diffusion from the outer sections is relatively faster. Also, despite the high mobility of the hydrogen ions, it is possible that local variations in acidity are due to local variations in the content of acetate.

STEX results in fewer compositional variations (Figure 4.4), possibly due to the disintegrating, rapid, pressure discharge that facilitates advective mass transport within the wood tissue. Moreover, as the heating up time is limited, the total resi-

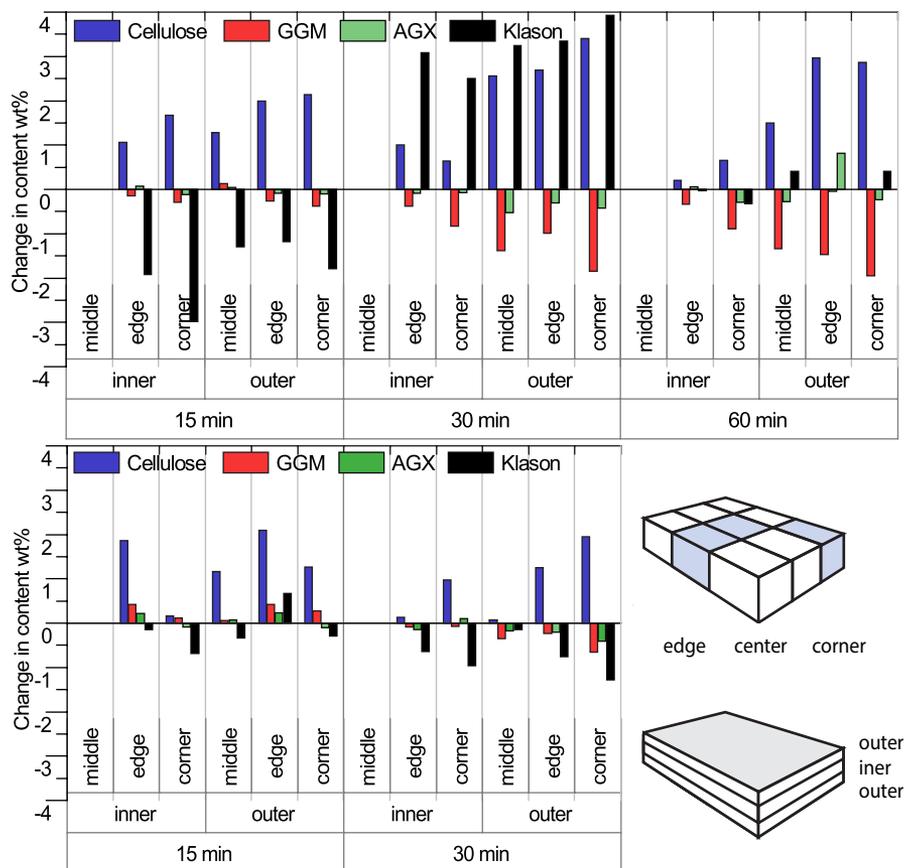


Figure 4.4: Variations in the local composition of HWE (upper) and STEX (lower) treated wood. The schematic illustration presents the wood sections selected.

dence time is shorter, which leads to a less extensive autohydrolysis.

Interestingly enough, short STEX treatment (15 min) induced an apparent increase in the content of hemicellulose and a decrease in Klason lignin in the external pieces, which actually indicates changes in the inner, i.e. reference, piece. This concurs with previous findings showing that the internal parts of steam-exploded chips are affected the most by the disintegrating effect of the treatment [Jedvert *et al.*, 2012]. A possible explanation for this may be that explosion causes an advective transport to occur, which enhances the removal of hemicellulose from the more disintegrated internal morphology of the wood chip, and results in a relative increase in the content of hemicellulose in the more outer fragments. After 30 min of pretreatment, a weak profile can be observed as the hemicelluloses are removed from the external part of the wood chips: this is due to autohydrolysis coupled with a more efficient mass transport from the outer sections, as discussed above. [DeMartini *et al.*, 2015] presented similar concentration profiles for hemicellulose subjected to short, but more severe, STEX-treatment.

