

Isolation of cellulose fibres from agricultural waste

Production of dissolving-grade pulp from oat husk and wheat straw

Master's thesis in Innovative and Sustainable Chemical Engineering

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Cover: Photographs of raw materials and pulps after acid pretreatment, soda pulping and EDTA-assisted hydrogen peroxide bleaching sequence. Wheat straw (top left), oat husk (top right), wheat straw pulp (bottom left), oat husk pulp (bottom right).

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Abstract

Recent decades have seen an increase in environmental awareness about the impact of everyday products. Cellulose is the most abundant natural polymer in the world and has long been used for production of films and textiles. The cellulose has traditionally been isolated from wood as a dissolving-grade pulp and then further processed into the desired product. Dissolving-grade pulps have narrow molecular weight distribution and contain high levels of cellulose, low hemicellulose and low amounts of lignin and ash and can be turned into a wide range of products. However, due to a future expected shortage of fibres, finding new raw materials is a must. One alternative source of cellulose could be to isolate cellulose from agricultural waste.

This project has been evaluating the suitability of using oat husk and wheat straw as alternative raw materials for the production of dissolving-grade pulp. These raw materials were chosen because of their abundance in Sweden, their low value and relatively high cellulose content. The process chosen was the prehydrolysis-soda pulping process, where a prehydrolysis step is used to remove hemicelluloses and facilitate delignification, and soda pulping is used as the main delignifying step.

An acid prehydrolysis-soda pulping process followed by a total chlorine-free (TCF) bleaching sequence was proven to be suitable for oat husk. The produced pulps had uniform molecular weights, high cellulose content, low hemicellulose content and little to no lignin content. The acid prehydrolysis was efficient in removing hemicelluloses and facilitating delignification in the soda pulping step.

With a higher liquid to solid ratio in the acid pretreatment and higher concentrations of NaOH during cooking, wheat straw exhibited similar properties regarding molecular weight distribution, cellulose and hemicellulose contents. However, ash and lignin removal was difficult. When the leaves were removed from the wheat straw, nearly all requirements for use as dissolving-grade pulp were met but the lignin levels.

Both of the raw materials assessed in this project show great potential to be used as raw materials for dissolving-grade pulps while also requiring milder process conditions than wood. Even though more research is needed to fully assess the suitability of the raw materials for dissolving-grade pulp production, the door of possibilities is wide open.

Keywords: Dissolving-grade pulp, cellulose fibres, soda pulping, acid pretreatment, autohydrolysis, hot water extraction, wheat straw, oat husk, agricultural waste, spruce

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Niclas Sjöstedt, Gothenburg, May 2022

List of Abbreviations

Below is the list of abbreviations that have been used in this thesis listed in alphabetical order:

AP	Acidic pretreatment
Ara	Arabinose
AS process	Acid sulfite process
ASL	Acid soluble lignin
DP	Degree of polymerisation
Gal	Galactose
Glu	Glucose
HWE	Hot water extraction
Klason	Klason lignin
l/s ratio	Liquid to solid ratio
Man	Mannose
M_n	Number average molar mass
MMD	Molecular mass distribution
M_p	Peak molecular weight
M_w	Mass average molar mass
MWD	Molecular weight distribution
M_z	Z-average molar mass
N/d	Not detected
PDI	Polydispersity index
PHK process	Prehydrolysis kraft process
Xyl	Xylose

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1 Introduction

1.1 Background

As reports on global warming have become more alarming, recent decades have seen a shift in focus on the environmental impact of our everyday products. Most of the polymers used in society today originate from fossil-based sources, but the non-biodegradable nature and the CO_2 releasing productions of these materials have made the need for biobased polymers even greater.

Cellulose is the major building block of green plants and it is the most abundant natural polymer on earth. It is also a perfect biobased alternative to use as starting material when replacing many fossil-based polymers. The cellulose has traditionally been isolated from wood as paper pulp or in a more pure form as dissolving-grade pulp, which can be used to produce for example films and textiles. But to further reduce the environmental impact and increase the economic feasibility of cellulose-based products, cellulose from low-value side-streams must also be considered.

Annual plants such as wheat and oat are grown in enormous amounts in Sweden. Parts of these plants, which are often seen as waste, also contain high levels of cellulose. Especially promising of these plant parts are the straw from wheat, which is often used as animal fodder or left on the fields to enrich the soil, and the husk from oats, which is separated from the grain during milling and mostly burned for energy. Although these agricultural waste streams are rich sources of cellulose, little research has been put into investigating the suitability of wheat straw and oat husk as starting materials in the production of dissolving-grade pulp. Available literature suggests different process challenges to those present when using wood as raw material, such as removal of high amounts of ash compounds[1].

While the production of dissolving-grade pulp from wheat straw or oat husk could create more value for agricultural waste in a forest-rich country like Sweden, it could also have a bigger impact in forest deficient countries. Countries like China and India have limited forest resources but a rich supply of non-wood raw materials, meaning that there are big opportunities should the production of dissolving-grade pulp from these materials be possible.

1.2 Aim

This project aims to assess the suitability of certain agricultural waste materials, namely wheat straw and oat husk, for the production of dissolving grade pulp. This is done to evaluate new uses for agricultural sidestreams and in the long haul increase the value of said sidestreams. This project also aims to gain a more complete understanding of the range of raw materials that can be used in the production of dissolving-grade, the specific process challenges posed by using these raw materials, and how to overcome them.

2 Theory

The following section will describe the raw materials used in this project, namely wheat straw and oat husks, as well as lignocellulosic materials in general and their basic components. The process steps present in the production of dissolving-grade pulp will then also be explained.

2.1 Lignocellulosic materials

Lignocellulosic material is the most abundant renewable feedstock on earth and makes up the most dry mass of vascular plants on earth[2]. Lignocellulosic materials are mainly made of carbohydrate-polymers called cellulose and hemicelluloses, as well as of aromatic polymers called lignin. These compositions vary depending on the type of plant, structure, and growing conditions[3][4]. Some extractives such as organic acids and water-soluble sugars as well as non-organic compounds are also present in small amounts in most lignocellulosic materials[5]. Lignocellulosic materials can roughly be classified as wood and non-wood materials. Wood lignocellulosic biomass refers to hardwood(broadleaf trees) and softwood(conifers), while non-wood refers to a much wider range of plants that lack the same structural integrity as wood[6].

2.1.1 Wheat straw

Wheat straw is the first of the two agricultural residual materials studied in this thesis. It is one of the most abundant agricultural residual products in the world with annual production exceeding 500 million tonnes[7]. Wheat straw is a by-product obtained after harvesting wheat grains with several different anatomical sections where the internodes make up the largest weight fraction of the plant of roughly 55%[8]. Leaves and nodes make up the remaining parts of the wheat straw[9]. As with all lignocellulosic materials, the presence of cellulose, hemicelluloses, and lignin can differ depending on growth conditions, but compositional analysis has shown that wheat straw consists of roughly 34-40% cellulose, 20-25% hemicelluloses and 20-25% lignin[9]. Wheat straw also comprises relatively high amounts of ash, around 9%, where silica makes up nearly 75% of the ash content[10].
There are currently several uses for wheat straw but very few of high economic value. Wheat straw is mostly used for cheap fibre supplements for animals, left in the fields to prevent erosion, or used as bedding material for livestock. If not used for this, it is often treated as waste or burned which releases CO_2 into the air[11]. The wheat straw used in the project can be seen in figure 1.



Figure 1: Wheat straw

2.1.2 Oat husk

The second agricultural residual material studied is oat husk. Oat husk is a by-product of oat milling and consists of the outer hard shell of the oat cereal grain. It is the largest by-product of the oat grain milling process, making up roughly 30% of the oat grain[12]. Oat husks consist of 15-25% of cellulose, 20-35% of hemicelluloses, and 10-30% of lignin[4]. The ash content in oat husks is typically between 5-7% and not as high in silica as wheat straw[4]. Oat husks have historically been used as a raw material for furfural production, but alternative sources of pentosan have since taken over. Oat husks are currently mostly used for energy production as clean-burned biomass. A small part is also used as dietary fibre supplements for animals[13]. Due to its high contents of hemicelluloses and especially arabinoxylans, oat husks could also provide an excellent starting material for the production of ethanol and xylitol[14].



Figure 2: Oat husk

2.1.3 Spruce

Spruce was used in the project as a comparison to the agricultural waste materials. Spruce is classified as a softwood and is commonly used in the pulping industry. The tree consists of several different plant parts where branches and needles are removed during harvesting and the bark prior to the pulping process. Spruce wood comprises roughly 40% cellulose, 35% hemicelluloses and 25% lignin[15]. Contrary to wheat straw and oat husk, spruce wood contains only around 0.3% ash compounds[16]. Due to the long fibres present in the wood of spruce, pulp made from spruce show increased strength properties compared to pulp made from shorter fibres[17]. Spruce is the most commonly grown tree in Sweden and is used in enormous amounts in both the timber and pulping industries[18].



Figure 3: Spruce shavings

2.2 Cellulose

Cellulose is the most abundant biopolymer in most lignocellulosic biomass and makes up roughly 38-50% of all biomass on earth[5]. Cellulose is a polymer comprised of glucose monomers, which is a six-carbon sugar molecule as seen in figure 4. The glucose units in the chain are linked together through $\beta - 1,4 - glycosidic$ bonds. The purpose of cellulose in plants is to provide rigidity and structural integrity to the plant[5].
As cellulose chains contain hydroxyl groups, there are possibilities of interactions between cellulose chains through hydrogen bonds. When these interactions between cellulose chains occur, the chains are organised in sheets through parallel stacking stabilised by interchain OH-O-bonds, van der Waals forces, and weak hydrogen bonds[19]. The stacking of sheets on top of each other results in a crystalline structure, where the cellulose is packed in an organised manner. Contrary to crystalline regions in cellulose, amorphous regions contain much shorter chain lengths as well as a wider distribution in chain lengths[20].
A higher proportion of amorphous regions make cellulose more reactive compared to cellulose with a high proportion of crystalline regions[20].

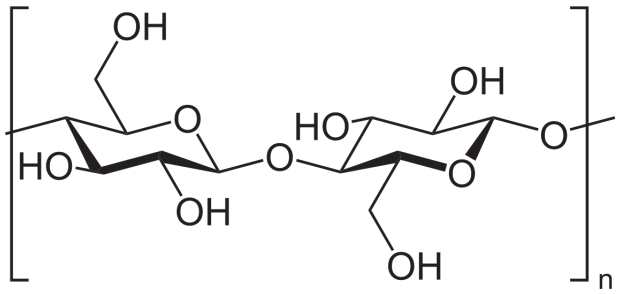


Figure 4: Structure of a cellulose molecule

2.3 Hemicelluloses

Hemicelluloses are a group of polysaccharides present in both wooden and non-wooden lignocellulosic materials as well as in some seaweeds. Hemicelluloses can both be composed of glucose as well as other water-soluble sugars. Apart from cellulose, which only differs in degree of polymerisation, hemicelluloses also differ in chemical composition, hence they can be split into different groups. Native hemicelluloses also have a significantly lower degree of polymerisation than native cellulose, usually between 50 to 200[21]. The most important function of hemicelluloses is to strengthen the cell walls by binding to cellulose with pectin to form cross-linked networks, and by interacting with lignin[22]. The hemicelluloses of the largest fraction in oat husks and wheat straw are arabinoxylan and arabinogalactan[23]. The most common hemicellulose in spruce is galactoglucomannan and arabinoglucuronoxylan[24]. Galactoglucomannan is a hemicellulose that consists of galactose, glucose, and mannose, while arabinoglucuronoxylan consists of arabinose, glucuronic acid, and xylose.

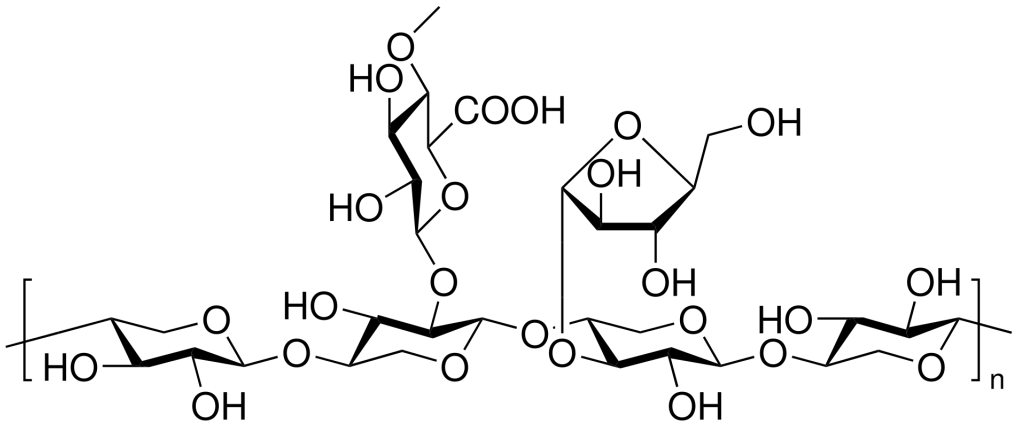


Figure 5: Structure of arabinoxylan

2.4 Lignin

The third component in lignocellulosic biomass is called lignin. Contrary to cellulose and hemicelluloses that have set molecular compositions, lignin is a class of complex aromatic and aliphatic structures with irregular compositions and placements in the cell walls. Lignin can form complexes with hemicelluloses to form naturally occurring composite

materials that provide structure and rigidity to the cell walls[25]. Most lignin is also hydrophobic by nature which acts as a physical barrier against hydrolysis of cellulose, as cellulose is highly hydrophilic[26]. For this reason, the content of lignin is often high in protective plant tissue such as bark.
While the structure of lignin is highly heterogeneous, the main structure is made up of three different molecules made up of phenylpropane that crosslink to form the lignin structure, as seen in figure 6. These three molecules called lignols are all alcohols and called coniferyl (4-hydroxy-3-methoxyphenylpropane), sinapyl, (3,5-dimethoxy-4-hydroxyphenylpropane) and coumaryl (4-hydroxyphenylpropane). All of these lignols are present in hardwood, softwood, and grasses but in vastly different amounts. Hardwoods and grasses both contain high contents of coniferyl and sinapyl while softwoods lignins are mostly made from coniferyl units[27]. The polymerisation of lignin occurs via oxidative radical polymerisation of these three lignols to form H, G, and S type lignin. H lignin is derived from coumaryl, G lignin from coniferyl, and S lignin from sinapyl, where H lignin is the least common lignin in nature[28].

