Improved Usage of Wood Raw Material through Modification of the Kraft Process

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Abstract

The kraft process is a complex system with many variables, and though the process is fairly well understood, there is still much we do not know.

This thesis examines some aspects of the kraft process that could prove to be of interest for the pulp and paper industry, specifically, the impact of wood chip impregnation and of the chemical structure of xylan on spruce kraft pulp. The intent is to suggest modifications to the kraft process as it is used today.

The effect of wood chip impregnation varies with the prevalent conditions, and increases the effect of the subsequent kraft cook. Longer impregnation at a lower temperature was found to increase screened pulp yield, reduce shives content, make it possible to reach a certain kappa number at a lower H-factor, and make it possible to reach a certain kappa number at a lower total alkali consumption.

Xylan has previously been found to have a strength-enhancing effect on pulp, and the chemical structure of the xylan in question was found to be the main strength-enhancing factor. For spruce xylan, the structure that provides the largest increase in strength is not the same as the structure that increases the yield the most. Removing xylan was determined to have a negative impact on pulp strength.

Xylan extracted from agro waste can be used as an additive to increase pulp strength. This could be viable, especially when combined with the production of green plastics from hemicelluloses extracted from the agro waste.

A suggested configuration of a future pulp mill is presented, incorporating the following modifications to the now standard kraft cooking system:

• impregnation at a lower temperature for a longer time;
• extracting xylan-enriched black liquor at an early stage of the impregnation or cook, and adding this liquor at a late stage of the cook;
• terminating the cook at a higher kappa number;
• increasing oxygen delignification to compensate for the increased kappa number at the end of the cook, keeping the kappa number constant going into the bleaching plant; and
• adding agro-waste xylan during oxygen delignification.
Foreword
There seems to be an ongoing trend in pulp and paper industry research to explore the opportunities offered by biorefineries to search for new opportunities for the forest industry. The focus of such research is on value-added chemicals and new materials made from wood, the raw material of the pulp and paper industry. This focus on new opportunities appears to me to be at the cost of research into pulp production, even though there is much that we still do not understand about this process and much that could still be improved.
Dedication

To Ingalill Gullman and Leif Baggman, my teachers in chemistry, physics, and math at Bergska skolan in Finspång: for conveying great passion for their subjects and for showing me the possibilities of natural science.

They set me on my way.

/Daniel
List of Papers

This thesis is based on the work presented in the three following papers:

**Paper I**

Tavast, D., Brännvall. E., Impact of Differing Time and Temperature during Impregnation on Kraft Cooking of Softwood Chips (Manuscript)

**Paper II**


**Paper III**

Conferences

The work presented here has been presented by Daniel Tavast at the following venues:

EWLP 2012 – Oral Presentation: Effect of Xylan Structure on Tensile Strength

Avancell 2012 – Poster Presentation: Optimal Utilization of Softwood Xylan

CRUW Final Seminar – Oral Presentation: Effect of Spruce Xylan Structure on Tensile Strength

Ekmandagarna 2013 – Oral Presentation: Bättre utnyttjande av vedråvaran [Improved usage of wood raw material]

WPCRN 2013 – Oral Presentation: Xylan as a Strength Enhancing Additive

ISWFPC 2013 – Poster Presentation: Xylan from Agro Waste on Softwood Kraft Pulp

FPRIC Summer Conference 2014 – Oral Presentation: Impact on Cooking Results of Differing Time and Temperature in the Impregnation of Softwood Chips

Avancell 2014 – Poster Presentation: Impact on Cooking Results of Differing Time and Temperature in the Impregnation of Softwood Chips

WPCRN 2014 – Oral Presentation: Impact on Cooking Results of Differing Time and Temperature in the Impregnation of Softwood Chips

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The Forest - A Natural Resource

The forest is a very important natural resource for Sweden, and how the forest is managed certainly affects its impact on the country. If the forest is treated properly it has great potential to provide sustainable raw material for the Swedish lumber as well as pulp and paper industries. However, to achieve this, it is important to maintain the ecosystem as well as its biological diversity and high productive capacity.

Surveys indicate that there has been net growth in the standing lumber supply in Sweden since the early 1900s (Figure 1). This is fortunate, as the forest is an important natural resource for the Swedish lumber as well as pulp and paper industries. One possible reason for this development is that sparsely populated areas have been harvested and planted with new, more productive trees; another possible reason is changes in how productive forests are maintained, as harvested areas are required by law to be replanted.

Although Sweden is mostly forested, not many species thrive in abundance. The species of trees most common in Swedish forests are spruce, pine, and birch, which are also the most common raw materials for the Swedish pulp and paper industry (Figure 1).

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Figure 1. Development of standing volume of common tree species in Swedish forests, including total volume (Riksskogstaxeringen 2014).
Wood - A Raw Material

Wood is a complex natural biocomposite, and it actually grows in trees. It’s a wondrous material with almost infinite potential uses, for building houses and furniture, for decoration, and, of course, for making paper.

Wood is anisotropic, meaning that it has different properties in different directions, due to its cellular structure. The properties in the transverse direction (along the trunk) differ the most from properties in the radial and tangential directions (perpendicular to the trunk), as most wood cells are oriented along the trunk.

The pith forms the very centre of the trunk, and is the remnants of the first growth of the tree. Outside the pith lies the heartwood, which no longer plays an active part in conducting nutrients. The heartwood is often far darker than the sapwood, which is located outside the heartwood, because the heartwood is the site of long-time extractive storage. Through the sapwood, the sap is distributed throughout the tree, but it is also in the sapwood that biochemicals are synthesized and stored (Hillis 1996). Between the sapwood and bark is the vascular cambium, a layer responsible, through cell division, for wood growth on its inside and bark growth on its outside (Larsson 1994) (Figure 2).

Growth rings occur because cells with different properties are produced depending on the growth conditions. In temperate areas with regular seasons, annual growth occurs. Cells growing early in the growth season, earlywood cells, are thin walled with large lumens, making them efficient at transporting liquid. Latewood cells, which form the darker parts of growth rings, have thicker and stronger walls.
Wood cells are held together by a matrix of lignin, which exists both inside the cell walls and between the individual cells (Figure 3). Aside from lignin, the cell walls consist of cellulose and hemicelluloses. The different cell wall layers consist of cellulose fibril aggregates with differing fibril angles. The variety of angles increases the structural strength of the fibres, the way re-bar is placed in several directions in concrete to increase its strength. The cellulose fibril aggregates consist of cellulose fibrils, which in turn consist of cellulose chains bound together.
Figure 3. The structure of wood. From smallest to greatest magnification: wood stump to wood cell (lignin matrix, cell wall structure, lumen, i.e., void inside fibre), to fibril aggregate, fibril, and cellulose molecule (illustration by Moser 2014).