4.2 Pretreatment of forest residues

4.2.1 Characterization of raw material

The starting material has to be characterized so that the effects of the treatment can be analysed. Unfortunately, forest residues are highly inhomogeneous in composition and their high content of extractives make analysis relatively difficult. Visual inspection allows the conclusion to be drawn that the material used in this study was constituted of a mixture of xylem and bark tissue from various parts of different tree species (Figure 4.5). In order to understand the composition of the material and its variations better, some fraction of wood chips (possibly originating from stem wood and bigger branches), small branches and bark were handpicked from it and analysed separately when the mixture was analysed, see Table 4.2.

The results obtained show that the content of lignin is relatively high in the bark and branches. This is related not only to an inherently high content of lignin in the material but also, as mentioned above, a high content of extractives affects the analyses and results by overestimating the content of Klason lignin (some extractives co-precipitate with the lignin during acid hydrolysis). Also, an “other fraction” (i.e. undetected compounds) comprised of extractives and ash is relatively large in these sections (compared to wood). The wood tissue has a significantly higher content of carbohydrate than the other samples that were analysed. Although the arabinose content is higher in bark and branches than in wood tissue (possibly due to the presence of arabinans and pectins in bark), the galactose fraction is highest in branches

Table 4.2: *The amount of anhydrosugars present in the sample, expressed as a weight fraction.*

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

*The deviation found from 3 samples.

and may be related to the presence of reaction wood. The relatively low contents of lignin (30.4%) and mannose (5.5%), together with a high content of xylose (14.2%), suggest a high fraction of hardwood [Raisanen and Athanassiadis, 2013; Teleman, 2016].

Forest residues were refined, milled and three samples were collected for analysis so that the overall composition of the material could be estimated accurately. As a result, the standard deviation from the average values obtained was in a similar range as measured previously for stem wood.

Extraction of the refined forest residues with acetone allowed the content of extractives to be measured (Table 4.3). Detecting acetone soluble extractives typical of softwoods (such as isopimaric, dehydroabietic and abietic acids), as well as those more commonly found in hardwood (such as β -sitosterol and botulin) [Fengel and Wegener, 1984], are other indications that the material is a mixture of softwood and hardwood. The overall content of extractives in the material was 16.9%. It is worth mentioning that this value may have been even higher in the original material, as it is possible that some of the extractives were vaporized during steaming and refining.

Table 4.3: *The contents of extractives in the forest residues, expressed as weight fraction.*

| 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 |
| Total | 16.9 |



Figure 4.5: *The material analysed. Above: untreated, steam exploded and refined forest residues. Below: separated fractions of wood chips, bark and branches.*

4.2.2 Steam explosion

Some of the changes rendered by steam explosion can be observed with the bare eye because the defragmentation of the material and the change in its colour are obvious (Figure 4.5), and some required chemical analysis (Table 4.4) to be detected, whilst others were seen as effects of the further delignification of the forest residues (and will be discussed later).

Table 4.4 presents the changes in the composition of the material after steam explosion at 4 or 7 bar (the amounts of the components are presented as weight percent of the sample, and not the original material). The most striking change is the decrease of the *other fraction* (from 10.5 to 8.7 and 6.1 wt% for 4 and 7 bar treatment respectively), a possible explanation for which is the evaporation and dissolution of extractives during steam pretreatment, although some of the extractives may react with the lignin during the treatment or precipitate with it when subjected to the acid treatment that forms a part of the Klason analysis procedure [Burkhardt *et al.*, 2013]. The changes in the content of extractives through both solubilisation/evaporation and co-precipitation with lignin result in a small increase of the Klason fraction.