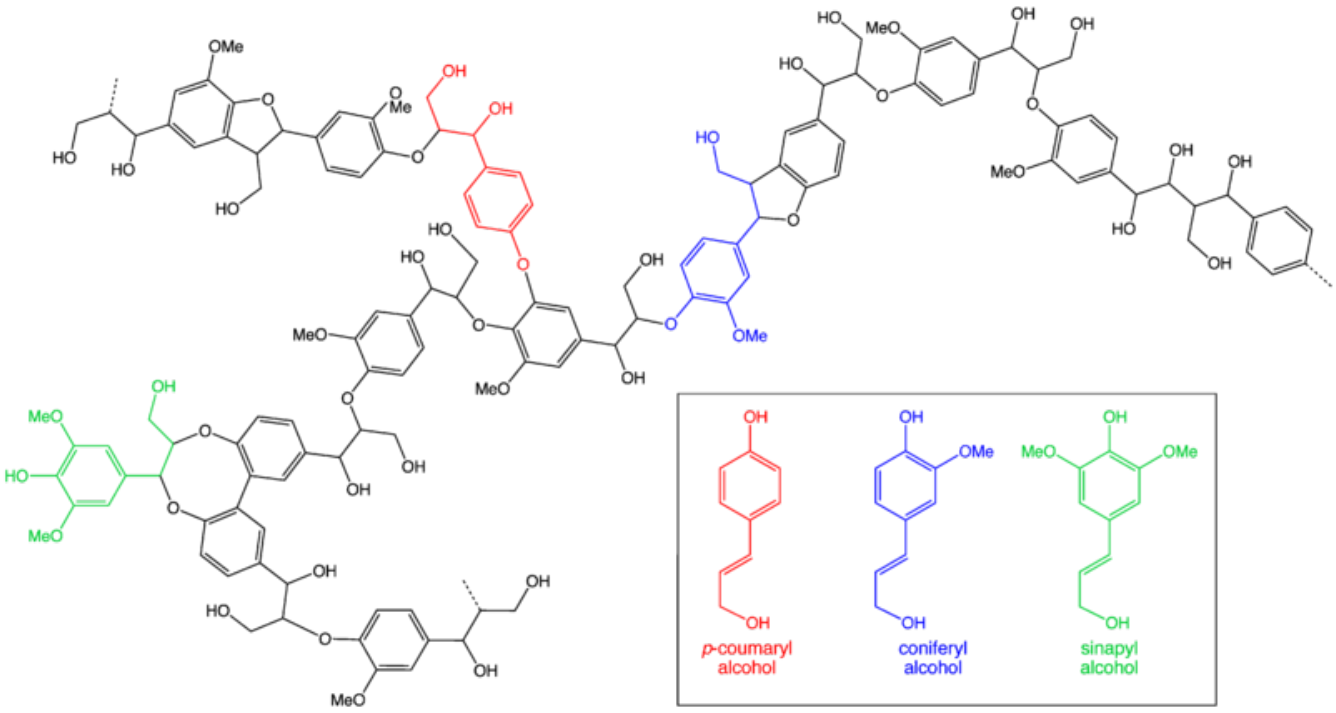


Figure 6: Lignin network with lignols

The lignin network is made from crosslinking these lignin monomers with both C-C and C-O-C-bonds, as seen in figure 6. The frequency of these bonds depends on the relative ratio of the different phenolic structures present in the lignin network[28].

2.5 Ash

Ash is defined as the inorganic residues that remain after combustion. Most non-wood lignocellulosic materials have significantly higher ash content than hardwood and softwood trees. Cereal straws have among the highest ash contents among all lignocellulosic

materials[29].
The ash content of wheat straw ranges from 5-11% depending on growth conditions and botanical part of the straw. The internodal parts of the straw have a relatively low ash content of roughly 3%, whereas the nodes and leaves have significantly higher ash contents[30]. Silica is the largest mineral component and is predominantly found as SiO_2. Silica makes up some 65-70% of the ash content in wheat straw and can severely limit the pulping process of wheat straw by complicating the recycling of cooking chemicals[31]. Other ash components of significant amounts in wheat straw are potassium, calcium and magnesium, but all these are less pronounced than silica[10]. The silica is present in the whole plant but is found in the highest concentration in the epidermal parts of the plant cells in the form of small structures called phytoliths[32]. The reason to the high silica content in non-wood plants is not yet fully known, but previous research indicates that silica is connected to plant growth and resistance to fungal infections in field-crops[33].
Oat husks have a similar composition of ash components as wheat straw, but normally in lower amounts. Oat husks contain roughly 5% ash where 75-85% consists of silica. Smaller amounts of calcium, potassium and magnesium are also present in oat husks[34].

2.6 Pretreatments of raw materials

To be able to produce a dissolving-grade pulp with the desired properties, a chemical pretreatment might be needed to extract excess hemicelluloses and open up the fibre structure to facilitate a greater removal of lignin and hemicelluloses in the subsequent pulping process. There are multiple types of pretreatments that are performed to achieve different purposes. Removing hemicelluloses is the primary target for oat husks and wheat straw, but the pretreatments can also open up the wood structure to make the cellulose more accessible. Disintegrating the lignin structures or removing ash compounds can also be targets of performing pretreatments of the raw materials. Mechanical pretreatments can also be of great importance in order to increase the accessible surface area and decrease mass transfer. Examples of mechanical pretreatments are grinding and chipping.

2.6.1 Prehydrolysis

One type of pretreatment that is frequently used in the commercial production of dissolving-grade pulp is an acidic prehydrolysis step. A prehydrolysis can both be performed with dilute acid as well as with water. At high temperatures and pressures, acidification of the prehydrolysis media occurs. This effect occurs due to a phenomenon called autohydrolysis and is a result of organic acids being released from the lignocellulosic material to cause partial deacetylation of the hemicelluloses. This releases acetic acid from bound acetyl groups in the hemicelluloses which causes an acidification of the prehydrolysis liquor[35]. Sulfuric acid is mostly used within the commercial process but other acids such as hydrochloric acid have also been proven to work for prehydrolysis purposes. The prehydrolysis step helps loosen the lignocellulosic matrix of the raw material before cooking to increase the accessibility of the lignin for the cooking chemicals[36]. However, condensation of lignin structures onto fibres is a risk of too severe prehydrolysis conditions which could make the lignin resistant to the delignification in the pulping step[37]. The most important purpose of prehydrolysis is to remove hemicelluloses. Due to the more branched

nature and shorter chain length of hemicelluloses, compared to cellulose, the hemicelluloses in the raw material are easier to hydrolyse[38]. The hemicelluloses are hydrolysed into their monomeric or oligomeric forms under acidic conditions. These monomers are easily dissolved into the prehydrolysis liquor and then washed away in the subsequent washing step.
The hemicelluloses separated from the raw material in the prehydrolysis can be used for fermentation for bioethanol production but can also be recovered for the production of high-value products. However, the standard procedure now is mostly to burn the prehydrolysis liquor for energy[39].

2.7 Pulping process

The main purpose of the pulping process is to liberate the cellulose fibres into individual fibres. Pulping can both be performed mechanically or chemically, where mechanical pulping liberates fibres by mechanical force, pressure, and temperatures, while chemical pulping liberates the cellulose fibres by solubilising the lignin that holds the fibres together. As only chemical pulping delignifies the raw material, it is the way of pulping used to produce dissolving-grade pulps. Chemical pulping is designed to break down the structures of lignin into smaller fractions which then become soluble in the cooking liquor.
Commercial pulping of wood is mostly performed with the Kraft process, also called the sulfate process. This process utilises sodium hydroxide in combination with sodium sulfide to delignify the raw material[40]. Soda pulping is also an alternative to Kraft cooking which only utilises sodium hydroxide as active chemical. Another process that is used commercially is the sulfite process, which is a process that uses a bisulfite solution to delignify the raw material[41].

2.7.1 Soda pulping

Soda pulping is the chemical process of using sodium hydroxide as the active chemical to produce pulp from lignocellulosic materials. Soda pulping only makes up a minor share of the commercially used pulping techniques for wood pulping but is the preferred process for pulping annual plants[42]. Soda pulping utilises sodium hydroxide (NaOH) as active chemical under high pressure and temperatures well above the boiling point of the cooking liquor, commonly between $150 - 170°$[43]. This achieves swelling of the fibres to increase the accessibility of the cooking chemicals and for better penetration into the raw material[43].
The soda pulping process achieves delignification mostly by breaking the non-phenolic β-O-4 linkages within the lignin networks yielding smaller fragments of the lignin, as seen in figure 7. These smaller fragments are easily dissolved in the highly alkaline cooking liquor and are then washed away in the subsequent washing step[42].

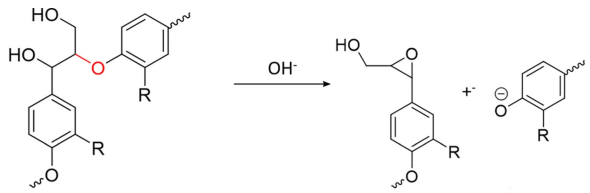


Figure 7: Cleavage of β-O-4 linkages under alkaline conditions

Phenolic lignin structures are not delignified as easily as non-phenolic structures in the lignin complex when only sodium hydroxide is used as a cooking chemical. During soda cooking, the phenolic lignin structures will form a quinone methide intermediate. This quinone methide will then under alkaline conditions either release formaldehyde to form an enol ether or partake in either reduction or condensation reactions[43]. These phenolic lignin structures will then subsequently become ionised which increases the solubility of the fragments and allows for dissolution in the cooking liquor.
Soda pulping can also be enhanced to reduce carbohydrate degradation and increase delignification by the addition of anthraquinone[44]. The degradation of other carbohydrates than lignin could be of big concern when using soda pulping. This will result in large yield losses as mainly hemicelluloses are degraded by peeling reactions and dissolved into the cooking liquor[42]. Some random alkaline hydrolysis of glucosidic bonds is also taking place during soda pulping[42]. This is however to some extent desired for the production of dissolving-grade pulp, as the carbohydrates that are especially prone to degradation are the hemicelluloses due to their lower degree of polymerisation compared to cellulose[42][44]. Previous studies have shown that the amounts of dissolved carbohydrates in the cooking liquor increase rapidly during the initial delignification of the cooking. The dissolution of carbohydrates then stagnates during the bulk delignification phase, to then increase again in the final delignification[42]. A depiction of this can be seen in figure 8 below.

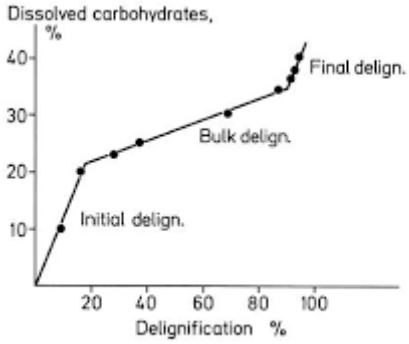


Figure 8: Dissolved carbohydrates during alkaline pulping[42]

One of the by-products formed from the cooking process is black liquor, which is the now dark coloured cooking liquor that contains dissolved lignin, degraded hemicelluloses as well as other extractives from the raw material. The black liquor contains many compounds that can be used in the production of value-added products. Soda cooking

has a major advantage for further monetisation of lignin compounds as it doesn't sulfonate the lignin molecules, as opposed to the sulfite and Kraft processes[45]. The lignin from the soda process can then be precipitated by lowering the pH of the black liquor and then used in the production of for example phenols and vanillin[45].

2.8 Dissolving-grade pulp

Dissolving-grade pulp is a pulp that is used to make products such as viscose, cellophane and cellulose ethers. The pulp is produced to contain high contents of cellulose and low levels of hemicelluloses, lignin, ash and other extractives. The exact amounts differ depending on the application, but in general, the pulp must contain at least 90% cellulose, below 5% hemicelluloses and trace amounts of lignin and ash[46]. Dissolving-grade pulps must also fulfil other requirements such as uniform molecular weight distribution, a degree of polymerisation adjusted for purpose of use as well as having a high cellulose reactivity[47]. A dissolving-grade pulp produced with the pre-hydrolysis Kraft (PHK) process usually has a polydispersity index (PDI) of 3.8-4.5[46], which is a measure of the heterogeneity of the produced pulp based on size of the polymer chains. The degree of polymerisation of the cellulose chains can differ depending on pulp application. For textile production such as viscose, the degree of polymerisation (DP) is usually kept in a range between 400-600[48], but there are also uses for pulps with higher and lower DPs as well.
Dissolving-grade pulp is commercially mostly produced from wood or cotton linters. 85% of the commercially produced dissolving-grade pulps are made from either hardwood or softwood and 10% from cotton linters[46]. Due to an increase in demand, much research has been devoted to the production of dissolving-grade pulp from non-wood materials such as bamboo and rice straw[46].
The main commercial processes for the production of dissolving-grade pulp from wood are the acid prehydrolysis Kraft process (PHK) and the acid sulfite (AS) process[49]. The AS process is better suited than the regular Kraft process for making dissolving-grade pulp. The reason for this is that the glycosidic bonds in the hemicellulose chains are cleaved spontaneously under the acidic conditions in the AS process[49]. To account for this, an acidic prehydrolysis is added to the Kraft process to remove hemicelluloses in the raw material before the alkaline cooking process[46]. To reach the desired purity of the pulp, a multi-stage bleaching step is usually also added to the process[46]. An additional extraction of hemicelluloses can also be required after the cooking process in the form of a cold caustic extraction[50].

2.9 Post-treatments

Post-treatment is the denomination of a treatment performed after the pulping process to either remove unwanted compounds or give the pulp the desired quality.

2.9.1 Bleaching

Bleaching is the process of whitening the wood pulp, mainly by removing chromophores - mostly found in the residual lignin. The bleaching is often conducted in several steps in a

so-called bleaching sequence. A bleaching sequence is often a series of different bleaching techniques. There are three main types of bleaching currently used commercially. These three methods are chlorine (Cl_2) bleaching, elemental Chlorine Free (ECF) bleaching and total chlorine-free (TCF) bleaching.
In the early days of pulp production and until the late 1980s, Cl_2 bleaching was the most used method. Bleaching with elemental chlorine is an efficient method of delignification but is currently rarely used due to the negative environmental effects of chlorinated organic matter produced in the process[42]. The pulping industry has since to a large extent transitioned to using chlorine dioxide-based bleaching methods instead of elemental chlorine. This transition has decreased environmentally harmful chemicals released from pulping wastewaters[51].
The most environmentally friendly way of bleaching pulp is done with the TCF bleaching method, where no chlorine is used. This method has been proven to drastically reduce emissions while still offering excellent bleaching properties[52]. TCF bleaching is often performed in a sequence of first using oxygen delignification before the primary bleaching steps where hydrogen peroxide bleaching and/or bleaching with ozone is used.