To make paper the fibres, which are the wood cells, must be liberated from the wood matrix. Fibre liberation can be achieved through mechanical or chemical means. Mechanical pulping uses mechanical force to tear the fibres from each other via the process of refining, which requires huge amounts of energy but gives a high yield of 97–98%. The amount of energy used can be reduced by heating the wood chips before refining, in thermomechanical pulping (TMP), or by a combination of chemical and heat treatments, in chemical-thermomechanical pulping (CTMP). As some of the lignin is degraded during the process, the yield is
slightly decreased in CTMP, though it is still far higher than that of chemical pulping.

There are several types of chemical pulping, the most common being the kraft process; see Figure 5 for a description. During chemical pulping, the fibres are liberated by removing lignin, the “glue” that holds the cells together, using chemicals (cooking liquor) and heat. The chemicals are used to break bonds in the lignin structure, which allows monomers and more complex molecules to be dissolved in the cooking liquor. The increased temperature increases the reaction rates of these reactions, reducing the cooking time. The yield of chemical pulping is typically approximately 50%, as about half the wood, mostly lignin, is dissolved into the cooking liquor. As the spent cooking liquor contains a high amount of biological material, it is usually burnt to extract energy and start the process of recovering the cooking chemicals.

**Paper - A Raw Material**

Paper is a very versatile material, although all qualities of paper are made from wood cells. For example, the behaviour during moisture uptake differs greatly between toilet paper and a paper cup, and a paper cup that dissolved as soon as you poured water into it would not be much use. Depending on the end product, an appropriate pulping method (e.g., mechanical or chemical) must be chosen and specified, for example, kraft pulping. Then there is the choice of raw material, as the species of tree used will affect paper properties. Depending on the end product, fillers and surface coatings will be added during the paper-making process.

Pulp mills in Sweden produced approximately 11 million tonnes of paper in 2013, over 9 million tonnes of which were exported. This production is divided into several groups (Figure 4), and the production of newsprint and other graphic paper qualities is in decline, though the production of packaging material is increasing (Skogsindustrin 2013, 2014).
Figure 4. Distribution of Swedish paper industry products (Skogsindustrin 2013)
The Kraft Process – from Wood to Pulp

The kraft process is the most common chemical process which turns wood into paper pulp.

Figure 5. A simplified overview of the kraft process. A: Trees, the raw material, are felled, de-branched, and transported to the mill. B: The logs are debarked and chipped. C: The chips are steamed to remove air from within them, and impregnated with cooking liquor. D: The impregnated chips are cooked at high temperature under harsh conditions. E: Delignification continues with the help of oxygen. F: The pulp is bleached to the desired brightness. G: The pulp is converted into paper using a paper machine.
### Raw Material

When trees are ready for harvest they are felled, de-branched, and loaded onto trucks for transportation to a mill (Figure 5A). When the timber arrives at its destination, it is measured by an independent agency working in collaboration with pulp mills and forest owners to register the volume of healthy wood delivered.

At pulp mills, there are often huge piles of logs waiting to be used. Mills usually stockpile only a few days’ supply, so new logs must keep arriving at all times.

The bark is removed (Figure 5B), as it will otherwise make the pulp darker and more difficult to bleach properly. One way to remove the bark is to place the logs in a large revolving drum, where abrasion between the logs and drum, and between the logs, physically removes the bark. A good printing quality, without spots, is very important, especially in languages where single characters are used to depict whole words, as a single dot in the wrong place can make the character mean something entirely different (Figure 6).

![Figure 6. The meaning of a Chinese character can change with the addition of a dot, making the paper quality very important (Ragnar 2003).](image)

The debarked logs are then cut into small pieces, called chips, which are temporarily stored in a large pile, waiting to be fed into the cooking stage.

### Cooking

The cooking starts with an impregnation stage (Figure 5C) the purpose of which is to distribute the active cooking chemicals throughout the chips, to produce as even a cook as possible. Without good impregnation (Figure 7), the fibres nearer the surface of the chip will be cooked far more than those nearer the middle of the chip. The active cooking chemicals are hydroxide ions and hydrogen sulphide ions. The concentration of hydroxide ions is usually above $1 \text{ mol L}^{-1}$ ($\text{pH} > 14$) at
the start of impregnation; as impregnation continues, alkali is consumed, mostly to neutralize the naturally acidic wood.

Figure 7. Incomplete impregnation of spruce chips. Chips impregnated with black liquor are cut in half to show that total penetration did not occur (Karlström 2009).

The conditions during a cooking stage (Figure 5D) are very harsh; although the alkali concentration is slightly lower than during impregnation, usually just below 1 mol L−1, the temperature is higher, usually 140–170°C. This high temperature speeds up the chemical reactions, so cooking time decreases with higher temperature. The purpose of cooking is to liberate fibres by removing lignin. However, it is not only the reaction rates of desired reactions that increase with the temperature; the reaction rates of undesired carbohydrate-degrading reactions that reduce pulp yield also increase. These undesired reactions that degrade carbohydrates are peeling and alkaline hydrolysis, which causes secondary peeling. Under the peeling reaction the reducing end groups of carbohydrate chains are attacked by hydroxide ions and terminal glucosyl units are split of. Alkaline hydrolysis shortens carbohydrate chains more significantly, as the attack of hydroxide ions can occur in random places on the chains, producing two shorter chains. How far the cook has proceeded is measured as the kappa number, which quantifies the amount of lignin remaining in the pulp. A pulp without lignin should have a kappa number of 0; however, this is not always the case, as other structures (e.g., hexuronic acid) can be oxidized, giving a false positive in the analysis.
The H-factor is used to calculate the effects of cooking conditions on the cooking process. The H-factor combines the relative reaction rate of the delignifying reactions, which depends on the temperature, and the time. As the reaction rate increases much faster than does the temperature (Figure 8), even a small temperature change will affect the time needed to achieve a certain cooking result, or kappa number. Therefore, a certain kappa number can be reached at a certain H-factor, depending on the system used. This is a complex matter, as a cooking system contains several variables, such as the cooking vessels, temperature, and chemical concentrations. A given H-factor can therefore be reached at different temperatures, which will give widely differing cooking times (Table 1). As the relative reaction rate varies greatly with temperature, 1 min at 170°C corresponds to 15 h at 100°C. The example in Table 1 uses an assumed target kappa number and an H-factor of 1200 h⁻¹ is needed to reach it, using a system with a cooking time of 18.2 to 1.3 h at 140–170°C. For such an H-factor, it would not be feasible to use a temperature as low as 140°C, as the retention time in the digester would be too long.