The amounts of the components are presented as fractions of the material, and

Table 4.4: *Composition of the refined untreated and steam exploded material, in wt % on refined wood residues*

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

thus they show apparent changes in the composition: a significant decrease in one fraction may imply an increase of a more stable component. In this case, the *other fraction* decreases, which is probably the reason for an apparent increase in the glucose content, as cellulose (being the main source of glucose) ought to remain stable during this treatment. In the same way, the relatively stable content of sugars originating from hemicelluloses indicates the partial extraction of hemicelluloses: if this were completely stable, a relative increase in the hemicellulose content would have been observed.

Compared to what was found for wood tissue, the removal of hemicelluloses seems to be limited: in particular, there seems to be no effect on xylan, while the mannan content decreases only at 7 bar treatment.

The somewhat limited effect of steam explosion on the composition of the material may be related to the fact that its composition and structure is different to the softwood used in the previous experiments. The properties of the forest residues, such as the contents and characteristics of the hemicelluloses, lignin and extractives, may have influenced the treatment. Apart from having different origins, the sizes of the treated material differed: steam explosion was performed on refined material and, in Paper I, on whole wood chips. The literature on steam explosion shows that the size of the wood pieces being treated influences the effect of the treatment significantly: the impact is higher on larger chips [Ballesteros *et al.*, 2000; DeMartini *et al.*, 2015; Jedvert *et al.*, 2012]. Since the material here was refined, its size was relatively small, and the pressure difference therefore had a very small/no influence on the solid material when the pressure dropped suddenly in the whole sample (the explosion effect). The limited effects of the explosion reduce the advective transport and thus explain the rather modest removal of solubilized structures from refined forest residues upon STEX.

4.2.3 Pulping of forest residues

The steam-exploded forest residues were cooked for 60 and 180 min in kraft and soda liquors; an additional series of cooks was performed on untreated material as a

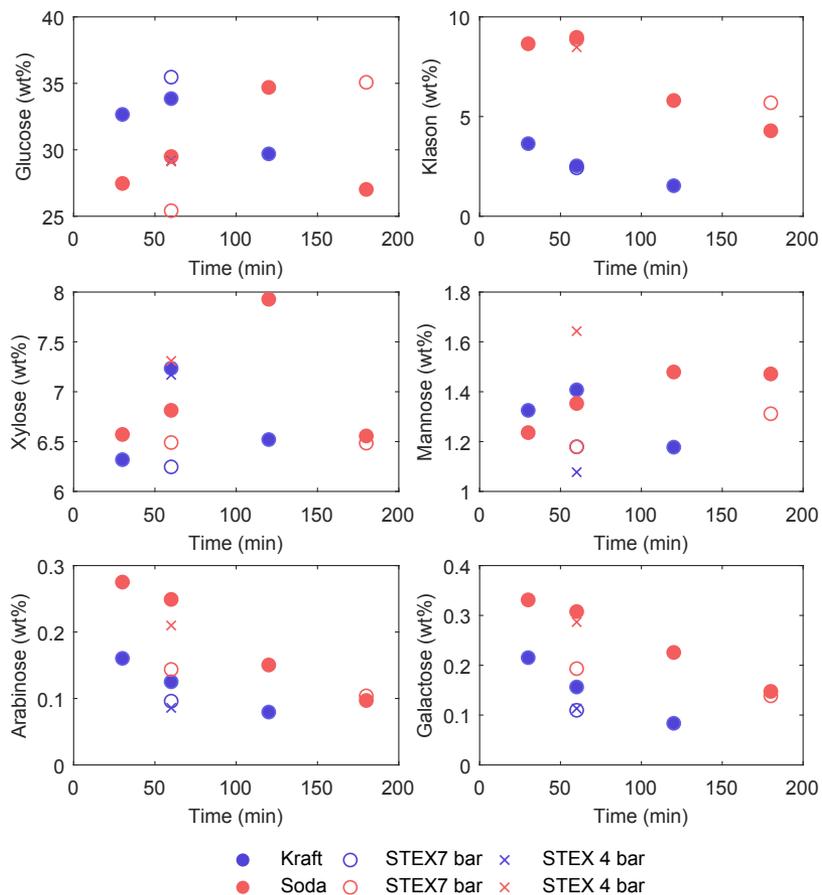


Figure 4.6: Changes in the composition of sugar and lignin upon cooking for 30 to 180 min (as wt% of the initial material)