2.9.2 Hydrogen peroxide bleaching

Hydrogen peroxide-based bleaching has long been a common bleaching method for bleaching mechanical pulp due to its ability to selectively remove chromophoric groups without significant losses in pulp yield[42]. In recent times it has also been of interest in TCF bleaching of chemical pulp due to its environmentally friendly properties. Bleaching pulp with hydrogen peroxide is carried out at a pH between 10.5-12 and temperatures between $80 - 100°C$. Higher pH is beneficial for the bleaching abilities, however, alkaline decomposition of the hydrogen peroxide can occur at pH higher than 10.8 [53]. Stabilising agents such as sodium silicate and magnesium sulfate can be added to the bleaching media to stabilise the hydrogen peroxide and prevent alkaline decomposition[42] In an alkaline solution the hydrogen peroxide reacts with a hydroxide ion in the solution to form a perhydroxyl ion and a water molecule as seen in the equation 2.1 below.

$$H_2O_2 + OH^- \longrightarrow OOH^- + H_2O \tag{2.1}$$

Hydrogen peroxide reaction under alkaline conditions

Formed perhydroxyl ions are highly unstable and will mainly react with side chains of the lignin molecule to degrade the lignin network into smaller pieces. Radicals formed in the decomposition of hydrogen peroxide will simultaneously yield oxidative degradation of the phenolic structures in the lignin network. This degradation of lignin is known as mild oxidation of lignin and is seen below in figure 9

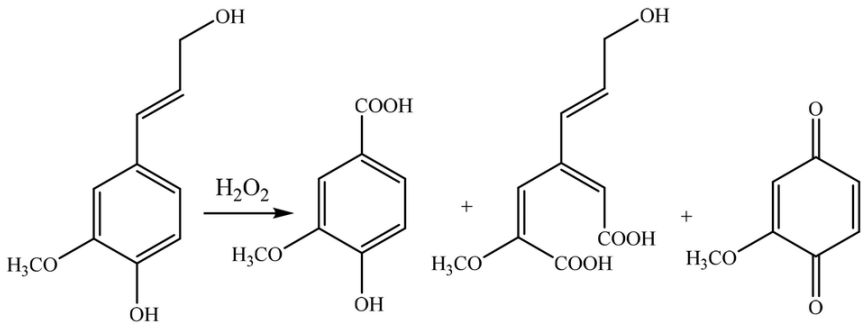


Figure 9: Mild oxidation of lignin molecule with hydrogen peroxide under alkaline conditions[54]

As the lignin molecules are decomposed into smaller pieces they become soluble in the alkaline bleaching media.
To increase the yield of the bleaching by avoiding degradation of the cellulose chains and to increase the bleaching properties of the hydrogen peroxide, the pulp must be virtually free of transition metal ions[42]. Transition metal ions catalyse the decomposition of the hydrogen peroxide by the Fenton reaction[42]. The Fenton reaction results in the formation of hydroxyl radicals, as seen in equation 2.2. The presence of hydroxyl radicals will then cause oxidative stress which leads to cellulose chain scissions[55].

$$Fe^{2+} + OH^- \longrightarrow Fe^{3+} + OH\bullet + OH^- \tag{2.2}$$

To remove the transition metal ions from the pulp prior to the hydrogen peroxide bleaching step, another step must be added to the bleaching sequence. This added step is either an acid wash or a pre-treatment with a chelating agent, namely EDTA or DTPA[42].

3 Materials & methods

The flowchart of the final process steps can be seen below in figure 10. The initial process conditions were chosen after analysing several different sources on prehydrolysis and soda cooking[56][57]. Materials were analysed for composition after each step in the process before deciding on changes in conditions and the next step of the process.

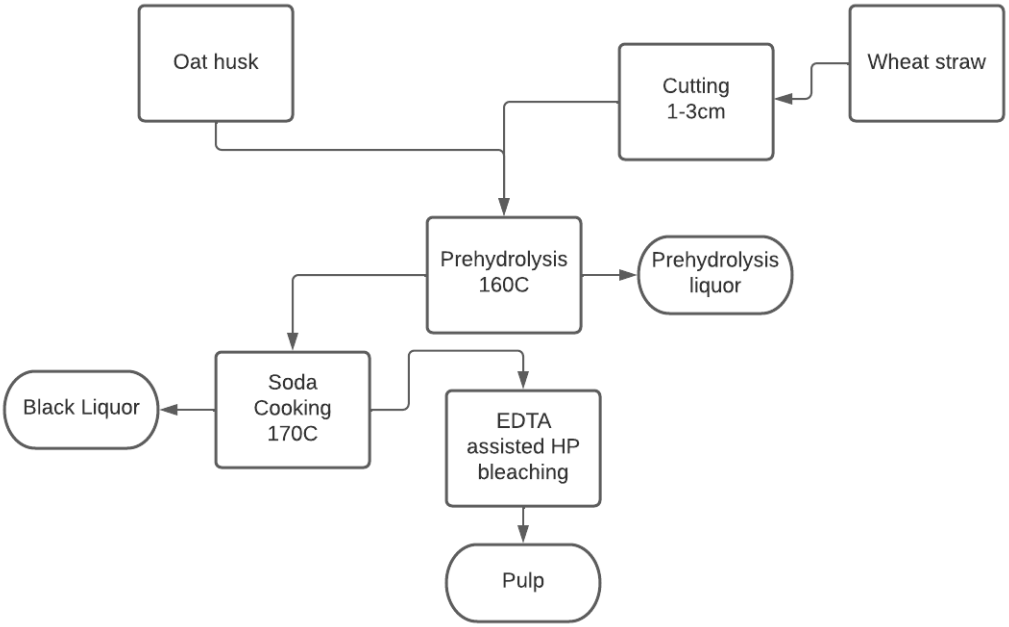


Figure 10: Flowchart of process for production of dissolving-grade pulp from oat husks and wheat straws

3.1 Raw materials

The raw materials used in this project were oat husks and wheat straw. Spruce shavings were also used as a raw material for comparison with the wheat straw and oat husks. The oat husks were supplied by Lantmännen and the wheat straw used in the project was grown in Sweden and sold as animal feed and bedding material. The spruce was supplied by Södra. The oat husks required no mechanical pretreatment prior to chemical pretreatments as the size distribution of oat husks is relatively homogeneous. The wheat straw however was cut into 1-3cm pieces using scissors to homogenise the material. The wheat straw was both used in the process with the leaves present and with the leaves removed by hand. A softwood prehydrolysis Kraft (PHK) dissolving-grade pulp with DP reduced to 195 was used as a benchmark for fibre analysis.

3.1.1 Prehydrolysis

The prehydrolysis step was performed at 160°C in 1.5-litre steel autoclaves, as can be seen below in figure 11, using a 6:1 liquid/solid (l/s) ratio for oat husk. For wheat straw 6:1 and 15:1 l/s ratios were tested. The steel autoclaves were placed in a rotating heating

vessel filled with polyethylene glycol and rotated at a speed of 15rpm. The dry content of the raw material was first assessed gravimetrically by weighing the samples before and after drying at 105°C overnight. Deionised water and hydrochloric acid were used and assessed as prehydrolysis liquids. Sulfuric acid was also tested in prehydrolysis liquid as a comparison to hydrochloric acid.



Figure 11: 1.5-litre steel autoclave used for prehydrolysis and cooking

The following procedure was used for all types of prehydrolysis: 50g(dw) of raw material was added to a steel autoclave under atmospheric pressures and cold prehydrolysis liquid was added to reach the desired l/s ratio. After placing the autoclave at 160°C in the heating vessel a heating time of 25 minutes, as previously determined by Wigell et al[58]., was assumed to reach the maximum temperature. The prehydrolysis time was then started after these 25 minutes had passed. After the full running time of the prehydrolysis the autoclave was placed in cold water for 5 minutes to cool to room temperature. The pretreated material was then transferred to a Büchner funnel where the prehydrolysis liquor was removed and recirculated once. The pretreated material was then washed extensively with deionised water until the filtrate was clear and at neutral pH.

3.1.2 Soda pulping

The soda pulping step was carried out at 170°C in the same 1.5L steel autoclaves used in the prehydrolysis step. The liquid content in the pretreated material was determined by subtracting the dry weight of the material from the total weight after pretreatment. The pretreated material was then added to the steel autoclave. The l/s ratio used in the cook was 8.3:1. The predetermined concentration of $NaOH$ (g $NaOH$/g total liquid) was dissolved in the amount of deionised water needed to reach an 8.3:1 l/s ratio and

subsequently added to the autoclave. After the full cooking time, the autoclaves were removed from the polyethylene glycol bath and cooled for 5 minutes in a water bath with running tap water. The pulp was then washed in a Büchner funnel once with its own black liquor and then with deionised water until the filtrate turned clear. Deionised water was then added to the pulp to reach a total slurry volume of 1L which was then transferred into a defibrator which ran for a total of 30 000 revolutions. After defibration the pulp was again washed in a Büchner funnel with deionised water until a clear filtrate could be observed.

3.2 Post-treatments

The following section describes the methodology of treatments to the pulp after the pulping step.

3.2.1 EDTA assisted hydrogen peroxide bleaching

The bleaching was carried out in a two-step sequence. The first step was a chelating step to remove transition metal ions. A pre-mixed solution of 0.5 weight-% on dry pulp of EDTA, 0.3 weight-% on dry pulp of H_2SO_4 and deionised water to reach a l/s ratio of 20:1 and then added to the pulp. The pulp slurry was then thoroughly mixed with a glass rod and placed in a water bath at 60°C for 1h with occasional stirring. The EDTA treated pulp was then washed with deionised water in a Büchner funnel and resuspended in 1 litre of deionised water once and then washed again with 2 litres of deionised water. The next step of the bleaching sequence was an alkaline hydrogen peroxide (H_2O_2) bleaching step. $NaOH$ pellets were dissolved in deionised water to reach a total slurry concentration of 0.01M. Enough $NaOH$ solution to reach a 10:1 l/s ratio for oat pulp or 20:1 l/s ratio for wheat pulp was transferred to a beaker. H_2O_2 (35%w/w) of desired concentration (on odw pulp) was then added to the beaker and mixed with a glass rod. 0.3% (on odw pulp) of the stabilising agent magnesium heptahydrate ($MgSO_4 * 7H_2O$) was added to the $NaOH + H_2O_2$ solution and stirred with a glass rod until complete dissolution. The mixture was then added to the beaker containing the pulp and mixed with a glass rod into a slurry. The pulp slurry was then transferred to polyethylene bags in which the bleaching was carried out in water baths at either 80°C or 90°. After the initial H_2O_2 bleaching step the pulp was washed in a Büchner funnel where the bleaching liquid was recirculated for washing once. The pulp was then washed extensively with deionised water until the filtrate reached neutral pH. The H_2O_2 bleaching step was then repeated.

3.3 Analysis methods

The following section describes the analytical methods used to characterise the properties and composition of the raw materials and produced pulps.

3.3.1 Carbohydrate quantification

The carbohydrate quantification is performed to quantify the monomeric sugar composition of the raw materials after complete hydrolysis. The hemicelluloses will then be

calculated back from the monomeric sugars.
200mg of oven-dried pulp was added to a 150ml beaker to which 3ml of 72% H_2SO_4 was added and stirred with a glass rod. The beaker was then placed in a vacuum desiccator for 15 minutes and then transferred to a 30°C water bath for 1h with occasional stirring. After removing the beaker from the water bath 84ml of deionised water was added to the mixture and stirred with a glass rod. The mixture was then placed in an autoclave at 125°C for 1h. The mixture was then filtered through a glass filter to remove solids and transferred to a 100 ml flask. After cooling to room temperature the flask was then filled to 100ml with deionised water. This mixture was then shaken thoroughly by hand to mix. An aliquot of 5ml was then transferred by pipette to a 50ml flask to which 2ml of 200mg/l of internal fucose standard was added. The mixture was then diluted to 50ml with deionised water. The final solution was then filtered through a 0.45mm PVDF filter prior to the analysis. The carbohydrate analysis was then determined as the amount of monomeric sugars using high-performance anion exchange chromatography (HPAEC). The system used was a Dionex ICS-5000 with a CarboPacTM PA1 column. The eluents used were $NaOH$ and $NaOH$ + $NaOAc$. The amounts of detected carbohydrates were then corrected to hydrolysis yields experimentally determined by Wojtasz-Mucha et al., using the same analysis method[59].

3.3.2 Klason lignin

The remaining material filtered off from the complete hydrolysis was considered to be Klason lignin. This was oven-dried at 105°C overnight and then quantified gravimetrically.

3.3.3 Acid soluble lignin

The amount of acid-soluble lignin (ASL) was determined from the filtrate of the acid hydrolysis of the carbohydrate quantification. The filtrate was analysed by measuring UV absorbance at 205nm using *Specord 205* from *AnalyticJena*. The concentration of acid-soluble lignin was then calculated using the Lambert-Beer law, as seen in equation 3.1, assuming the absorptivity constant to be 110 $Lg^{-1}cm^{-1}$[60].

$$A = \epsilon \cdot l \cdot C \tag{3.1}$$

Where A is the absorbance, ϵ is the absorptivity constant, l is the length of the cuvette in centimetres and C is the concentration of acid-soluble lignin in g/L.

3.3.4 Ash content

The ash content was determined by placing a ceramic crucible containing 1g of oven-dried material in a *Nabertherm L9/S27* furnace at $525°C \pm 25°C$. The material was considered completely combusted when no black spots remained. The ash content was then cooled and placed in $105°C$ overnight before being determined gravimetrically.

3.3.5 Molecular weight distribution

Pulp samples were sent to *MoRe research Örnsköldsvik AB* for analysis of molecular weight distribution. Wheat and oat pulps were analysed for parameters seen in table 1 The samples were dissolved in 0.5 w/v-% DMAc/LiCl and analysed in a PL-GPC 220 with RI-detector at a flow rate of 1ml/min

Value	Abbreviation
Peak molecular weight	M_p
Number average molar mass	M_n
Mass average molar mass	M_w
Z-average molar mass	M_z
Polydispersity index	PDI

Table 1: Values of analysed molecular weight distribution

3.3.6 Fibre image analysis

The fibre dimensions of the produced pulps were analysed in a Kajaani FS300 fibre image analyser. 50mg of never dried pulp was transferred to 2L deionised water and defibrated in a pulp disintegrator for 30 000 revolutions. Roughly 50mL was then poured into a beaker and left overnight to let the fibres swell before analysis.