Figure 8. The H-factor: relative reaction rate (\(k_{rel}\)) of delignification as a function of temperature
Table 1. Example of the effect of temperature on cooking time, assuming a target kappa number reached at an H-factor of 1200 h\(^{-1}\). Showing temperature, relative reaction rate and time

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>k(_{rel}) [h(^{-1})]</th>
<th>t [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1</td>
<td>1200</td>
</tr>
<tr>
<td>140</td>
<td>66</td>
<td>18.2</td>
</tr>
<tr>
<td>150</td>
<td>165</td>
<td>7.3</td>
</tr>
<tr>
<td>160</td>
<td>401</td>
<td>3</td>
</tr>
<tr>
<td>170</td>
<td>927</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Oxygen Delignification**

The purpose of oxygen delignification (Figure 5E) is to remove additional lignin, as the pulp still contains a fair amount of lignin after the cooking stage. Oxygen delignification can be used to increase the yield of the process, as it makes it possible to terminate the cook at a higher kappa number, resulting in a higher yield (Figure 9) while maintaining the kappa number going into the bleaching sequence. This minimizes the demand for bleaching chemicals per tonne of pulp.

Figure 9. Increased yield with oxygen delignification. If the cook is terminated at a higher kappa number, and the pulp is oxygen delignified to compensate, the overall yield of fully bleached pulp is increased (Ragnar 2002).
Bleaching

Unbleached kraft pulp is usually quite dark, even though wood entering the process is rather light in colour, because coloured groups are created under the harsh alkaline conditions of the kraft cook. Sulphite pulp is usually brighter. To produce lightly coloured paper, especially printing qualities of paper, it is necessary to bleach the pulp (Figure 5F). There are many chemical treatments for bleaching paper pulp, and due to a ban on chlorine bleaching, two styles of bleaching are now used: totally chlorine-free (TCF) and elementary chlorine-free (ECF) bleaching. TCF bleaching uses no chlorine whatsoever, but ECF bleaching uses chlorine dioxide (ClO₂) (Table 2).

Table 2. Bleaching stage: abbreviation and full name.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Oxygen gas</td>
</tr>
<tr>
<td>C</td>
<td>Chlorine gas</td>
</tr>
<tr>
<td>D</td>
<td>Chlorine dioxide</td>
</tr>
<tr>
<td>E</td>
<td>Alkaline extraction</td>
</tr>
<tr>
<td>P</td>
<td>Hydrogen peroxide</td>
</tr>
<tr>
<td>T</td>
<td>Peracetic acid (or Paa)</td>
</tr>
<tr>
<td>Z</td>
<td>Ozone</td>
</tr>
<tr>
<td>Q</td>
<td>Chelating, EDTA</td>
</tr>
<tr>
<td>A</td>
<td>Acid wash</td>
</tr>
</tbody>
</table>
Impregnation - A Deeper Look

A satisfactory impregnation stage is needed to ensure a pulp that meets product specifications. The impregnation stage should cause the even distribution of cooking chemicals throughout each chip, which in turn provides for uniform cooking conditions throughout the chip bed. If the cooking conditions vary between the surface and the centre of a chip, the cooking will progress further on the surface, as it is more difficult for the active cooking chemicals to reach the centre of the chip. This leads to fibres with a large kappa number distribution, and therefore to a less homogeneous pulp. Fibres nearer the surface will also experience relatively greater carbohydrate degradation under inhomogeneous conditions.

To understand chip impregnation, consider the process as a combination of two phenomena: first, liquor penetration, which can be understood as the flow of liquid through the chips; second, diffusion, which is the movement of ions through the chip matrix (Malkov 2002; Määttänen and Tikka 2012).

Impregnation Factors

The impregnation of wood chips is a complex system with several variables.

Concentration of Active Cooking Chemicals

During impregnation, the concentration of active cooking chemicals will vary throughout a chip, as diffusion and liquor flow are hindered by the wood matrix (Figure 10). The chemical concentration in the chip varies, decreasing when moving deeper into the chip, and in fully impregnated areas the concentration in the chip can be the same as the bulk concentration (Zanuttini et al. 2000; Costanza et al. 2001). A higher concentration of active cooking chemicals in the cooking liquor (i.e., the bulk) will result in more homogeneous impregnation (Wirspa et al. 1950; Ban et al. 2003; Zanuttini et al. 2005), possibly because increased osmotic pressure results in a greater initial driving force for equalization. This increases the diffusion rate, as the diffusion constant is dependent on the concentration of hydroxide ions, which can further magnify concentration differences (Costanza et al. 2001). Lehto et al. (2013) demonstrated that small alkali additions, i.e., effective alkali (EA) 1–4%,
were not enough to neutralize the acidic groups native to birch (*Betula pendula*), and that larger alkali additions (EA 6–8%) increased the polysaccharide degradation. Increased EA was also demonstrated to cause higher dissolution of organic matter in the liquor.

When considering the concentration of active cooking chemicals, it is important to note the difference between a high concentration and a high effective alkali (EA, kg NaOH per tonne of wood). The effective alkali only considers the relationship between NaOH and dry wood, while the concentration of active cooking chemicals can be seen as a relationship between effective alkali and the ratio of liquor to wood (L:W, litres of water per kg of dry wood; see Example 1).

**Example 1**

18% EA corresponds to 180 kg of NaOH per tonne of dry wood.
At an L:W of 3.5:1, the corresponding concentration of NaOH is 51 g L⁻¹, or 1.29 mol L⁻¹.
At an L:W of 5:1, the corresponding concentration of NaOH is 36 g L⁻¹, or 0.90 mol L⁻¹.

**Time**

It can be difficult to vary reaction times in a mill, as a certain product flow must be maintained. However, it has been found that increased time in the impregnation stage will improve cooking conditions in chips by providing more homogenous conditions in the chips (Hartler et al. 1972; Zanuttini et al. 2000; Costanza et al. 2001; Ban et al. 2003; Hultholm 2004; Reddysuresh 2013). An increased impregnation time results in a more complete impregnation, causing improved cooking conditions and a more homogeneous cook (Figure 10).

**Temperature**

Temperature is a variable that is easily changed in a mill, and small temperature changes can greatly change a system. Increasing the temperature during the impregnation stage will speed up the impregnation rate (Ban et al. 2003; Hultholm 2004; Reddysuresh 2013) and increase the amount of organic matter in the impregnation liquor (Lehto et al. 2013). This might not always be beneficial, as the rates of unwanted reactions will also increase with increased temperature (Wedin
The impregnation temperature will also affect the rate of alkali consumption (see below).