reference. The latter had the same hydroxide ion concentration and cooking times of 30 to 180 min (60 or 180 min for pretreated samples). The kraft cooks had higher total ion concentrations, due to the addition of hydrogen sulphide and carbonate ions. The material, obtained in the form of pulps, was analysed for composition as was precipitated black liquor lignin; the results are presented in Table 4.5.

Comparison between soda and kraft pulping

Analysis of the pulps indicates that the cooking yields were relatively diverse for the samples and treatment conditions selected. Generally, soda cooking resulted in higher total yields (due to the greater amount of residual lignin present after cooking). The delignification and removal of carbohydrates seem to be rapid initially (i.e. during heating-up and 30 min cooking) and slower later on in the treatment: this is similar to the cooking behaviour known for xylem (with differences in the cooking efficiency). As expected, the removal of lignin was more efficient when kraft cooking was applied, as the cleavage of phenolic β -O-4 bonds in lignin is mediated by hydrogen sulphide ions. When compared to kraft [Jedvert *et al.*, 2013] and soda cooks of wood [Wigell *et al.*, 2007], pulps based on forest residues contain less lignin, which can be related to the different composition and morphology of the starting material.

Hemicelluloses undergo rapid dissolution and peeling during heating-up (GGM) and at the beginning of the cooking process (both GGM and AGX), followed by alkaline hydrolysis of the glycosidic bonds and secondary peeling later on in the cook. As a result, kraft cooking of softwood causes degradation of ca. 75% of the galactoglucomannan and 40% of the araminoglucuronoxylan present [Sjostrom, 1977]. It seems that arabinose, galactose and mannose follow this trend when forest residues are pulped.

Nonetheless, the xylan fraction declines rapidly only at the beginning of the cook: the remainder (roughly half of the initial value) is relatively stable throughout the rest of the cook, showing a minimal increase with time (Figure 4.6). The behaviour of xylan follows the changes in the content of Klason lignin in the precipitate obtained from the black liquor. The content of xylan and lignin in pulp is known to show a linear relation for wood subjected to both soda [Wigell *et al.*, 2007] and kraft cooking [Matthews, 1974]. This trend was not found for forest residues.

The content of xylan is generally higher in soda pulps, possibly due to the degradation and removal of some lignin carbohydrate complexes during the course of kraft cooking. A possible explanation of the behaviour found for xylan may be an increase in its re-adsorption on cellulose fibres: this is commonly associated with the chemical pulping of wood, and depends on the cooking conditions and concentration of xylan in the liquor [Jan-Åke and Nils, 1969; Jan-Åke, 1970; Meller, 1965]. The increase in resorption could be a consequence not only of the higher ionic strength of the kraft