3.3.7 Intrinsic viscosity

Intrinsic viscosity was analysed to give an estimation of the average length of the cellulose chains.
200mg of odw pulp was carefully shredded by hand and transferred to a 50mL plastic flask. Two small copper rods and 25mL of deionised water were added to the flask. The flask was sealed and shaken by hand for 3 minutes. 25mL of 1M CED (Copper(II)ethylenediamine) was added to the flask to reach a 0.5M concentration in order to dissolve the cellulose. All air was squeezed out of the flask and sealed again. The flask was shaken by hand for 5 minutes and left in a $25°C$ water bath for 30 minutes. The samples were analysed using the SCAN-C 15:62 method where the sample is pressed into a 1mL capillary and the efflux time is measured with a stopwatch.

3.3.8 Scanning electron microscopy (SEM)

To get a better understanding of the fibre morphology of the produced pulps, a scanning electron microstopy (SEM) was performed on the finished pulps. Air-dried samples were analysed using a Phenom ProX Desktop SEM from ThermoFisher Scientific with an electron beam operating at 10kV or 15kV.

3.3.9 Nuclear magnetic resonance spectroscopy (NMR)

Three different pulp samples were sent to Swedish NMR Centre (SNC) in Umeå for cross-polarisation solid-state NMR analysis to examine the molecular compositions of the pulps.

4 Results & Discussion

4.1 Raw materials

This section will present the results of the analyses performed on the untreated raw material. The compositions of the raw materials will be discussed in regard to suitability as a raw material in the production of dissolving-grade pulp.

4.1.1 Oat husks

	Glu	**Xyl**	**Gal**	**Ara**	**Man**	**Klason**	**ASL**	**Ash**	**N/d**
Oat husks	29.69	29.74	1.28	3.34	0	22.22	2.61	5.85	11.12

Table 2: Composition (wt %) of untreated oat husks. Glu = Glucose, Xyl = Xylose, Ara = Arabinose, Man = Mannose, Klason = Klason lignin, ASL = Acid-soluble lignin, Ash = Ash compounds, N/d = Not detected

Previous studies have shown that the composition of oat husk is dependent on the climate and growth conditions. The composition seen in table 2 is within the range of previous studies [4].
As can be seen in table 2, oat husks have a high content of hemicelluloses. Xylose makes up the largest composition of the hemicelluloses and is present in roughly the same amount as glucose when the raw material is fully hydrolysed. However, the raw material might contain starch from the grains which implies that the detected glucose might not all originate from the hydrolysed cellulose. The extent of starch fraction was not determined, so the fraction of starch in the raw material remains unknown. Oat husks contain roughly 25% lignin (22.22% Klason lignin and 2.61% ASL). The ash in oat husks is expected to be mostly SiO_2 which has low solubility in acidic solutions[34]. Therefore, ash contributes to the Klason fraction, as the Klason lignin fraction is measured as the amount solid remains after complete acid hydrolysation. 11.12% of weight fraction in oat husks were not detected by the analysis methods used in this project. This fraction is most likely made up of fats, proteins and acid-soluble ash[61]

4.1.2 Wheat straw

	Glu	**Xyl**	**Gal**	**Ara**	**Man**	**Klason**	**ASL**	**Ash**	**N/d**
Wheat straw	38.16	18.42	0.99	2.54	0.40	21.62	2.77	9.41	15.1
Wheat leaves	29.43	11.34	1.71	6.32	0	20.50	3.56	14.73	27.14
Wheat stalks	41.56	12.08	0.80	2.15	0	23.86	2.55	6.80	17.00

Table 3: Glucose, hemicellulose monomers and lignin content in wheat straw, wheat stalks and wheat leaves

Wheat straw comprises mainly of two different anatomical fractions: leaves and stalks. The stalks can also be divided into anatomical fractions with nodes and internodes, but

these two fractions will be referred to as the stalk fraction in this project. The original material, as well as separated fractions, were analysed for composition and the results are presented in table 3.
The glucose contents in the samples were 38.16% for the entire fraction of wheat straw, 29.43% for the leaf fraction and 41.56% for the stalk fraction. The glucose originates primarily from cellulose and hemicelluloses. Therefore it could be assumed that both straw and stalks contain high levels of cellulose and could be promising in the context of dissolving-grade pulp.
The levels of hemicelluloses present in the analysed samples varied between the different plant parts and they correspond well to levels reported by previous research[62]. Previous papers have also shown that wheat straw comprises some uronic acid which cannot be quantified in the system used[63].
Wheat straw contains more hemicelluloses than both the leaves and the stalks being 22.4% of the mass fraction and for the leaves and stalks 19.37% and 15.03% respectively. The reason for this is unclear, but one reason can be that the fractions that were analysed were from different batches. Previous research has shown that the composition of wheat straw can differ significantly depending on growing season, climate and soil condition[62].
Another major difference between the fractions is the amount of ash. Leaves in the analysed samples contained 14.73% of ash while the stalks contained 6.80%. Should the leaves be present in the pulped material, the high amounts of ash can cause issues in the recovery of the cooking chemicals[64]. Early tests in this project also indicated that with the leaves present, the finished pulp still contained more than 2% ash.
As wheat straw contains both leaves and stalks, the amount of ash is much higher in wheat straw than in the stalks. Similarly, as discussed for oat husks, some acid insoluble ash compounds will end up in the Klason lignin fraction.

4.2 Pretreatment

The major purpose of the pretreatment is to remove as much of the hemicellulose fraction as possible while maintaining the cellulose fraction within the material. Another purpose of the pretreatment is to open up the fibre structure of the raw material to facilitate the delignification during the cooking step.

4.2.1 pH after hot water extraction depending on raw material

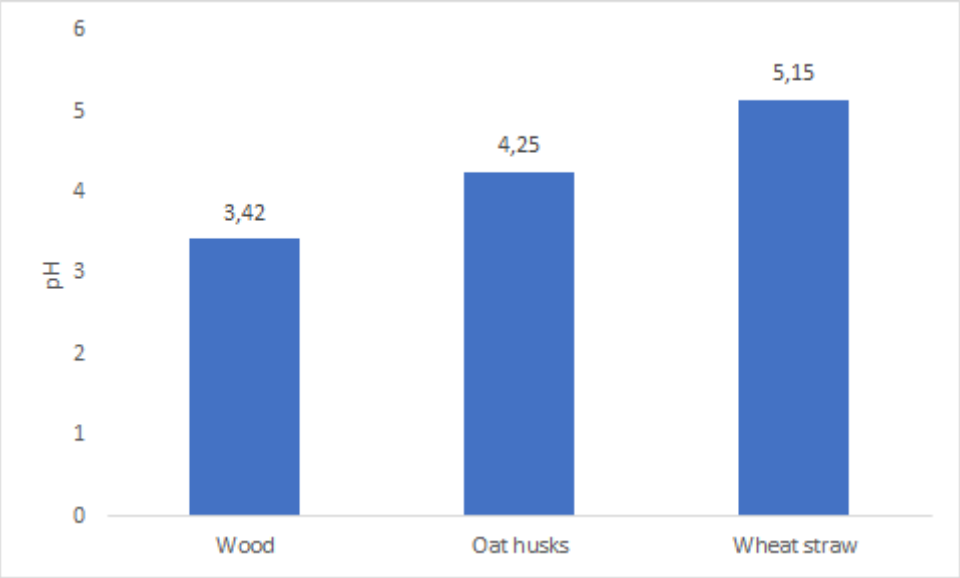


Figure 12: pH of pretreatment liquor after 60 min hot water extraction (HWE) at 160°C of spruce shavings, oat husks and wheat straw (6:1 l/s)

Effects of HWE on oat husks, wheat straw and spruce shavings were analysed. The materials were treated at 160°C for 60 minutes with an l/s ratio of 6:1. The effects of the treatment were analysed in terms of the pH of the media with a pH meter and reported in figure 12 This was done to gain knowledge on the amounts of hydrogen ions released from each of the raw materials into the prehydrolysis liquor during the HWE pretreatment.
Some of the mechanisms involved in the autohydrolysis of wood remain unknown. However, the main contributing factors are believed to be the release of organic acids from the raw material combined with the deacetylation of hemicelluloses to cause acidification of the media[59].
The results indicate that autohydrolysis is more pronounced in spruce than in oat husks as the pH prehydrolysis liquor of wood was at 3.42 compared to 4.25. The same can be said for oat husks and wheat straw, as the hot water extraction on wheat straw resulted in a prehydrolysis liquor of pH 5.15 after treatment. There is currently no literature describing autohydrolysis of either oat husks or wheat straw which makes it difficult to reason about the source of the differences. However, it is easier to consider the implications of the difference in pH. One assumption could be that even with the addition of the same amounts of acid to the prehydrolysis liquid before the pretreatment, the pretreatment of oat husks will be more severe than that of wheat straw due to the more pronounced autohydrolysis in oat husks.
These results indicate that HWE under the used conditions is an inefficient method to use for the pretreatment of wheat straw. However, when the pH of the pretreatment liquor from oat husks is compared to that of wood shavings, the results differ about as much as those between oat husks and wheat straw.

4.2.2 Pretreatment of oat husks

As oat husks have high hemicellulose content (>30%), the prehydrolysis step is crucial in the production of dissolving-grade pulp.

Pretreatment	Glu	Xyl	Gal	Ara	Man	Klason	ASL	Ash	N/d
No pretreatment	29.69	29.74	1.28	3.34	0	22.22	2.61	5.85	11.12
30 min HWE	32.17	26.00	1.09	2.46	0	24.76	3.17	-	10.35
60 min HWE	37.34	24.74	0.80	1.81	0	26.49	2.90	-	5.92
30 min 0.1% HCl	43.11	18.56	0.66	1.44	0	25.09	2.81	-	8.33
60 min 0.1% HCl	43.34	15.57	0.63	1.19	0	27.02	2.74	6.61	9.51

Table 4: Composition (wt %) of untreated and pretreated oat husks at $160°C$ (6:1 l/s ratio)

As can be seen in table 4, oat husks have high levels of monomers, originating from hemicelluloses. The most abundant is xylose. It can be noticed that both HWE and the acidic pretreatment (AP) were efficient in removing hemicelluloses. The effects on hemicelluloses are more pronounced than the effects on cellulose. This is mostly due to the shorter degree of polymerisation and more amorphous structures of the hemicelluloses compared to the cellulose which makes the hemicelluloses more prone to acid hydrolysis. All hemicelluloses present in oat husks were hydrolysed to some extent in the pretreated samples. However, the levels of arabinose decreased by 64% in the 60 minutes acid pretreated sample. This is a more significant decrease than the levels of galactose and xylose, which dropped by 51% and 48% respectively. As the most common hemicellulose polymer in oat husks is arabinoxylan, which consists of long xylan chains with few substituted arabinose residues, it could be possible that the arabinose residues are easily cleaved off from the xylan chains during the pretreatment and dissolved into the pretreatment liquor.
The apparent Klason lignin content in the sample increases, which was expected. The reason for this is lignin units being mostly unaffected by the pretreatments with only small fractions of acid-soluble lignin removed, while the big fraction of hemicelluloses is extracted. It was observed that the amounts of ASL are lower in the sample exposed to 60 minutes acid prehydrolysis compared to 30 minutes HWE pretreated sample despite that a bigger fraction of hemicelluloses are removed. This indicates that more ASL is removed in the AP compared to the HWE.
As can be seen in table 4, the ash content of oat husks remains largely unaffected by an AP and the apparent increase stems mainly from a decrease in the hemicellulose fraction rather than an increase in ash compounds. This is to be expected as the largest portion of ash in oat husks is expected to be silica oxide[34], which has very low solubility in acidic media. An acidic pretreatment could help with removing some inorganic compounds such as MgO, K_2O and CaO.

4.2.3 Pretreatment of wheat straw

Pretreatment	Glu	Xyl	Gal	Ara	Man	Klason	ASL	Ash	N/d
No pretreatment	38.16	18.42	0.99	2.54	0.40	21.62	2.77	9.41	15.10
30 min HWE	39.20	19.86	0.84	2.29	0.37	23.16	2.98	-	11.30
60 min HWE	38,93	19.13	0.86	1.90	0.39	25.77	2.94	-	10.08
30 min 0.1% HCl	38.52	19.06	0.72	1.67	0.37	25.75	3.11	-	10.80
60 min 0.1% HCl	41.50	17.94	0.66	1.21	0.36	26.48	2.88	7.49	8.97

Table 5: Composition (wt %) of untreated and pretreated at 160°C wheat straw (6:1 l/s ratio)

When using a 6:1 l/s ratio for pretreatments of wheat straw, the effects of the pretreatment were less pronounced compared to what was seen for oat husks. All pretreatments of wheat straw show partial removal of arabinose and galactose, but xylose and mannose remain largely unaffected. Only the samples pretreated for 60 minutes in acid shows lower xylan levels than the untreated sample. A possible reason for this is that the wheat retained much of the liquid within the fibres, which results in insufficient mixing during the pretreatment. This also resulted in too small amounts of free liquid to enable diffusion of the dissolved compounds out of the material
However, levels of undetected substances in the samples are decreasing which indicates that something is still removed from the material. This is most likely due to the evaporation of volatile compounds and partial dissolution and degradation of proteins and starch.
To counter the high liquid retention of the wheat straw and ensure sufficient mixing during the pretreatment a higher l/s ratio of 15:1 was tested and evaluated, which can be seen in table 6

Pretreatment	Glu	Xyl	Gal	Ara	Man	Klason	ASL	Ash	N/d
30 min 0.1% HCl	49.02	18.28	0.41	1.04	0	22.89	2.15	-	6.21
60 min 0.1% HCl	52.86	14.97	0.19	0.51	0	24.27	1.62	-	5.58

Table 6: Composition (wt %) wheat straw pretreated at 160°C (15:1 l/s ratio)

A higher l/s ratio allows for obtaining more pronounced effects on the material. Not only does it decrease the amounts of hemicelluloses present in the samples but also it decreases the fraction of non-detected components in the samples compared to all other samples pretreated with the lower l/s ratio.
The reason for the increase in efficiency of the pretreatment for the higher l/s ratio is likely caused by increasing the total amount of hydrogen ions in the liquid as well as increasing the sheer forces of the mixing. Unlike in the pretreatments using a 6:1 l/s ratio, the wheat straw does not retain most of the liquid within the fibres when using a 15:1 l/s ratio. This makes the shear forces act more on the raw materials as well as ensures that there is an even distribution of hydrogen ions acting on the raw material.
As can be seen in table 5, wheat straw contains relatively high amounts of ash. The apparent ash fraction decreased slightly in the acid pretreatment. It could be related

to mild effects of the treatment or the presence of acid-soluble inorganic compounds. Another reason could also be found in the heterogeneity of the wheat straw material and different proportions of anatomical fractions between samples. It could therefore be the case that the material analysed for ash in the non-pretreated material contained more leaves, resulting in higher ash content.