Malkov (2002) demonstrated that temperature is important for impregnation due to changes in liquor behaviour, and at temperatures of approximately 40°C the difference in penetration behaviour between white liquor (WL) and water is noticeable. However, this difference disappears as the temperature reaches 60°C, indicating that the impregnation behaviour will remain consistent at the temperatures used during impregnation under mill-like conditions.

Impregnation for a longer time at a lower temperature can influence the pulp properties by producing straighter fibres with fewer kinks (Antonsson et al. 2009); this is beneficial as tensile stiffness is dependent on fibre shape (Page et al. 1979).

**Pressure**

An increased process pressure during impregnation has been demonstrated to cause a more homogenous impregnation process (Malkov 2002).

**Wood Chip Properties**

Chip dimensions are important as they determine how far into the chip chemicals need to penetrate. According to Zanuttini et al. (2000), the most important dimension is the thickness, which is unsurprising, as chip thickness is usually far smaller than chip height or width (Figure 10). Penetration behaviour also differs depending on whether penetration occurs tangentially or radially (Inalbon et al. 2013), though this difference is too small to negate the thickness being far smaller than the other dimensions. This is corroborated for kraft pulping by findings indicating that the direction of penetration is unimportant for alkalis, but not for acids (Fuller 1983).

Chip thickness has been demonstrated to affect pulp properties (Hartler et al. 1962) such as kappa number (Gullichsen et al. 1992) and shives content (Hellström 2008). A thicker chip also displays a more pronounced concentration gradient (Hartler et al. 1962, 1972; Johansson et al. 1984; Gullichsen et al. 1992). Rayal et al. (2005) demonstrated that
a larger thickness distribution gives an increased kappa number distribution measured on individual fibres in a pulp. However, if an even impregnation profile is achieved, any chip size distribution will be negated.

Figure 10. Concentration profiles during impregnation of a wood chip. Concentration in the chip is relative to concentration in the bulk phase, a darker concentration profile indicating a later point in time.

The properties of the wood chip also depend on where in the tree the chip originates, as impregnation behaviour differs markedly between heartwood and sapwood (Wirspa et al. 1950; Malkov 2002; Tellki et al. 2012; Inalbon et al. 2013; Reddysuresh 2013). This difference in behaviour is unsurprising, as wood displays different properties in the radial and tangential directions. A piece of wood cracks radially between centre and bark, indicating that the fibres shrink more in the tangential than the radial direction (Figure 2 and Figure 11). Depending on the growth site, seasonal conditions will vary, affecting the distribution between earlywood and latewood fibres; this in turn affects wood density
and impregnation behaviour, wood containing more earlywood fibres being lower in density and more easily impregnated.

Figure 11. Cracks in wood form almost exclusively radially between centre and bark, due to how wood cells behave during drying.

Air inside chips or individual fibres will make impregnation more difficult (Wirspa et al. 1950; Maas 1953; Stamm 1953; Woods 1956; Gullichsen and Fogelholm 2000), as air trapped in the lumen of a fibre will stop liquid from filling the fibre.

Fresh chips are more easily impregnated than are dried chips (Malkov 2002; Solar et al. 2008; Solar et al. 2009; Solar et al. 2011), possibly due to changes in the fibre walls as the fibres are dried.

Wood Species

The species used is an important factor affecting impregnation (Hartler et al. 1972; Sjöström 1981; Matsumura et al. 1999), as different wood
species have different fibre structures and chemical constituents; these differences, however small, affect how chips behave during impregnation. The most prominent differences are found between hardwoods and softwoods; there are, of course, behavioural differences within these groups, but they are not as important as those between the groups. One important aspect of impregnation is the extractives content: softwoods contain more extractives than do hardwoods, and the presence of more extractives negatively influences impregnation, as extractives can block pathways for liquor penetration (Chen 1994).

Where the tree grew should also be considered (Rydholm 1965; Singh et al. 1999), as the growth site might influence variables such as density, earlywood:latewood ratio, and mineral content (Figure 12).

![Figure 12. Both wood cuts are from pine. The large one grew in Brazil and was cut at 12 years of age, while the smaller one comes from northernmost Norway, and was cut at 167 years of age. The larger cut is far less dense than the smaller one, and visual inspection confirms that the larger cut contains a far lower percentage of latewood fibres. The larger cut is also far softer than the smaller one.](image)

There are large differences in hemicellulose content between species; for example, birch contains far more xylan than do most other species.
Birch xylan also has a more linear and less branched structure than do most other xylans. In softwoods, it is generally the glucomannan that contains acetyl groups, not the xylan as in hardwoods. In addition, the formation of aliphatic acids during the kraft process depends on the species (Pakanen et al. 2013)

**Swelling**

Wood swelling is dependent on pH and temperature (Zanuttini et al. 1999; Inalbon et al. 2008), as these parameters influence the effective capillary cross-sectional area (ECCSA) and high-alkali treatment causes enough swelling to almost close the lumen (Maximino et al. 1988). Swelling is affected by pH and salt (NaCl) concentration, where a very low or very high pH reduces the water retention value. However, at a NaCl concentration of 0.25 mol L$^{-1}$, this effect is absent from kraft and sulphite pulps (Grignon and Scallan 1980).

**Alkali Consumption**

During the impregnation stage, aliphatic carboxylic acids are formed; these include formic and acetic acids, which are considered volatile, and non-volatile hydroxyl monocarboxylic and dicarboxylic acids. These acids are degradation products of both carbohydrates and lignin (Alén 2000). Under kraft conditions, carbohydrates are degraded at relatively low temperatures (>100°C) (Sjöström 1981; Alén 2000). As the temperature is relatively low during the impregnation stage, usually 130°C or less, neither primary nor alkaline hydrolysis has a high reaction rate, reducing the importance of these reactions compared with their effect in the cooking stage (Nevell 1985; Fengel and Wegener 1989).

If the alkali concentration is increased, more acetyl groups are neutralized until all acetyl groups are neutralized (Zanuttini et al. 2000; Ban et al. 2003; Costa et al. 2008). That the acetyl groups are important for alkali consumption is supported by findings indicating that an absence of acetyl groups reduces alkali consumption in the cook (Sjöström 1981). The occurrence of acetyl groups in a chip is strongly correlated with the progression of impregnation, and can be correlated with pulp quality (Costanza et al. 2001).
Regarding the rate of alkali consumption, it has been demonstrated that alkali is consumed faster at higher temperature (Zanuttini et al. 1997; Ban et al. 2003; Karlström 2009), at higher alkali concentration (Zanuttini et al. 1999; Ban et al. 2003), with decreasing chip thickness (Inalbon et al. 2011), and with increasing ionic strength (measured as concentration of Na⁺), though the impact of ionic strength was determined for low concentrations, not under mill-like conditions (Inalbon et al. 2011; Kuitunen et al. 2012).