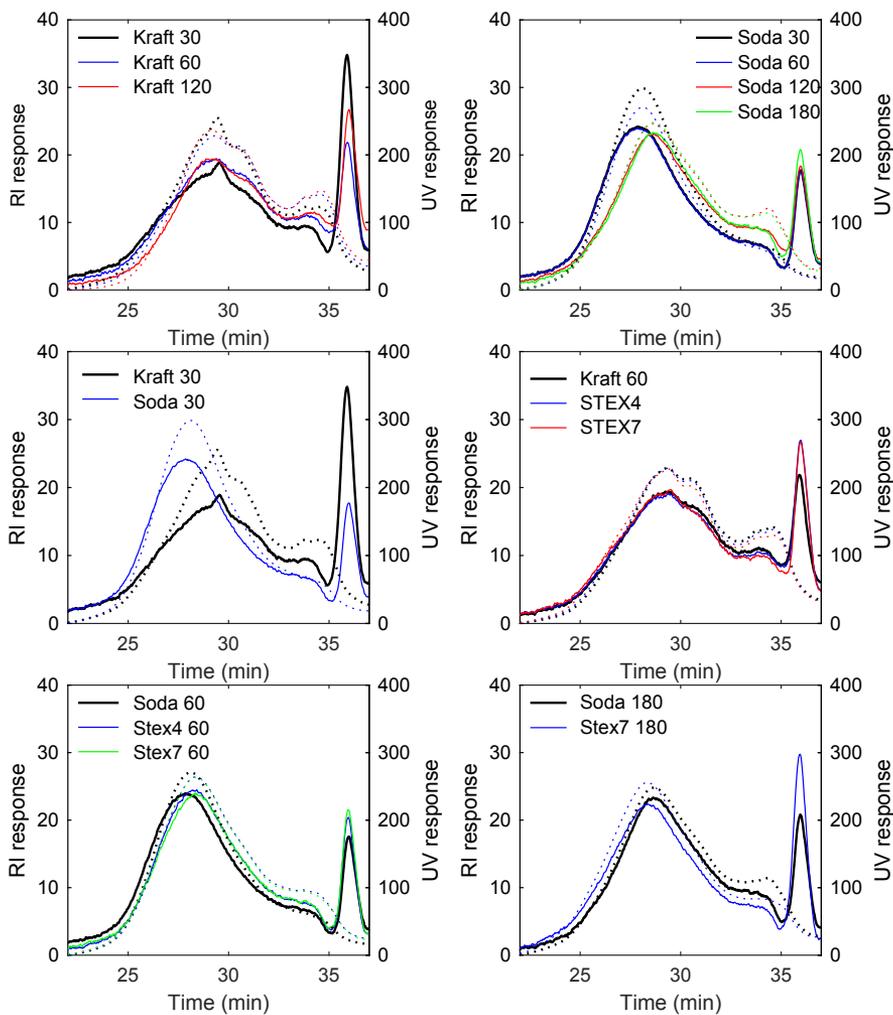


Figure 4.7: The GPC results obtained. RI response: solid lines. UV: dotted lines.

cooking liquor, which leads to a decrease in the repulsive forces between xylan and cellulose chains (as both are negatively charged), but also the decrease in the molecular extension of xylan, which favours the penetration of xylan molecules into the pores [Ström *et al.*, 1982]. Moreover, the somewhat different structure of the cellulose promotes the resorption, or presence, of xylan with different types/structures that have different re-adsorption properties and this could also contribute to resorption.

The glucose originates mostly from cellulose and is therefore stable under cooking conditions. The content of glucose decreases slightly upon cooking, possibly due to the peeling of hemicelluloses and cellulose as well as to the degradation of starch (Table 4.5). The variations detected in the glucose content can also be a reflection of the aforementioned inhomogeneity of the material. Kraft cooking seems to yield a higher glucose content than soda cooking, as is commonly observed in wood pulping.

The lignin extracted from the material during cooking was analysed (after precipitation from the black liquors) for molecular weight by GPC; the results are reported in Figure 4.7. As expected, the RI and UV signals overlap but, at the long elution time, the RI responses of all the samples show a peak indicative of low molecular non-aromatic compounds. The molecules detected originate most probably from extractives and are possibly degradation products.

Comparison of the results from different pulping experiments shows that lignin obtained from soda cooking generally has a higher molecular weight, which concurs with that observed for wood: a possible explanation is that it is extracted without cleaving phenolic β -O-4. In the case of soda pulping, plots obtained for the 30 and 60 min cooks overlap: the prolonged treatment induced a shift towards a lower molecular weight, suggesting degradation of the lignin in the liquor.