4.2.4 Effects of pretreatments on different raw materials

To compare oat husk and wheat straw with the commercially used raw materials, spruce shavings were analysed. The results can be seen in table 7.

Pretreatment	Glu	Xyl	Gal	Ara	Man	Klason	ASL	N/d
No pretreatment	44.31	5.68	1.61	0.92	11.12	27.89	0.75	7.73
30 min HWE	48.80	5.03	1.12	0.17	8.45	30.81	0.70	4.91
60 min HWE	50.93	4.53	0.66	0.12	7.09	31.69	0.70	4.27

Table 7: Composition (wt %) of untreated and pretreated at 160°C spruce shavings (6:1 l/s ratio)

As can be seen above in table 7, spruce shavings comprises larger fractions of glucose, mannose and lignin than both the oat husk and wheat straw. The largest share of glucose fractions originates from cellulose, but as previously showed by Wojtasz-Mucha, some of the glucose in spruce also originates from hydrolysed glucomannan. Glucomannan is the most abundant hemicellulose in spruce and in a ratio of on average 1 glucose for every 3.5 mannose[65].

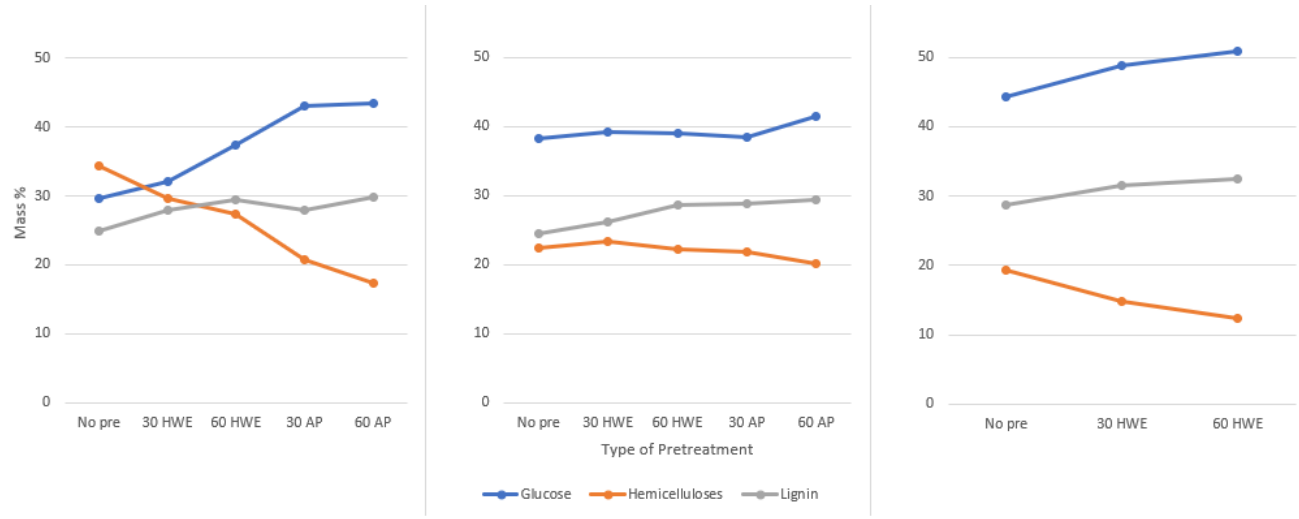


Figure 13: Compositions of glucose and hemicellulose monomers in oat husk (left), wheat straw (middle) and spruce shavings (right) depending on pretreatment at 160°C

When comparing the three raw materials, three trends can be seen for all raw materials in figure 13: The glucose and lignin fractions increases with treatment severity while the hemicellulose fraction decreases. This is expected as one of the main purposes with

the pretreatment is to remove hemicelluloses, and due to the shifting of fractions the glucose and lignin fractions increase. However, the trends were different depending on raw material. The hemicelluloses of oat husk are easily removed with the current 6:1 l/s pretreatment ratio, while the effects are much less pronounced in wheat straw. While acid pretreatment wasn't used at all as a pretreatment on spruce shavings, the effects of HWE on spruce shavings were significantly more pronounced in spruce shavings than in oat husk and wheat straw. This was also expected as autohydrolysis yielded the lowest pH of the pretreatment liquors in spruce shavings out of all the raw materials.
All raw materials exhibited darkening in coulour with pretreatment severity. While the mechanisms behind this are not fully determined for all the raw materials, it can be assumed that destruction of native lignin chemical structures and formation of C-C bonds in the lignin structure due to condensation reactions contribute to this darker colour[66].

4.3 Pulping

The following section contains the results obtained from pulp analysis after the pulping process of oat husks and wheat straw. As the main purpose of the pulping process is delignification, results were compared for the same pulping conditions but different pretreatments to analyse how different pretreatments facilitate delignification.
Removal of ash components is another key aspect of the pulping process for oat husks and wheat straw, as the raw materials contain roughly 6.0% and 9.4% of ash respectively. The degree of polymerisation for the cellulose will also be affected by the pulping process and will therefore be compared for the different pulps. The results will then be discussed regarding the obtained pulp's suitability as a dissolving-grade pulp. The content of lignin in the samples will only be mentioned as Klason lignin, as the levels of ASL in the cooked pulp were so low.

4.3.1 Pulping of oat husks

The raw materials previously compared in table 4 were all pulped at 170°C and a NaOH concentration of 4% (8.3:1 l/s) for 2h. The composition of the pulps after the pulping process can be seen below in table 8.

Pretreatment	**Glu**	**Xyl**	**Gal**	**Ara**	**Man**	**Klason**	**Ash**	**DP**
No pretreatment	75.82	18.41	0.09	0.60	0	0.89	1.84	577
30 min HWE	82.49	16.02	0	0.37	0	0.70	-	582
60 min HWE	83.91	12.54	0	0.28	0	0.42	-	553
30 min 0.1% HCl	87.70	4.85	0	0.13	0	0.79	-	437
60 min 0.1% HCl	93.89	3.71	0	0	0	0.31	0.11	405

Table 8: Composition (wt %) and DP of pulped oat husks with different pretreatments at 170°C and 4% NaOH (8.3:1 l/s ratio) ratio)

For comparison purposes, the same pulping was performed at materials pretreated at various conditions. The compositional analysis is presented in table 8. The results indicate that the hemicellulose content decreases and cellulose fraction increases with treatment severity.

As previously discussed and shown in figure 12 hot water extraction only achieves a pH value of roughly 4.3, while the theoretical pH of 0.1% HCl is around 1.6. It is therefore expected that the dissolution, degradation and extraction of hemicelluloses are more efficient. This not only leads to lower hemicellulose content at the beginning of the pulping for the acid pretreated samples but also a more accessible structure. This can be seen in figure 14 where the removal of the total amount of hemicelluloses during the pulping process is depicted.

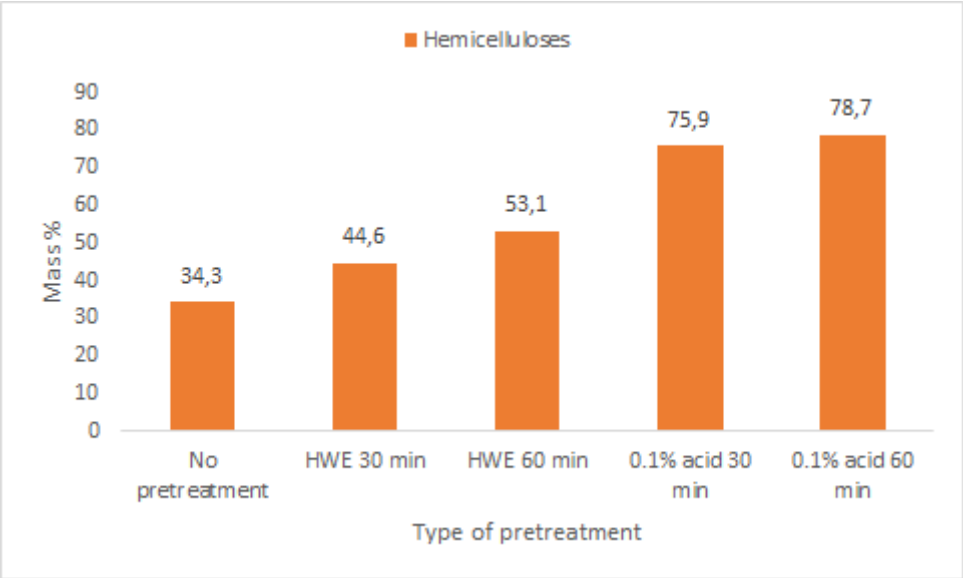


Figure 14: Total amount of hemicelluloses removed from oat husk during pulping for 2h at 170°C and 4% NaOH (8.3:1 l/s ratio)depending on type of pretreatment at 6:1 l/s ratio

Not only does a more severe treatment seem to facilitate hemicellulose removal during pulping but also delignification, as seen in table 8. The pulp with the lowest Klason lignin content is the pulp pretreated with acid for 60 minutes. However, the pulp pretreated with acid for 30 minutes has a higher Klason lignin content than both the HWE pretreated pulps, but this could be a result of not hydrolysing the pulp completely during analysis. After pulping, the hemicellulose of highest abundance is still xylan. This is to be expected as xylan was by far the hemicellulose of the highest weight fraction in the raw material. The pulp pretreated for 60 minutes with acid shows an 87.5% removal of xylan when compared to the untreated raw material. However, the removal of all other hemicelluloses from this pulp was complete. This leads us to the conclusion that xylan is the most difficult hemicellulose to remove from oat husk.
Of the different oat pulps, only the 60 minutes 0.1% HCl pretreated pulp seems to fulfil the requirements of dissolving-grade pulp with >90% cellulose and <5% hemicelluloses. The DP of the pulp is in the lower range of viscose purpose dissolving-grade pulps of 400-600 even before adding a necessary bleaching step, to achieve a higher brightness, which reduces the DP of the pulp even more.
Just like for hemicelluloses and lignin, the removal of ash from oat husks during the pulping process is more efficient when exposing the raw material to an acidic pretreatment.

As can be seen in table 8, the pulp from non-pretreated oat husks still contains 1.84% ash while the 60 minutes 0.1% HCl pretreated pulp only contains 0.11% of ash. This is another important aspect of dissolving-grade pulp as the pulp can only contain trace amounts of ash to be suitable as dissolving-grade pulp. However, as the ash in oat husks is mainly silica, the more ash that is removed during the pulping the higher the silica content will be in the black liquor. This can cause problems in the recovery of the cooking chemicals in large scale operations, and it is, therefore, important to find a way around this.

4.3.2 Oat husk process improvements

To increase the recyclability of chemicals, sulfuric acid(H_2SO_4) was used instead of hydrochloric acid(HCl) in the acidic pretreatment. The 0.1 wt% of HCl in the prehydrolysis liquor is equivalent to 0.0274M. As H_2SO_4 donates two protons in reaction with water, concentrations of both 0.0274M and 0.0137M of H_2SO_4 were tested in the prehydrolysis liquor. The oat husk samples were then pulped with 4% NaOH for 120 minutes and bleached with the same bleaching sequence used for previous pulps. The compositions of the pulps can be seen below in table 9

Pretreatment	**Glu**	**Xyl**	**Gal**	**Ara**	**Man**	**Klason**	**DP**
0.0137M H_2SO_4	95.34	4.89	0	0	0	<0.1	279
0.0274M H_2SO_4	98.10	1.91	0	0	0	<0.1	238

Table 9: Composition (wt %) and DP of pulped oat husks with different concentrations of H_2SO_4 pretreatment (6:1 l/s ratio) at 170°C and 4% NaOH (8.3:1l/s ratio) and bleached with EDTA assisted HP bleaching

The produced pulp that was pretreated with 0.0137M of H_2SO_4 was very similar in composition and DP to the pulp pretreated with 0.1% (0.0274M) HCl, as expected. On the other hand, the pulp produced with 0.0274M had a significantly smaller fraction of hemicelluloses than the previously produced pulps. Even compared to a commercially produced dissolving-grade pulp, 1.91% hemicelluloses is a relatively low amount. The ash content and lignin content were just trace amounts which further concludes that the composition of the produced pulp is suited for dissolving-grade pulp purposes. Although the DP is relatively low in this pulp, there are still applications for dissolving-grade pulps with DP around 200 such as adapted Lyocell production[67].

4.3.3 Pulping of wheat straw

Pretreatment	Glu	Xyl	Gal	Ara	Man	Klason	Ash	DP
No pretreatment	77.36	12.07	0.08	0.44	0	3.55	4.21	485
30 min HWE	83.79	10.12	0	0.27	0.40	1.43	-	395
60 min HWE	84.14	9.74	0	0.28	0	2.12	-	409
30 min 0.1% HCl	86.01	10.39	0	0.28	0.40	2.48	-	426
60 min 0.1% HCl	89.17	10.34	0	0.26	0.29	1.62	3.95	439

Table 10: Composition (wt %) and DP of pulped wheat straw with different pretreatments (6:1 l/s ratio) at 170°C and 4% NaOH (8.3:1 l/s ratio) ratio)

As previously discussed, HWE pretreatment of wheat straw only shows a slight decrease in the pH of the cooking liquor. For this reason, it is expected that the removal of hemicelluloses with HWE pretreatment is only going to be minor. As can be seen in table 10, this was the case with the 30 min HWE and 60 min HWE. The weight fraction of hemicelluloses were only 10.8% and 10.1% respectively for these samples compared to the pulp that was not pretreated which had 12.6%. After the pulping process the fraction of cellulose increased from 77.4% to 83.8% in the 30 min HWE pretreated pulp and 84.10% in the 60 min HWE pretreated pulp. This indicates that components that are not detected in the analysis of the pulps are removed in the HWE pretreatment as well, as the total weight fractions of cellulose and hemicelluloses are increasing. The components removed in this stage are likely to be proteins and water-soluble extractives.