**Xylan**

Pulp and paper products are sold with certain specified properties to meet customer demands. These properties are affected by, among other factors, chemical constituents such as lignin, cellulose, and hemicellulose. Xylan is a hemicellulose with interesting properties, as it can function as a strength-enhancing agent in paper.

**Chemical Structure**

In nature, xylan can be found in most plants, including trees, though the amount of xylan found varies greatly. Hardwoods can contain as much as 30% xylan, whereas softwoods usually contain no more than 8%. Although all xylans are based on xylopyranosyl chains, the chemical structure of xylan differs between species (Erbringerová et al. 2005).

The most prominent difference between native xylans from differing plants is the constitution of the substituents. Uronic acid and arabinose are the most common substituents; other substituents, including galactose, glucose, and rhamnose groups, can be found on methyl glucuronic acid groups (Shatalov et al. 1999; Evtugin et al. 2003). It is not only the structure of the substituents that varies, but also the ratio in which they occur on the base chain (Erbringerová et al. 2005).

Birch xylan is acetylated and has an uronic acid ratio of approximately 1:10. The structure of spruce xylan, on the other hand, differs from the long straight structure of birch xylan, having a branched structure and mainly containing arabinose and uronic acid (Erbringerová et al. 2005) (Figure 13).
Figure 13. A xylose chain substituted with A) uronic acid, B) an acetyl group and C) an arabinose unit.

**Behaviour of Xylan in the Kraft Process**

During the kraft process, xylan is dissolved as molecules in the alkaline cooking liquor (Axelsson et al. 1962; Figure 14). This behaviour is the basis of why xylan is such an interesting molecule during the kraft cook. An interesting concept is the possibility of redistributing a strength-enhancing agent from inside the fibre wall, where it will not interact in fibre-fibre bonds, by dissolution and subsequent redeposition on fibre surfaces where interaction in fibre-fibre bonds can occur.

Figure 14. Xylan is dissolved as molecules during the kraft process, and later re-deposited on the fibre.
During the kraft process and the dissolution of xylan molecules, the dissolution behaviour depends on the molecular characteristics of the xylan, where a higher degree of substitution increases solubility. Which substituents are present is not as important as is the degree of substitution, whether it involves uronic acid groups (Saake et al. 2003; Westbye et al. 2006), arabinose groups, or acetyl groups (Saake et al. 2003). Dissolved xylan molecules often contain bound lignin, called lignin carbohydrate complexes (LCC). Precipitated birch xylan contains up to 10–15% lignin (Axelsson et al. 1962; Danielsson et al. 2007; Jansson and Brännvall 2011), while precipitated spruce xylan can contain up to 75% lignin (Jansson 2011). A higher amount of bound lignin reduces the solubility (Saake et al. 2003; Westbye et al. 2006).

The xylans of differing wood species do not behave the same way in solution, as they are influenced by both cell wall structure and the chemical composition of the wood matrix. For birch xylan, the dissolution occurs very quickly and large xylan molecules are released into solution after a very short time. These high-molecular-weight structures are then degraded as the kraft process continues (Danielsson et al. 2005). For spruce xylan, Jansson and Brännvall (2011) found a different behaviour, in which the molecular weight distribution of xylan in the black liquor (BL) shows evidence, first, of smaller molecules and, later, of the release of higher-molecular-weight xylan. The molecular weight distribution of the spruce xylan also decreases due to degradation as the cook continues. It was also demonstrated that spruce xylan dissolved early in the cook contains more uronic acid, which increases the xylan solubility (Silva et al. 2011), than is found at later stages.

Like cellulose, hemicelluloses can be degraded due to peeling during the kraft process. The chemical structure of the xylan affects how it is degraded, and a xylan with arabinose units can be more stable during the kraft process, as arabinose substituents favour the stopping reaction rather than the peeling reaction (Sjöström 1981).

As cooking progresses, the solubility of xylan decreases (Bosmans et al. 2014) and xylan starts to redeposit on the fibre walls, though only a portion of the xylan will be redeposited (Yllner et al. 1956, 1957; Hansson et al. 1969). Kabel et al. (2007) found that lower-molecular-weight xylan reprecipitated to a lesser degree, and that at least 15 xylose groups were
needed in the backbone chain to permit reprecipitation. The substituents on the xylose chain affect the precipitation, and a lower uronic acid ratio increases precipitation (Silva et al. 2011).

**Effects on Pulp**

The redeposited hemicelluloses on the fibre surfaces can increase the tensile strength of a paper sheet by strengthening the fibre-fibre bonds (Sjöberg et al. 2004). However, there is no simple correlation between the amount of xylan on a fibre surface and the resulting strength increase; it has been demonstrated that the chemical structure of the xylan is more important than is the amount of xylan reprecipitated on the fibre surface (Danielsson et al. 2005; Köhnke et al. 2007; Danielsson et al. 2009). As Sjöberg et al. (2004) found that more xylan on the surface reinforces the strength increase, it must be assumed that this applies per xylan structure, and not simply to all possible xylan structures. Additions of high-molecular-weight birch xylan to a spruce kraft cook results in a higher pulp strength than does the addition of a lower-molecular-weight birch xylan (Danielsson et al. 2005). Unlike the strength increase with the addition of higher-molecular-weight birch xylan, Danielsson et al. (2009) demonstrated that a higher degree of substitution in eucalyptus xylan reduced its strength-enhancing effects. This behaviour may occur because the disassociation of acetyl groups from birch xylan leaves long xylan chains with a comparatively low branching ratio, resulting in a system of molecules that are easily packed together. In contrast, other xylans, such as spruce or eucalyptus xylan, have a much more branched structure, even at a late stage of the cooking process, which makes effective packing behaviour unlikely. The dense packing behaviour of the long, straight birch xylan could explain why birch xylan can greatly increase pulp strength (Figure 15), as it can form a cohesive bond with a dense and stable structure between two fibres farther apart from each other than can more branched xylans.
Figure 15. Possible packing behaviour of A) birch xylan, and B) a more branched xylan, such as spruce or eucalyptus xylan.

It has been demonstrated that xylan influences the pulp properties in more ways than simply by increasing pulp strength. It can also increase the effect of beating, which in itself increases pulp strength by means of delamination and internal fibrillation, causing the fibres to swell more (McIntosh 1967; Page et al. 1967), and an increased xylan content reduces the beating energy needed to reach a certain tensile index (Sjöberg et al. 2004; Danielsson et al. 2005; Colodette et al. 2011).