Table 4.5: *Composition of the pulps and the precipitate obtained from acidified black liquor.*

| Pretreatment STEX (bar) | Cooking Conditions | | | Composition of Pulp | | | | | | | | Composition of Precipitate | | | |
|-------------------------------|--------------------|---------------|-----------------|---------------------------|------|-------|-------|------|--------|------|-------|----------------------------|-----|------|--------|
| | Type | Time (min) | Yield (wt %) | Ara | Gal | Glu | Xyl | Man | Klason | ASL | Other | Ara | Gal | Xyl | Klason |
| | | | | (wt% on initial material) | | | | | | | | (wt% on lignin) | | | |
| - | - | - | - | 1.16 | 1.60 | 36.69 | 14.17 | 5.50 | 30.37 | 0.12 | 10.27 | | | | |
| - | Kraft | 30 | 42.2 | 0.16 | 0.22 | 32.66 | 6.32 | 1.33 | 3.64 | 0.41 | -2.52 | 0.6 | 0.4 | 7.3 | 71.2 |
| - | Kraft | 60 | 44.7 | 0.13 | 0.16 | 33.85 | 7.24 | 1.41 | 2.53 | 0.31 | -0.93 | 0.6 | 0.6 | 6.3 | 71.9 |
| - | Kraft | 120 | 39.8 | 0.08 | 0.08 | 29.69 | 6.52 | 1.18 | 1.53 | 0.39 | 0.31 | 0.4 | 0.4 | 2.3 | 66.1 |
| 4 | Kraft | 60 | 39.0 | 0.09 | 0.11 | 29.17 | 7.17 | 1.08 | 2.53 | 0.38 | -1.49 | 0.5 | 0.5 | 5.0 | 73.5 |
| 7 | Kraft | 60 | 45.7 | 0.10 | 0.11 | 35.47 | 6.25 | 1.18 | 2.43 | 0.27 | 0.17 | 0.2 | 0.2 | 1.2 | 78.7 |
| - | Soda | 30 | 46.6 | 0.28 | 0.33 | 27.47 | 6.57 | 1.24 | 8.65 | 0.66 | 1.46 | 0.7 | 0.4 | 13.8 | 70.8 |
| - | Soda | 60 | 48.8 | 0.25 | 0.31 | 29.49 | 6.81 | 1.35 | 8.97 | 0.63 | 1.02 | 0.7 | 0.5 | 10.2 | 72.9 |
| - | Soda | 120 | 50.1 | 0.15 | 0.23 | 34.69 | 7.93 | 1.48 | 5.81 | 0.56 | -0.70 | 0.5 | 0.5 | 5.3 | 76.1 |
| - | Soda | 180 | 42.2 | 0.10 | 0.15 | 27.02 | 6.56 | 1.47 | 4.29 | 0.00 | 2.59 | 0.4 | 0.5 | 3.3 | 76.0 |
| 4 | Soda | 60 | 51.2 | 0.21 | 0.29 | 29.11 | 7.31 | 1.64 | 8.48 | 0.54 | 3.60 | 0.5 | 0.4 | 8.8 | 73.2 |
| 7 | Soda | 60 | 49.5 | 0.14 | 0.19 | 25.42 | 6.49 | 1.18 | 8.87 | 0.50 | 6.75 | 0.3 | 0.2 | 2.6 | 82.3 |
| 7 | Soda | 180 | 49.5 | 0.10 | 0.14 | 35.08 | 6.48 | 1.31 | 5.69 | 0.25 | 0.70 | 0.1 | 0.1 | 0.2 | 77.0 |

Effects of pretreatment on pulping

Comparing the steam-exploded material prior (Table 4.4) and after kraft and soda cooking (Table 4.5), it can be ascertained that the *other fraction* in pulps is much smaller and most likely indicates the dissolution of extractives. As the extractives were removed, the mass balance improved. A comparison between steam-exploded and untreated material cooked for 60 min shows that the pulps have similar contents of Klason lignin, which is in contrast to the behaviour observed previously for wood where the pretreatments enhanced delignification [Jedvert *et al.*, 2013]. The difference can be related to the aforementioned effect of the size of the treated material reducing the effect of the steam explosion. It is interesting to note that although the content of Klason lignin was the same in the pulps, it was found to be higher in the precipitates of black liquor taken from the pretreated samples. This discrepancy can be a result of the generation of pseudo-lignin (lignin condensed with degradation products from hemicelluloses) during the steam explosion [Heitz *et al.*, 1991].