Figure 15: Total amount of hemicelluloses removed from wheat straw during pulping for 2h at 170°C and 4% NaOH (8.3:1 l/s ratio)depending on type of pretreatment at 6:1 l/s ratio

As can be seen in figure 15, the content of hemicelluloses from the raw material is barely affected by a 6:1 l/s ratio pretreatment. The trends even show that the amount of hemi-

celluloses removed during the pulping step is lower for the acid pretreated samples than the HWE pretreated samples. It is possible that the easily accessible hemicelluloses are removed during the acid pretreatment but not in the HWE pretreatment. The same hemicelluloses are then instead removed during the pulping step for the HWE pretreated samples. Thus, the pulped samples that were pretreated with acid show similar compositions as the HWE pretreated samples.
The fraction of cellulose is increasing slightly after pulping of the acid pretreated samples compared to those pretreated with HWE, but the hemicellulose fractions are slightly lower in both HWE pretreated samples. A likely reason for this could be that the acid pretreatment is more efficient in removing components from the not detected fraction. However, the contents of hemicelluloses and lignin are still too high for a dissolving-grade pulp. In order to remove bigger fractions of hemicelluloses of lignin the following pulps were produced with a 15:1 l/s ratio pretreated raw material and pulped with a 6% concentration of $NaOH$ instead of 4%.
As can be seen in table 10, the ash contents of the wheat straw pulps were still relatively high post pulping. As a dissolving-grade pulp requires to only comprise trace amounts of ash, more of the ash must be removed from the pulp.

4.3.4 Wheat straw process improvements

To determine whether the high ash content in the wheat straw pulps was due to pulping of leaves, which are very high in ash content, the stalks were separated from the raw material and pulped after acidic pretreatment. This resulted in a pulp with an ash content of 0.66%. Several different causes of this were considered. One possible reason is that the solubility of ash compounds was saturated in the cooking liquor. Acid pretreated wheat straw was therefore pulped with a 15:1 l/s ratio with the same NaOH concentration and the pulp was analysed for ash content. This resulted in pulp with an ash content of 3.20%. This is slightly lower than the pulp produced with an 8.3:1 l/s ratio but the ash content is still relatively high compared to the requirements for dissolving-grade pulps and compared to the ash content of the wheat stalk pulp.
The wheat stalks were pretreated with acid using a 15:1 l/s ratio to increase the efficiency of the pretreatment to increase the removal of hemicelluloses. To increase the delignification, the concentration of $NaOH$ in the cooking liquor was increased from 4% to 6%.

Pretreatment	**Glu**	**Xyl**	**Gal**	**Ara**	**Man**	**Klason**	**DP**	**Ash**
60 min 0.1% HCl	94.80	2.45	0	0.08	0.59	1.30	329	0.60

Table 11: Composition (wt %) and DP of pulped wheat stalks with acidic pretreatment (15:1 l/s ratio) and pulped at 170°C and 6% NaOH (8.3:1 l/s ratio)

As can be seen in table 11, the Klason lignin and ash content are much lower in the pulp from wheat stalks compared to pulps from wheat straw. As a result of the increased l/s ratio during the pretreatment, the levels of hemicelluloses are also significantly lower. However, for this pulp to meet the requirements of a dissolving-grade pulp, some more lignin and ash must be removed.

4.3.5 Effects of soda pulping on different raw materials

Pulping of spruce shavings using similar process conditions as in the pulping of oat husks and wheat was performed to increase the understanding of the different raw materials. Initially, both HWE and 0.1% HCl were intended to be used as pretreatment for the spruce shavings. However, after the initial pretreatment of the spruce shavings, the lignin in the sample was resistant to pulping. That the acid pretreatment on spruce shavings was most likely too severe and caused lignin condensation reactions which precipitated condensated lignin onto the fibres, rendering the lignin resistant to pulping.
The pulps produced from spruce shavings under different process conditions can be seen below in table 12.

HWE time and NaOH %	**Glu**	**Xyl**	**Gal**	**Ara**	**Man**	**Klason**
No pretreatment 4%	73.57	5.75	0.49	0.28	7.37	11.10
30 min 4%	81.35	2.84	0.12	0	3.55	8.52
60 min 4%	83.55	3.10	0	0	1.73	6.21
No pretreatment 6%	79.49	2.36	0.24	0.11	8.00	6.31
30 min 6%	88.31	2.82	0.09	0	4.80	3.76
60 min 6%	89.25	2.28	0	0	2.26	4.81

Table 12: Composition (wt %) of pulped spruce shavings with different HWE pretreatment times and pulped at 170°C with 4% and 6% NaOH (8.3:1 l/s ratio)

Soda cooking under the chosen conditions is enough to liberate the fibres to produce a pulp. However, pulping of spruce shavings using these conditions isn't as efficient in removing lignin as the same conditions were for oat husk and wheat straw. The lowest lignin value of the pulped samples was achieved using 30 minutes of HWE and 6% $NaOH$ concentration. The reason why the 30 minutes pretreated pulp comprises lower lignin than the 60 minutes pretreated pulp could be due to more condensation of lignin with more severe pretreatment resulting in less accessible lignin. This lignin content of 3.76 is still much too high for a dissolving-grade pulp. This was expected as much more severe pulping is needed to obtain dissolving-grade pulp from wood.
Compared to wood chips which are most commonly used in the pulping industry, wood shavings have a very high surface area and all parts of the shavings are readily available to pretreatment and cooking chemicals. Wood chips would likely need much longer pretreatment times to achieve the same removal of hemicelluloses. This, in combination with the low values of pH achieved during HWE of spruce shavings, as seen in figure 12, makes HWE an efficient way of removing hemicelluloses in spruce shavings.
The glucose fraction in the HWE pretreated samples using 6% $NaOH$ is close to 90%, but the bleaching needed to bleach a pulp from roughly 4% Klason lignin to only trace amounts is likely going to be extensive.

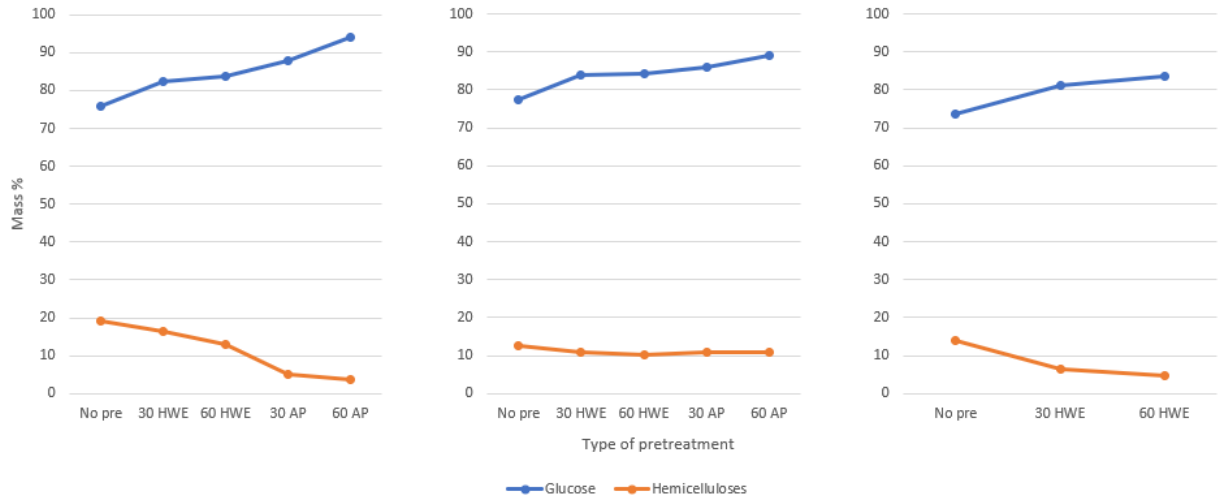


Figure 16: Compositions of glucose and hemicellulose monomers in oat husk (left), wheat straw (middle) and spruce shavings (right) pulped at 170°C with 4% NaOH (8.3:1 l/s ratio) depending on pretreatment.

All three raw materials show an increase in removal of hemicelluloses with pretreatment severity. However, the effect is significantly more pronounced in the oat husk and spruce pulps than in the wheat straw pulps. This can also be seen in the glucose and hemicellulose trends of oat husk and spruce shavings, where there is a clear correlation between lowering of the hemicellulose fractions and the increase in the glucose fractions. As previously shown in figure 15, pretreatment performed at a 6:1 l/s ratio was ineffective for wheat straw, resulting in low removal of hemicelluloses. The removal of hemicelluloses during HWE is more pronounced in spruce shavings than in oat husk and wheat straw. This is expected as HWE of spruce shavings achieves the lowest pH out of the three raw materials, as can be seen in figure 12.

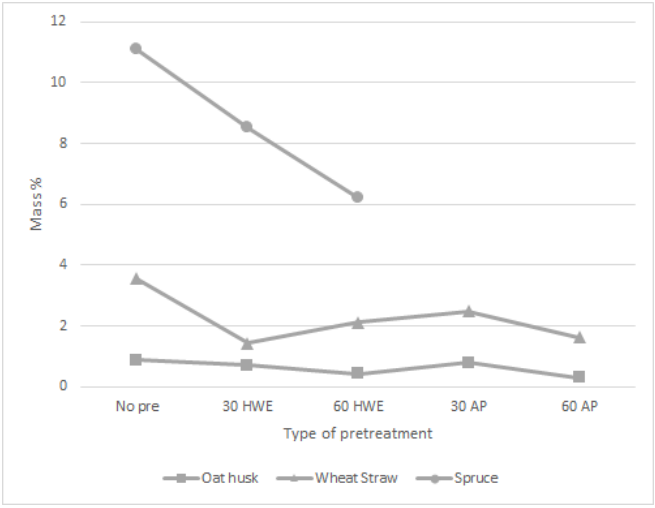


Figure 17: Amounts of lignin in oat husk, wheat straw and spruce shavings pulped at 170°C with 4% NaOH (8.3:1 l/s ratio) depending on pretreatment.

Delignification of the different raw materials differs substantially. Delignification of oat

husk is efficient with a prehydrolysis-soda process, while the amounts of lignin left in the spruce pulps show that the process is much less efficient for spruce shavings. The delignification of wheat straw during soda pulping is also much more efficient than in spruce. It remains unknown if the big differences in removed lignin between the agricultural waste materials and the spruce are caused by big differences in lignin structures, the higher lignin content of spruce or accessibility of the lignin in the different materials. However, it is likely that all of these factors influence the final lignin content of the pulp. Oat husk and wheat straw contain roughly the same amount of lignin, while the finished oat husk pulps contain significantly less lignin than the wheat straw pulps, proving that the lignin content in the raw material is of less significance for delignification when comparing these two materials.

4.4 Post-treatments

After the pulping process, pulps with compositions most suited for dissolving-grade pulps were selected for further treatment. Both pulps from oat husks and wheat stalks showed promising results and were used in an EDTA assisted hydrogen peroxide bleaching process. The pulps selected were the oat husk pulp that was pretreated with 0.1% HCl for 60 minutes with a 6:1 l/s ratio and pulped at 4% $NaOH$ concentration for 2h. The wheat stalk pulp chosen for bleaching was pretreated with 0.1% HCl for 60 minutes with a 15:1 l/s ratio and pulped at 6% NaOH concentration for 2h.
The compositions of the pulps prior to bleaching can be seen in table 13.

Pulp	**Glu**	**Xyl**	**Gal**	**Ara**	**Man**	**Klason**	**Ash**	**DP**
Oat husk pulp	93.89	3.71	0	0	0	0.31	0.11	405
Wheat stalk pulp	94.80	2.45	0	0.08	0.59	1.30	0.60	329
Spruce shaving pulp	89.25	2.27	0	0	2.25	4.81	-	-

Table 13: Compositions and DP of pulps before EDTA assisted HP bleaching

4.4.1 Bleaching

The pulps were bleached with a bleaching sequence that consisted of chelating EDTA step before a two-step hydrogen peroxide bleaching. This sequence is industrially called a Q-P_1-P_2 bleaching sequence. The EDTA step prior to the bleaching is to remove unwanted transition metal ions in the pulp that catalyse the decomposition of the hydrogen peroxide and eventually cellulose chains. The selected pulps were then bleached with 5% HP (on oven-dried pulp) at 80°C for 120 minutes. The pulps were then extensively washed and bleached again with 3% HP at 80°C for 120 minutes. The compositions of the pulps can be seen below in table 14.

Pulp	**Glu**	**Xyl**	**Gal**	**Ara**	**Man**	**Klason**	**Ash**	**DP**
Oat husk pulp	95.37	4.31	0	0	0	0.05	0.05	291
Wheat stalk pulp	95.40	2.38	0	0.08	0.79	0.74	0.19	273
Spruce shaving pulp	90.18	2.29	0	0	2.17	3.21	-*	-*

Table 14: Compositions and DP of pulps after EDTA assisted HP bleaching

EDTA assisted HP bleaching had a significant effect on lignin and ash content on both the oat husk and wheat stalk pulp. In the oat husk pulp, only trace amounts of lignin and ash compounds remained, while 0.7% lignin and 0.2% ash remained in the wheat stalk pulp. The degree of polymerisation was lowered in both pulps. Obtained pulps showed major brightening from the bleaching process as can be seen in figure 18 and figure 19.



Figure 18: Unbleached oat husk pulp (left) and oat husk pulp bleached with EDTA assisted HP bleaching (right)



Figure 19: Unbleached wheat stalk pulp (left) and wheat stalk pulp bleached with EDTA assisted HP bleaching (right)

To meet the requirements for a dissolving-grade pulp, the wheat stalk pulp needs more extensive bleaching. Several bleaching alternatives could be considered. One option could be to use an oxygen bleaching step first in the bleaching sequence. Oxygen bleaching has the advantage of being a TCF bleaching method, which is more environmentally friendly than bleaching methods containing chlorine. However, another option to achieve a more extensive delignification would be to use chlorine dioxide (ClO_2), which is the best method to delignify pulps. However, the bleaching would not be considered TCF bleaching if ClO_2 bleaching is used.



Figure 20: Unbleached spruce shavings pulp (left) and spruce shavings pulp bleached with EDTA assisted HP bleaching (right)

Further testing was also performed on the wheat stalk pulp by doubling the l/s ratio as well as the HP concentrations. These tests did not show any major improvements in delignification but lowered the ash contents of the pulp to <0.1%. These tests also showed further degradation of the cellulose chains, which decreased the DP.
The pulp obtained from spruce shavings was also bleached with the same bleaching sequence. The bleaching step removed a significant lignin fraction, however, the pulp is still far from dissolving-grade pulp quality. While the bleaching removed some of the lignin, it is clear that in order to meet dissolving-grade pulp requirements in this pulp it either needs to be delignified more in the pulping step or more severe bleaching methods. Due to the lignin present in the bleached pulp, the pulp had a yellow colour rather than white as seen in figure 20.