If a paper mill is not directly connected to a pulp mill, then pulp must of course be transported to the mill; this pulp is dried before transport, so as to transport as little water as possible. This drying process changes the properties of the pulp. Compared with never-dried fibres, dried fibres retain less water in the fibre wall. As a wet kraft fibre is dried and reaches the fibre saturation point (FSP), there is no more water in the lumen, and water from inside the fibre wall will be removed with further drying. As the water content of the fibre wall decreases, pores in the outer layer of the fibre wall close irreversibly, while pores farther inside the fibre wall close reversibly (Stone and Scallan 1966). If xylan is present in the fibre wall, the severity of this hornification can be decreased (Oskanen et al. 1997; Köhnke et al. 2007; Köhnke et al. 2010), and the more xylan, the less severe the hornification (Silva et al. 2011).
Wood is, by its nature, designed to work in a wet state, but when used as a raw material it is almost always intended to be used in a dry state. It is important to consider how the properties of the wood material change during drying.

As a fibre wall absorbs liquid, it will swell through internal fibrillation (Scallan 1974), greatly increasing the pore volume in the fibre wall (Figure 16). Cooking affects the fibre wall structure, and the pore radius of fibres is dependent on the kappa number (Andreasson et al. 2003) and, therefore, on the chemical composition of the pulp. Hornification negatively affects pulp strength, because any fibre swelling decreases as hornification occurs. Swelling makes the fibres more flexible and increases the number of fibre-fibre joints created in a sheet. Swelling also affects the water retention value (WRV), and Zanuttini et al. (1999) have demonstrated that an increase in the number of acid groups increases the WRV, while remaining acetyl groups in the fibre wall reduce the WRV.

Figure 16. Internal fibrillation during swelling (Scallan 1974).
Yield

Raw material is a pulp mill’s largest expense, which makes the pulp yield the determining factor of profitability. Imagine a mill called Bruket (which simply means “the mill” in Swedish). Bruket is fairly old, not very big, and uses the kraft process, with spruce as the raw material.

The yearly production is 365,000 tonnes of bone dry (b.d.) pulp, which means that it produces 1000 tonnes of dry pulp per day. The current system has a yield of b.d. pulp of 50.0% at a kappa number of 35. It is common to give production numbers in ADMT year\(^{-1}\), which is the number of air-dry metric tonnes of pulp produced per year. Even if pulp is dried to 100% dry content, it will soon absorb considerable moisture from the air, and even a Licentiate thesis like this one contains approximately 5–10% water depending on the prevailing conditions. To address the fact that fibres are so good at retaining moisture, all weights used in this thesis are dry weights, unless otherwise specified.

Increased Pulp Yield

If the engineers at Bruket managed to increase the yield by 1% by modifying the process, Bruket would produce another 10 tonnes of pulp per day, without extra raw material costs. That is, however, not the whole picture: Assume that the current bottleneck is the recovery boiler, which is working at maximum capacity. The increase in yield means that less biological material will be dissolved in the cooking liquor, i.e., the BL. This reduces the load on the recovery boiler, which means that Bruket can increase production even more, to a degree that increases the load on the recovery boiler to the same level as before (Example 2).

Example 2

\[ P = \text{Production} \]
\[ Y = \text{Yield} \]
\[ m = \text{mass} \]

\[ P_0 = 1000 \text{ tonnes day}^{-1} \]
\[ Y_{\text{PULP}} = 50.0\% \]
\[ Y_{\text{NEW PULP}} = 51.0\% \text{ (an increase in yield of } 2.0\%, \text{ or } 20 \text{ tonnes/day)} \]
\[ m_{\text{NEW PULP}} = 1020 \text{ tonnes day}^{-1} \]
Increased material inflow should therefore produce 20 tonnes of biological material in the BL per day.
0.2 tonne = 49% of material inflow ≥ 51% = 20*51/49 tonnes = 20.8 tonnes
P_{NEW} = 1000 + 20 + 20.8 = 1040.8
\[
\frac{1040.8}{1000} \times 100 - 100 = 4.08\%
\]

The result is a 4% increase in production.

Example 1 shows that an increase in yield can ultimately result in even larger overall increases, and that even a very small yield increase can be beneficial.

**Increased Pulp Quality**

The pulp that Bruket produces must achieve specified properties such as tensile strength, viscosity, and brightness. If Bruket produces pulp of lower-than-expected quality, its customers might be dissatisfied. However, if Bruket’s engineers manage to tweak the pulping process to increase the pulp quality, it might be possible to make a paper product with the same specified properties, but using less pulp. To make this profitable, the pulp would have to be sold by function, i.e., for its physical properties, instead of by weight. For example, a printing paper with a grammage of 80 g m$^{-2}$ might meet the same specifications at a grammage of 76 g m$^{-2}$. Such a change could increase the volume of final products by 5% without using more pulp, assuming that the weight differences lie only in the fibre portion of the paper. Whether such a venture would be profitable would also depend on how the pulp quality was improved, on whether the methods used reduced the yield, or even on whether an overly expensive system change was required.
Objective

There is still much to learn about the kraft process, and about what happens as wood is turned into paper pulp.

This thesis examines how the conditions during impregnation of wood chips and how the chemical structure of xylan in spruce kraft pulp affect yield and quality of the resulting paper pulp. This is done with the intent of presenting suggested modifications to the kraft process as it is used today.
Materials and Methods

The following are descriptions of the raw materials and methods used in performing the studies included in the thesis.

Raw Materials

Swedish spruce chips were, if moist, first dried at 40°C in a Termaks TS 8430 drying cabinet, then sorted by hand, and a 2–8-mm thickness fraction, without knots or bark, was used. Rice husks came from Tanzania, whereas wheat straw came from Sweden.

The stock solution of NaOH was made by dissolving puriss-grade pastilles (VWR Prolabo) in deionized water, while the stock solution of Na₂S (VWR) was prepared by dissolving technical-grade flakes in deionized water. These stock solutions were used to prepare the WL. The sodium chloride used to adjust the ionic strength was of puriss grade (VWR Prolabo). The acetic acid was 99.83% pure (VWR Prolabo), the acetone 99.9% pure (VWR Prolabo), and the ethanol 96.3% pure (VWR Prolabo). The hydrochloric acid used for the conductometric titration had a concentration of 37% (Fischer Scientific). The sulphuric acid used for carbohydrate analysis had a concentration of 72% (Labservice AB).

Steel Autoclave Cooking System

A cooking system based on steel autoclaves rotating in a heating bath was used at several stages in the research.