Steam explosion affected the sugar composition of the pulps. It resulted in a lower xylan content after 60 min of cooking independent of cooking method and, when performed at 7 bar, the xylan content in the lignin precipitate from the black liquor was also found to be lower. The latter can be a result of the partial extraction and degradation of xylose into furfural in acidic conditions during steam pretreatment [Abatzoglou *et al.*, 1990; Janzon *et al.*, 2014; Li *et al.*, 2005]. Last but not least, the glucose content was somewhat decreased in the pulps, possibly as a consequence of the removal of hemicelluloses and pectins during pretreatment

The GPC results reflect the molecular weight distribution after pretreatment and cooking, making it difficult to evaluate the effect of the steam explosion itself. The plots for Kraft lignin, shown in Figure 4.7, for untreated and steam-exploded material overlap fully. For the 60 min soda cook, steam explosion 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 lignin MWD of the pretreated sample was shifted towards the higher molecular mass region. Depending on which lignin fractions are extracted from the material, the effects 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), which will not be visible until these fragments have been transported out from the material, i.e. only after long delignification times.

The $^1\text{H}^{13}\text{C}$ HSQC NMR-spectra of the lignin rich fractions extracted in 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: $\text{CH}_2\text{-COOH}$ (34.2/2.2 ppm), CH_2 (25/1.5, 29.1/1.1, 31.8/1.2 ppm), CH_3 (15/0.7 ppm) (Appendix, Figure A1). The latter concurs with the low molecular

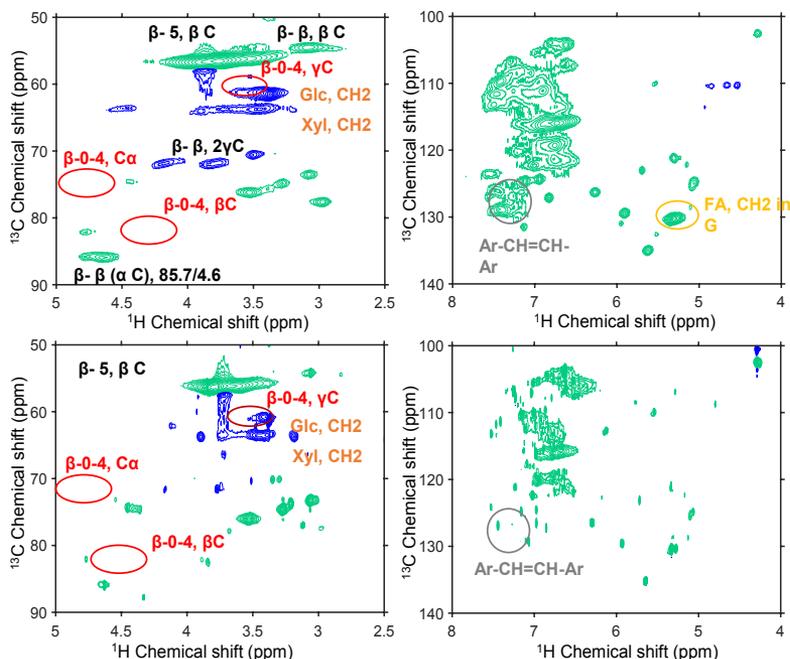


Figure 4.8: The NMR-spectra of the lignin rich fractions extracted in 180 min soda cook of steam exploded (top) and non-pretreated forest residues (bottom)

mass signal observed in the MWD chromatograms.