4.5 Solid-state NMR analysis

A solid-state analysis was performed to establish whether the cellulose present in the sample consisted of cellulose I or cellulose II. The transformation from cellulose I to cellulose II starts at 12.5% of $NaOH$ in ambient temperatures and therefore it is important to examine whether this happens during the process[68]. The presence of cellulose I will result in peaks around 64.9ppm from the 6th carbon (C-6). Should cellulose II be present, the peak will instead be located between 62.2-62.8ppm[69]. The pulps that were analysed can be seen in table 15 below.

Raw material	**Pretreatment**	**Pulping**	**Bleaching**	**Colour**
Oat husks	0.1% HCl 6:1 60 min	4% NaOH 120 min	EDTA+5% HP+3% HP	Green
Oat husks	0.1% HCl 6:1 60 min	4% NaOH 120 min	None	Red
Wheat straw	0.1% HCl 6:1 60 min	6% NaOH 120 min	None	Blue

Table 15: Pulps analysed with solid-state NMR

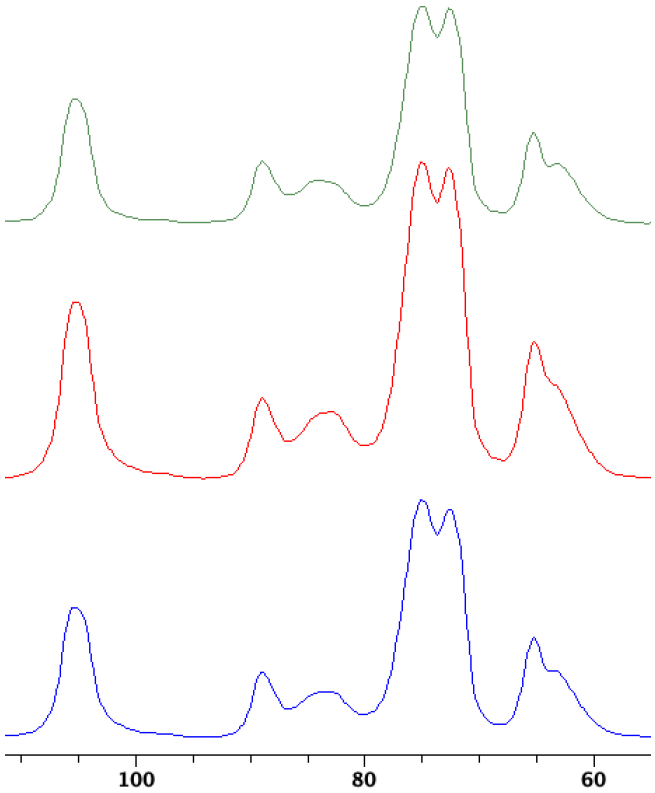


Figure 21: Chemical shift (ppm) for bleached oat pulp (green), acid pretreated oat pulp (red) and acid pretreated wheat pulp (blue)

As can be seen in figure 21, the three pulps are very similar in composition. The analysis also shows that the cellulose appears to be of Cellulose I type, as the peak is located at 64.9ppm with no visible peak between 62.2-62.8ppm. The peaks for all of the samples correspond well to previous studies of solid-state NMR on cellulose I[69]. That there are no indications of cellulose II in either of the samples is a good thing for a pulp that is to be used as a dissolving-grade pulp as the presence of cellulose II negatively affects the reactivity of the pulp due to a denser structure and the increased influence of hydroxyl groups in the hydrogen bonds of cellulose II[70].

4.6 Molecular mass distribution

The pulps analysed for molecular mass distribution are listed below in table 16.

Pulp	**Pretreatment**	**Pulping**	**Bleaching**
Oat husks	None	4% NaOH 120 min	None
Oat husks	0.1% HCl 6:1 60 min	4% NaOH 120 min	EDTA + 5% HP + 3% HP
Wheat straw	None	6% NaOH 120 min	None
Wheat straw	0.1% HCl 6:1 60 min	6% NaOH 120 min	EDTA + 5% HP + 3% HP

Table 16: Pulps sent for molecular mass distribution analysis to *MoRe research Örnsköldsvik AB*

The molecular weights and polydispersity indexes were determined for selected pulps. The results can be seen below in table 17 for the individual pulps.

Pulp	Mp	Mn	Mw	Mz	PDI
Oat no pretreatment	391175	38654	427142	1404533	11.05
Oat full process	55351	19004	89431	266580	4.706
Wheat no pretreatment	292061	40537	353335	1188730	8.716
Wheat full process	42266	14361	58091	151875	4.045

Table 17: MMD analysis results. Units in g/mol

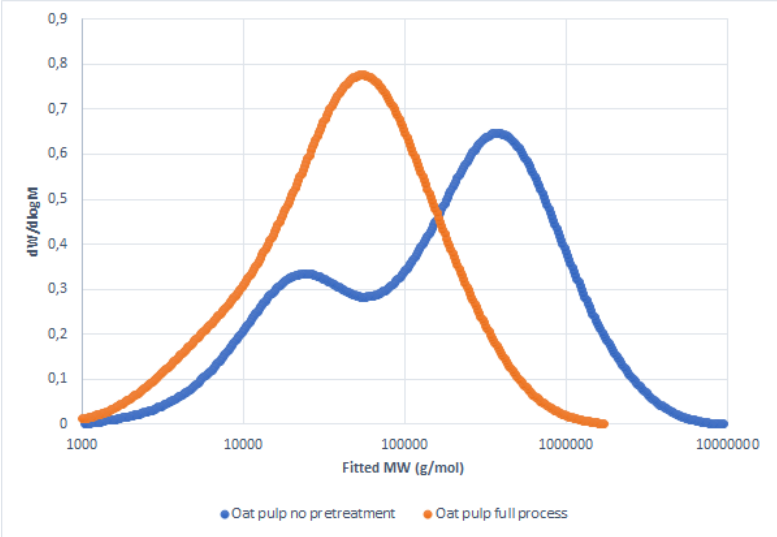


Figure 22: Logarithmic molecular weight distribution of non-pretreated oat husk pulp and pretreated and bleached oat husk pulp

What is generally the most used value to measure the molecular mass distribution of dissolving-grade pulps is the polydispersity index (PDI), which is defined as M_w/M_n. As can be seen in table 17, the PDI of the oat pulp without pretreatment and bleaching is 11.05 indicating a broad range of molecular weight distribution in the sample. However, when the oat pulp is both pretreated and bleached, the PDI drops significantly to a value of 4.706. This PDI value is similar to commercial dissolving-grade pulps that are produced by the prehydrolysis kraft (PHK) process from wood and significantly lower than for dissolving-grade pulps produced with the acid sulfite (AS) process[49]. A major difference between commercially produced dissolving-grade pulps from wood and the fully processed oat husk pulp is that both the mass average molar mass and the number average molar mass are much lower in the oat husk pulp. This is to be expected since the degree of polymerisation is much lower in oat husks than in wood.
As can be observed in figure 22, there are two peaks in the untreated pulp. The shoulder peak at lower molecular weights is most likely a result of signals from different hemicelluloses present in the sample. The main peak of higher molecular weight molecules is then made from the cellulose present in the sample. As most of the hemicelluloses are removed in the acidic pretreatment and subsequent pulping, there is no clear shoulder

peak in the fully processed sample. The fully processed sample only has one clear peak, which is to be expected as this sample mostly contains cellulose. The cellulose peak is now at much lower molecular weights than for the pulp without the pretreatment and bleaching. This is due to acid hydrolysis in the pretreatment and alkaline hydrolysis and peeling reactions in the pulping process. Some degradation during the bleaching step also plays a part in the degradation of the cellulose chains.

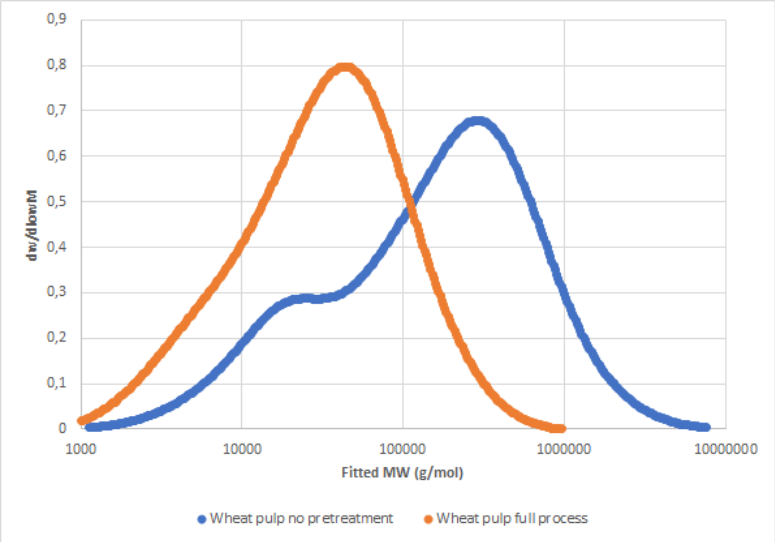


Figure 23: Logarithmic molecular weight distribution of non-pretreated wheat straw pulp and pretreated and bleached wheat straw pulp

The wheat straw pulp has a molecular mass distribution that is very similar to the pulp produced from oat husks. We can once again see a shoulder peak representing the hemicelluloses in the sample. The shoulder peak is slightly smaller in the wheat pulp sample as the wheat pulp comprises fewer hemicelluloses than the oat pulp. The fully processed wheat pulp also has slightly lower values for M_n, M_w and PDI. The PDI for the wheat pulp is 4.045 which is considered well within the range of PHK dissolving-grade pulps[49]. As the wheat pulp is pulped at a higher $NaOH$ concentration than the oat husk pulp, it is difficult to compare the properties of the material. However, the molecular weights of the polymers in the pulp produced by both oat husks and wheat straw are lighter than those in dissolving-grade pulp produced from wood[49].

4.7 Fibre morphology

Three different fully processed pulps were analysed for fibre morphology in a Kajaani FS300 fibre analyser. The pulps analysed can be found in table 18. Fibre morphology such as fibre length, length distribution and width of the cellulose fibres are of utmost importance for the physical properties of the final pulp[71].

Pulp	Glu	Hemi	Klason	DP	Average fibre length (mm)	Fibre witdh (μm)
Softwood PHK	92.17	7.05	0.19	195	0.97	23.72
Oat husk	96.47	3.10	<0.1	236	0.40	18.13
Wheat stalk	96.17	3.17	0.76	274	0.42	11.51

Table 18: Weight fractions (%), DP and average fibre lengths and widths of analysed pulps

The length and width distributions can be seen below in figure 24, 25 and 26.

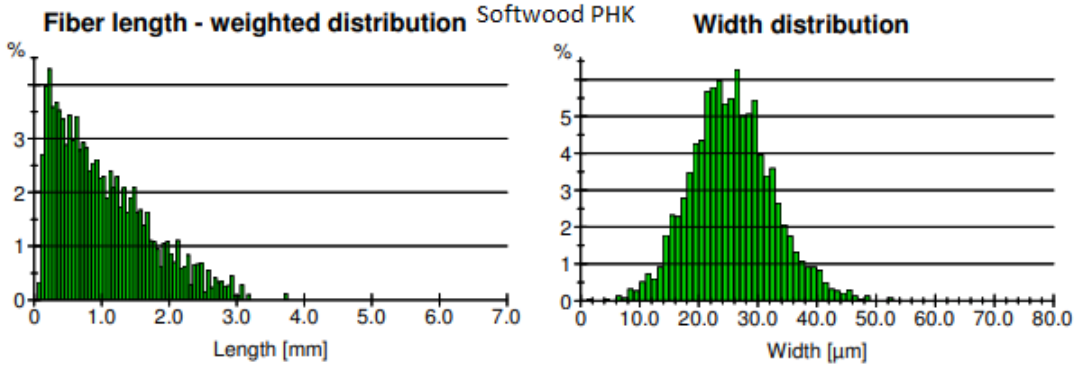


Figure 24: Weighted fibre length distribution and width distribution for softwood PHK dissolving-grade pulp

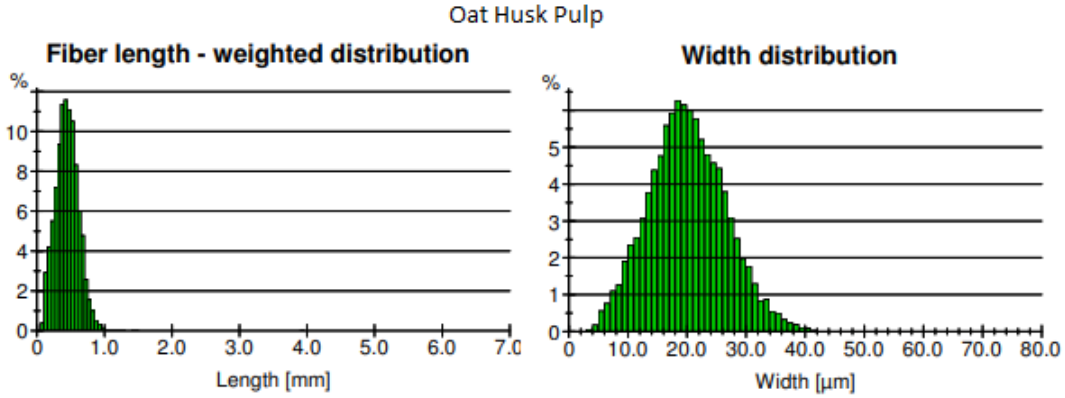


Figure 25: Weighted fibre length distribution and width distribution for oat husk pulp

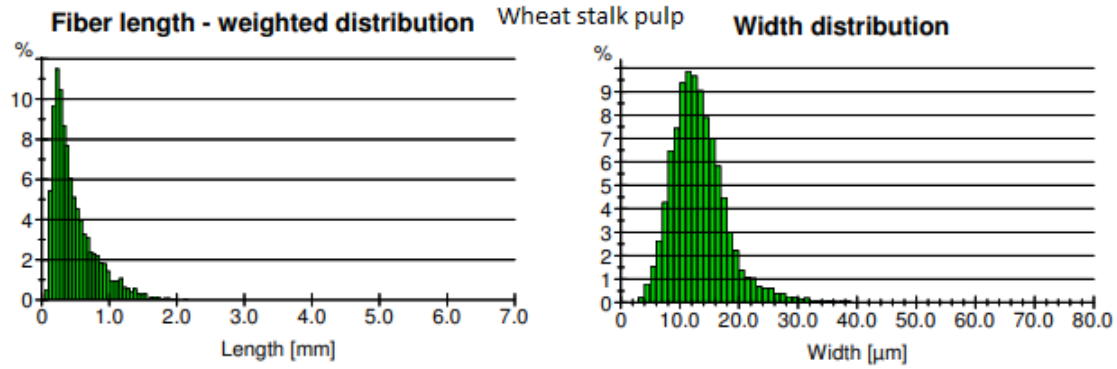


Figure 26: Weighted fibre length distribution and width distribution for wheat stalk pulp

The softwood PHK pulp has a DP of 195, which is close to the IV of the pulps produced from oat husks and wheat straw and could therefore serve as a good fibre morphology comparison for the pulps produced in the project.
The softwood PHK pulp has a large number of fibres below 0.5mm and the length distribution decreases almost linearly up to 3mm where the average fibre length is 0.97mm. The width of the fibres has a distribution that resembles a normal distribution with an average of 23.72μm. This gives an average length to width ratio of 42.17. Previous studies have shown that Norway spruce has an average fibre length of 1.88mm[72], while other studies report softwood pulps with fibre lengths of between 2.5-3mm before acid hydrolysis[73]. This indicates that the process and subsequent hydrolysis to lower the DP has also lowered the average fibre length of the pulp, while the arithmetic fibre width remains in the range of softwood pulps[72].
As can be seen in figure 25, the fibre length distribution shows shorter lengths in the oat pulp than in the PHK softwood pulp. As expected, fibres in the oat husk pulp are shorter than those in the softwood PHK pulp.
While pulps of short fibres have lower strength than pulps produced from long fibres, it is expected that smaller fibres will have a better reactivity due to an increased surface area leading to better accessibility for the dissolving chemicals[74]. Despite having a quite narrow fibre length distribution of short fibres, the width distribution of fibres in the oat pulp is quite similar to that of the softwood PHK pulp. The most narrow fibres in both pulps are just short of 10μm and the widest just over 40μm. However, the length to width ratio of the oat pulp fibres is just 22.19, roughly half that of the softwood PHK pulp.
The wheat stalk pulp has fibres that are similar in average length to the oat pulp, but more narrow. The length distribution describes a pulp that has a major share of fibres between 0.2-0.6mm but some fibres have a length up to 2mm. The average length to width ratio of the fibres in the wheat stalk pulp is 36.49 which puts it closer in shape to the softwood PHK pulp than the oat husk pulp.