Raw material was placed in steel autoclaves (2.5 dm³ capacity); the air within the autoclaves was removed by vacuum suction for 30 min, to remove air from within the raw material. Cooking liquor was then added to the autoclaves without releasing the vacuum. The autoclaves were rotated in a polyethylene glycol bath while in a slightly inclined position, to ensure good mixing of dry matter and cooking liquor. In addition to the impregnation and cooking times, the autoclaves were allowed 10 min to reach the target temperature. The process was terminated by reducing the temperature in the autoclaves by submersion in a cold water bath.

Impregnation Trials

The impregnation trials were performed using the steel autoclave cooking system described above. After impregnation and subsequent
cooling, 150 mL of liquor was extracted for analysis. The alkali concentration in the autoclave was adjusted to 0.725 mol L\(^{-1}\) (EA 10\%) by adding the same total volume of WL and deionized water as that of the removed sample. The autoclaves were returned to the heating baths and removed after specific cooking times at 157°C, creating a series of differing cooking times for each impregnation stage. After cooling, the BL was collected for analysis and the chips were washed for 14–16 h with deionized water. The fibres were separated in a Nordiska Armaturfabriken defibrator using deionized water and then centrifuged to a dry content of 25–30\%. The centrifuged pulp was manually disintegrated into smaller pulp pieces, which were dried at 40°C in a Termaks TS 8430 drying cabinet and then placed in plastic bags. The bags were sealed and stored for at least 12 h to achieve a homogeneous moisture content throughout the pulp sample before the dry content was analysed.

**Liquor-Exchange Cooks**

To determine the impact of the chemical structure of xylan present in the BL at the end of the cook, we used a cooking procedure in which half the BL was exchanged with liquor containing xylan with a specified chemical structure.

**Exchange Liquors with Specified Xylan Structures**

Exchange liquors were produced according to Jansson and Brännvall (2011). This resulted in BLs enriched with xylans having specific chemical structures, by cooking 300 g of oven dry (o.d.) spruce chips using the steel autoclave cooking system described above. After cooling, the BL was separated from the chips, and stored at 4–6°C for 20–24 h before further experimentation.

**Agro-Waste Xylan**

Rice husk and wheat straw xylans were obtained by subjecting rice husks or wheat straw to kraft conditions using the steel autoclave cooking system described above. Cooking liquor was prepared from stock solutions to obtain \([\text{OH}^-] = 1.20\) mol L\(^{-1}\) and \([\text{HS}^-] = 0.26\) mol L\(^{-1}\). Sodium chloride was added to reach a total sodium ion concentration of \([\text{Na}^+] = 2.57\) mol L\(^{-1}\). The volume of cooking liquor added to each autoclave corresponded to a liquor-to-wood ratio of 4 L kg\(^{-1}\) of dry...
material. The autoclaves were kept in the glycol bath for 30 min at a cooking temperature of 157°C. The BL was then separated from the delignified material.

Xylan Precipitation

Xylan was precipitated from the obtained BLs using the procedure presented by Axelsson et al. (1962), except that acetone (not ethyl ether) was used in the final washing stages. A volume of acetic acid equal to that of the BL was slowly added during mixing, to reach pH 3. The mixture was then poured into three times as much ethanol and kept in a fridge at 4–6°C for 16–24 h, while the precipitated xylan was allowed to sediment. The supernatant was decanted off and the precipitate was washed twice with an ethanol:water mixture (1:2), three times with pure ethanol, and finally three times with acetone. The precipitate was centrifuged in a Rotofix 32A centrifuge at 4000 rpm for 20 min between all washing stages. The precipitate was then dried overnight in a desiccator under vacuum. The dry content of the xylan was determined using a Mettler PM 460 IR balance. Birch xylan was precipitated using the same procedure, but from industrial BL.

Standardized Cook with Liquor Exchange

The cooking procedure for BL exchange cooks was as follows: 500 g of o.d. spruce chips were subjected to kraft cooking in a pilot-scale forced-flow circulation digester. The WL had an effective alkalinity (EA) of 20% and a sulphidity of 34% (calculated as NaOH), corresponding to [OH⁻] = 1.25 mol L⁻¹, [HS⁻] = 0.26 mol L⁻¹, and [Na⁺] = 2.5 mol L⁻¹ with a liquor-to-wood ratio of 4:1. The chips were steamed for 5 min to remove air from within them, after which the WL was pumped into the digester. Liquor circulation was started and the temperature was raised quickly to 100°C, and then to the cooking temperature of 157°C at a rate of 1°C min⁻¹. The cooking proceeded for 120 min (Figure 17A), after which the liquor circulation was stopped and half the BL removed. The removed BL was replaced with BL produced as described above in “Exchange Liquors with Specified Xylan Structure”, or with WL containing xylans previously precipitated as described above in “Agro-Waste Xylan” (Figure 17B). At the point of exchange, the alkali concentration in the BL was determined to be 0.3 mol L⁻¹ by analysing the removed BL. To ensure the same alkali profile in all cooks, the [OH⁻] of the exchange liquors was adjusted to 0.3
mol L\(^{-1}\). For reference, a cook was performed without BL exchange, referred to as Ref\(_{\text{NO-EXCH}}\), incorporating a 10-min rest to simulate BL exchange, before the cook was resumed by restarting the liquor circulation. As a second reference, a cook was performed in which BL was exchanged with WL corresponding to [OH\(^{-}\)] = 0.3 mol L\(^{-1}\), [HS\(^{-}\)] = 0.26 mol L\(^{-1}\), and [Na\(^{+}\)] = 2.5 mol L\(^{-1}\) (referred to as Ref\(_{\text{WL}}\)). After the liquor exchange, the cook was continued for a further 48 min (Figure 17C), after which BL was removed for analysis and xylan precipitation. The system was prewashed with deionized water to cool it. The chips were washed for 14–16 h with deionized water. The fibres were separated in a Nordiska Armaturfabriken defibrator using deionized water and then centrifuged to a dry content of 25–30%. The centrifuged pulp was manually disintegrated into smaller pulp pieces, which were placed in a plastic bag. The bag was sealed and stored for approximately 12 h to achieve a homogeneous moisture content throughout the pulp sample.

**Black Liquor Analyses**

The residual hydroxide ion concentration was determined according to SCAN N 33:94 and the hydrogen sulphide ion concentration according to SCAN N 31:94.

**Pulp Analyses**

The yield was determined gravimetrically.