As observed previously in our studies, no signals of $\beta - O - 4$ could be found after soda cooks were performed (Figure 4.8) [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/vague in the samples cooked without pretreatment, namely signals indicating:

- the increased presence of $\beta - \beta$ linkages: α CH (85.7/4.6), β CH (54.1/3.1) and γ CH₂ (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 (CH₂, 62.1-64.3/3.3-3.8) and Glc (CH₂ 60/3.-3.8)

- an increased presence of fatty acids such as: CH=CH(128.2/5.3 130.1/5.3).

These findings point out an enhanced mass transport of material during soda cooking upon steam explosion pretreatment (carbohydrates, extractives and conjugated/condensed lignin structures). At the same time, they call attention to the possibility of condensation of lignin during STEX, indicated by occurrence of β - β linkage along with shift to higher molecular weight in the GPC chromatograms. However, it should be kept in mind that these structures are also to a varying extent present in native lignin and the relatively strong β - β NMR signals observed can simply be a result of enhanced extraction of these structures due to STEX combined with a relatively long delignification (180 min).

5

Conclusions and Future Work

5.1 Conclusions

- Steam explosion achieves a comparably greater removal of hemicelluloses from wood than hot water extraction, as the compositional effects are influenced strongly by the rapid pressure-release step. During the prolonged treatment, however, the autohydrolysis, coupled with mass transport resistance, becomes important in the development of different composition profiles within the wood chips.
- Hot water extraction, when applied for a short time, introduces significant variations in the local composition within the treated wood: it leaves the composition of the inner part of the tissue less affected. Prolonged treatment, on the other hand, leads to a more severe overall hydrolysis.
- The delignification rate of forest residues is faster than that of wood.
- The behaviour of xylan during delignification differs for forest residues when compared to wood: rapid initial extraction followed by a rather stable content during the rest of the pulping process, along with no commonly-observed co-extraction of xylan - lignin, indicates the possibility of the enhanced re-adsorption on celluloses and/or occurrence of different types of xylan.

- The impact of steam explosion was found to be limited when material of smaller size was pretreated.
- There are some indications that pseudo-lignin forms in pulps during STEX of forest residues, although this is possibly connected to presence of extractives.

5.2 Future work

Future work should focus on more detailed investigation of the molecular weight and structure of the hemicelluloses recovered in relation to the pretreatment conditions and raw material. It could also involve investigating structural changes that are possibly induced in lignin upon steam explosion pretreatment. In a broader perspective, the prospect of integrating steam explosion with existing pulping processes, and applying it in combination with other pretreatments, is a topic of interest.

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Appendix

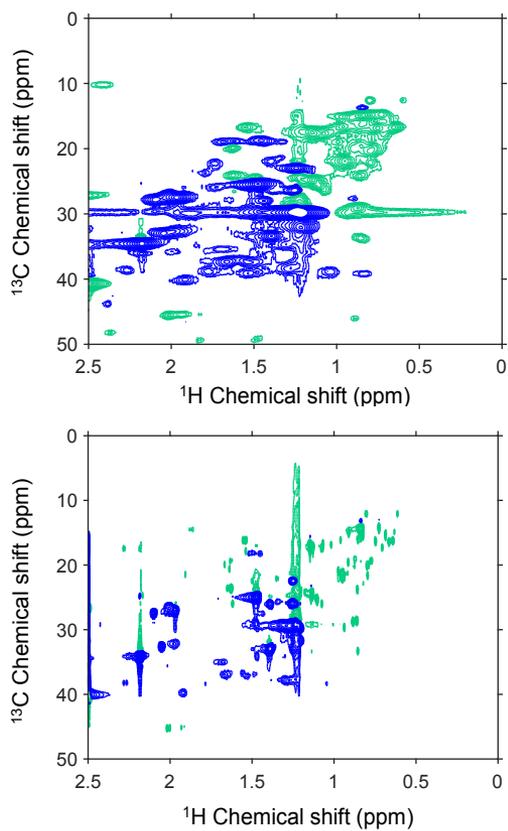


Figure A1: The NMR-spectra of the lignin rich fractions extracted in 180 min soda cook of steam exploded (top) and non-pretreated forest residues (bottom)