4.7.1 Scanning electron microscopy

The three pulps previously analysed for fibre morphology were also analysed with a scanning electron microscope (SEM) to further evaluate the fibre morphology of the

different pulps. SEM is an excellent tool for imaging samples at high magnifications.

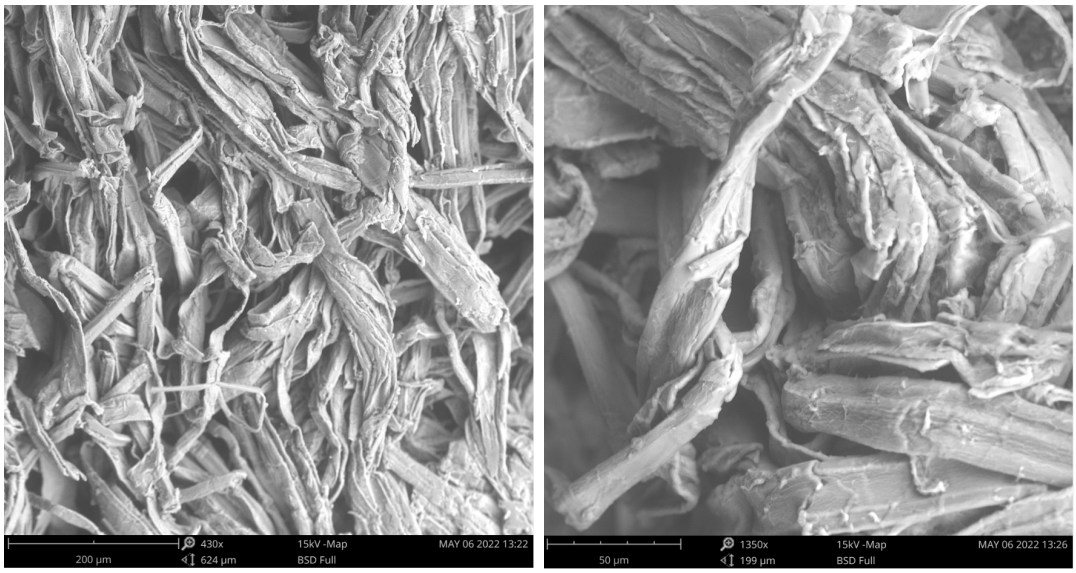


Figure 27: 430x and 1350x magnification of softwood PHK pulp

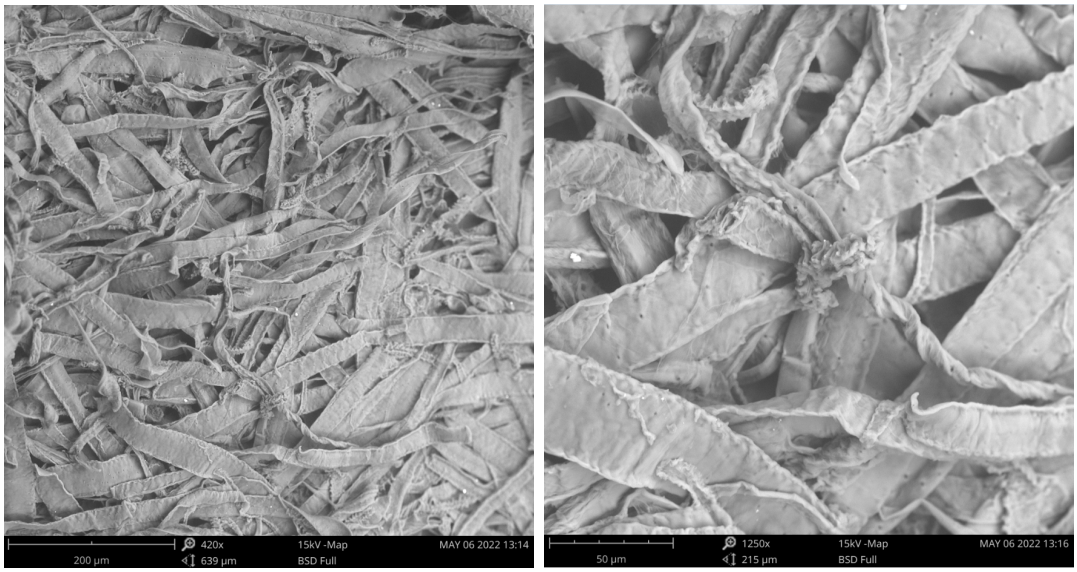


Figure 28: 420x and 1250x magnification of oat husk pulp

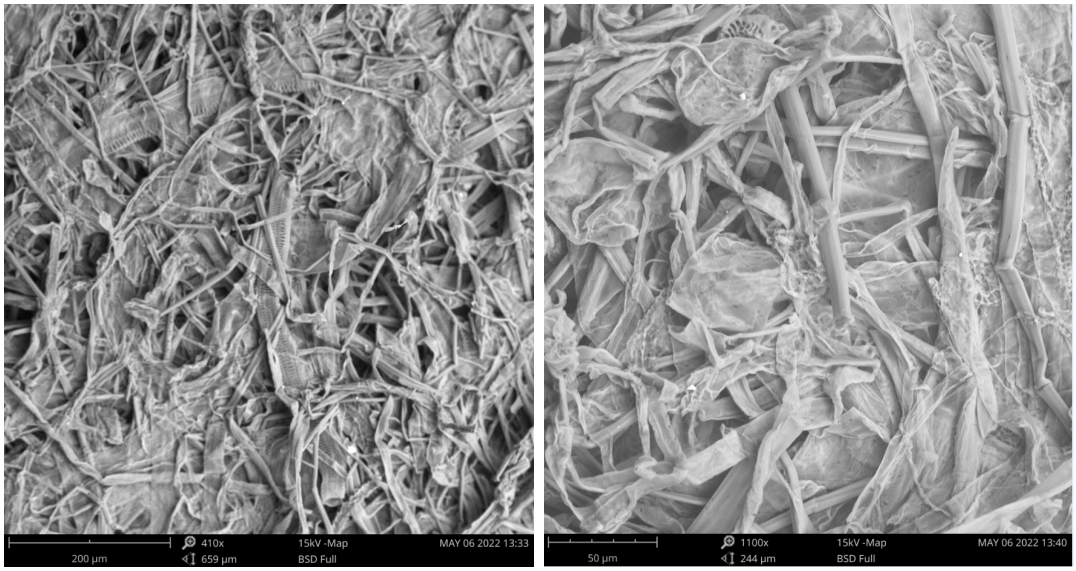


Figure 29: 410x and 1110x magnification of wheat stalk pulp

The fibres of the softwood dissolving-grade pulp show a relatively uniform shape distribution with a high portion of long fibres. The fibres have a rugged surface which gives the fibres an increased surface area. At the bottom of the 1350x magnification picture, a cracked fibre can be seen. This could be a result of the acid hydrolysis treatment used to decrease the viscosity of the pulp.
The fibres of the oat husk pulp are just like the softwood fibres quite uniform in shape. However, the shape is very different to the softwood fibres. The oat husk fibres appear to be smooth and shaped like flat sheets. This gives a much smaller surface area than the softwood fibres. Despite the smaller surface area, the flat nature of the oat husk fibres should allow for high accessibility for dissolution chemicals, as there are very few regions of the fibres that require deep penetration. The black spots that can be seen on the fibres are most likely pits.
The pulp fibres appear to be mostly separated with very few bundled areas. This could also be a result of the flat nature of the oat husk fibres.
The wheat stalk pulp shares very few similarities with the oat husk pulp. While some relatively flat areas can be observed, the fibres seem to be mostly long and thin. The fibres in the pulp also show a more heterogeneous size distribution compared to the other two pulps. It is also clear from the 1110x magnification in figure 29 that there are some flat and round shapes in the pulp that appear very different to the long and thin fibres. These fibres could originate from leaves that were left in the pulping process due to insufficient removal during the separation of the wheat stalks. Another type of tissue that also appears can be seen at the top of the 1110x magnification picture, which appears as a round shape with small holes. This is most likely vascular tissue that is used for liquid transportation within the fibres.

4.8 Summary of results

Pretreatment with hot water extraction at 160°C for 30 or 60 minutes was insufficient for both oat husk and wheat straw due to the relatively low amounts of hydrogen ions

released from the raw materials under these conditions. The best results for oat husks were instead achieved by pretreatment with 0.0274M of H_2SO_4 at 6:1 l/s ratio for 60 minutes before pulping with 4% NaOH at 8.3:1 l/s ratio for 120 minutes. The lignin content in the oat husk pulp was then lowered to only trace amounts with a subsequent TCF bleaching sequence which consisted of a chelating EDTA step prior to two HP bleaching steps at 5 and 3 wt% (on o.d pulp).

For wheat straw, the leaves had to be removed from the wheat straw mixture due to their high ash content. The stalks that were left were then pretreated with 0.1% (0.0274M) HCl at 15:1 l/s ratio for 60 minutes and then pulped with 6% NaOH at 8.3:1 l/s ratio for 120 minutes to achieve the best results. The same bleaching sequence that was used for the oat husk pulp was unable to reduce the lignin content of the wheat stalk pulp to lower than 0.74%. Despite testing higher concentrations of HP during bleaching, no lower lignin levels were reached. This indicates that the current TCF bleaching method was insufficient for delignification of wheat stalk pulp and that harsher conditions or bleaching methods should be applied for further delignification. NMR analysis also indicates that cellulose II isn't present in either of the finished pulp samples, proving that the process doesn't generate any regenerated cellulose.
The acidic pretreatment at a 6:1 l/s ratio was both efficient in removing hemicelluloses from oat husk as well as in making the remaining hemicelluloses and lignin structures more susceptible to removal in the pulping step. The wheat straw needed a higher l/s ratio to achieve similar results and it was concluded that a 15:1 l/s ratio was sufficient when pretreating wheat straw. The reason why wheat straw needed a higher l/s ratio was likely that wheat straw can retain higher amounts of liquids than oat husk, which results in insufficient mixing and reduced physical forces affecting the material.
While dissolution studies of the different pulps are yet to be performed, the composition of the oat husk pulp satisfies the requirements of dissolving-grade pulp with a high cellulose content, low lignin, ash and hemicellulose content, high brightness and homogeneous molecular weight distribution. The same applies to the pulp produced from wheat stalks, except that lower lignin levels need to be achieved.

5 Conclusion

This master's thesis work has been focusing on testing the concept of production of dissolving-grade pulps from oat husk and wheat straw by way of a prehydrolysis-soda process. The use of this method could be beneficial to find new uses for low-value materials to achieve a more circular bioeconomy. The experimental approach in the project has not been focused on optimisation of each process step but rather on starting from set process conditions (160°C for prehydrolysis and 170°C for cooking). The pulps have then been analysed for compositions and properties before further modifications in chemical concentrations and process times have been decided upon. This approach was chosen to reduce the complexity of the project as the process consists of two different raw materials as well as several different process steps.

The main conclusions of this work are:

- Both oat husk and wheat straw show good potential in producing relatively pure cellulose pulps.
- The agricultural waste analysed were easier to process compared to wood. The prehydrolysis-soda combined with an EDTA assisted two-step hydrogen peroxide bleaching is sufficient to obtain pulp with specifications close to dissolving-grade pulp, which is not true for wood due to its inherent resilience to treatments caused by chemical and morphological structure.
- The prehydrolysis step is essential in removing hemicelluloses and facilitating delignification. For oat husk, acid is just enhancing the prehydrolysis process and for wheat straw it is needed due to poor autohydrolysis.
- Wheat straw causes problems due to inherent lignin fraction and high ash contents. The ash fraction can be controlled by removal of leaves.

6 Future work

There are several areas that need to be further analysed before a final assessment of the suitability of oat husk and wheat straw as raw materials for production of dissolving-grade pulp can be made.
Reactivity should be assessed for the pulps to evaluate if the pulps meet dissolving-grade pulp standard.
It should be assessed whether removing the leaves is the only way to achieve low levels of ash content in pulp made from wheat straw or if a specific ash-removing pretreatment can be implemented in the process. Should removing the leaves be the only way to achieve low ash content, it must be further assessed how the leaves can be removed in an efficient and sustainable way. Further bleaching in order to remove the lignin from the wheat pulp should also be looked into.
To keep the process financially and environmentally sustainable, a proper analysis on scale-up and recovery of process chemicals must be done. Possible uses for side-streams such as prehydrolysis and cooking liquors should also be evaluated in order to increase the utilisation of the raw materials as much as possible.

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