The kappa number was analysed according to ISO 302:2004, for Papers II and III using a kappa number titrator from Metrohm and for Paper I using an automated system from Mettler Toledo, based on the T70 titrator. The old Metrohm equipment used to perform this analysis was replaced due to failure, and the replacement Mettler Toledo equipment was found to be at least as stable, providing values well within the error margins of the old system, ensuring the compatibility of the two systems.
Figure 17. Flowchart of the liquor-exchange cook using a pilot-scale forced-flow circulation digester. A) Standardized cook, 120 min. B) Liquor exchange: After 120 min, half the black liquor was removed and replaced with the same volume of black liquor containing xylan of a specified structure, or with white liquor containing previously precipitated xylan. C) The cook continued for 48 min, before termination (Papers II and III).
For mechanical testing, the pulps were wet disintegrated in accordance with ISO 5263. Specifically, they were beaten in a PFI mill (according to ISO 5264) for 500, 1000, 2000, and 5000 revolutions, the mildest beating simulating the fibre wear occurring when passing through the pipes and pumps of a mill. °SR was determined according to ISO 5267-1:1999 followed by sheet making using the Rapid-Köthen sheet former (according to ISO 5269-2:2004). The tensile strength was tested using a Frank Tensile Tester (Horizontal TS, model 81502) (according to ISO 5270:1999 and ISO 1924-2).

The pulp carbohydrate content of was analysed, after acid hydrolysis, according to SCAN-CM 71:09 using a high-performance anion-exchange chromatograph equipped with pulsed amperometric detection (HPAEC-PAD) and a CarboPac PA1 column (Dionex).

The total number of charged groups in the pulp was determined using conductometric titration according to Katz et al. (1984), except that the time between NaOH additions was increased to 30 s. The method has a standard deviation of ±6 μmol g⁻¹.

The zeta potential was determined using a Mütek SZP-10 instrument in pulps beaten for 500 PFI revolutions. The beaten pulp was disintegrated for 2000 revolutions in a Lorentzen and Wettre disintegrator at a fibre concentration of 1.5%, and the conductivity was adjusted to 0.11 ± 0.01 mS cm⁻¹ with [NaCl] = 0.1 mol L⁻¹.
Results and Discussion

The kraft process has many variables, some easy to change in a mill, and others less easy to manipulate. How these variables interact can have unexpected effects: an increase in one variable might have a negligible effect under certain conditions, but completely change the outcome under other conditions.

Impregnation

To investigate the impact of time and temperature on a subsequent kraft cook, softwood chips were impregnated at different temperatures for different lengths of time; see Table 3 for the impregnation conditions. The impregnated chips were cooked in a standardized kraft process at 157°C.

Table 3. Conditions for the reference stage and new impregnation stages used in the study (Paper I).

<table>
<thead>
<tr>
<th>Impregnation stage</th>
<th>Reference</th>
<th>New</th>
</tr>
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<tbody>
<tr>
<td>Liquor-to-wood ratio</td>
<td>3.5 : 1</td>
<td>3.5 : 1</td>
</tr>
<tr>
<td>Retention time (t) [min]</td>
<td>30</td>
<td>60–120</td>
</tr>
<tr>
<td>Temperature (T) [°C]</td>
<td>130</td>
<td>105</td>
</tr>
<tr>
<td>Sulphidity [%]</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>Effective alkali [%]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Impregnation</td>
<td>18.2</td>
<td>18.2</td>
</tr>
<tr>
<td>- Cook</td>
<td>1.2</td>
<td>0.4–2.5</td>
</tr>
<tr>
<td>[OH⁻] [mol L⁻¹]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Start of impregnation</td>
<td>1.30</td>
<td>1.30</td>
</tr>
<tr>
<td>- Start of cook</td>
<td>0.725</td>
<td>0.725</td>
</tr>
<tr>
<td>[Na⁺] [mol L⁻¹]</td>
<td>2.5</td>
<td>2.5</td>
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</table>

Time and Temperature

That the temperature affects the rate of alkali consumption is clearly shown in Figure 18a, where the rate of consumption at 130°C is considerably higher than at 105°C. Figure 18a also shows that more alkali was expended with increasing time, which is in agreement with earlier

Figure 18.  a) Alkali profile of impregnation at 130°C for 30 min and at 105°C for 60–120 min. Trend line for 30/130 approximated based on Zanuttini et al. 2000 and 2005.

b) Alkali profile of a standardized cooking stage following by differing impregnation stages; alkali charge adjusted to 0.725 mol L⁻¹ at start of cook (time at start of cook set to 0), the adjustment varying depending on the parameters of the impregnation stage (Table 4) (Paper I).
To examine the effect on the alkali profile of a kraft cook following the impregnation stages used in Paper I, a standardized kraft cook in which the alkali concentration was initially adjusted to 0.725 mol L\(^{-1}\) was used. The results indicate that a certain amount of alkali was expended in the impregnation and cooking (Figure 18 and Table 4), apparently dependent on the cooking time. As more acetyl groups were removed during the longer impregnation (Zanuttini et al. 1997), resulting in increased alkali consumption, the need for neutralization during the cook decreases (Sjöström 1981).

Table 4. Variations in effective alkali (EA\%) during the impregnation stages and cooking, calculated by measuring hydroxide ion concentration in liquor. The longest cooking time was 290 min, corresponding to “End of Cook” in the table (Paper I). “Imp.” stands for impregnation and “cons.” stands for consumption. The error margin of the analysis is ± 0.3 percentage points.

<table>
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<tbody>
<tr>
<td>30/130</td>
<td>18.2</td>
<td>9.0</td>
<td>1.2</td>
<td>10.2</td>
<td>19.4</td>
<td>4.8</td>
<td>14.6</td>
</tr>
<tr>
<td>60/105</td>
<td>18.2</td>
<td>9.8</td>
<td>0.4</td>
<td>10.2</td>
<td>18.6</td>
<td>4.2</td>
<td>14.4</td>
</tr>
<tr>
<td>90/105</td>
<td>18.2</td>
<td>8.2</td>
<td>1.9</td>
<td>10.2</td>
<td>20.1</td>
<td>4.8</td>
<td>15.3</td>
</tr>
<tr>
<td>120/105</td>
<td>18.2</td>
<td>7.6</td>
<td>2.5</td>
<td>10.2</td>
<td>20.7</td>
<td>5.9</td>
<td>14.8</td>
</tr>
</tbody>
</table>

As the amount of alkali expended during the cook, for a certain cooking time, is dependent on how much alkali is expended during the impregnation, the temperature in the impregnation stage is also shown in Figure 19. The results show that a certain kappa number can be reached with lower alkali expenditure during the cook if impregnation occurs at a lower temperature for a longer time. This decreased neutralization in the cooking stage should benefit the carbohydrate yield, as the reactions...
impairing the carbohydrate yield are slower at relatively low impregnation temperatures than at normal cooking temperatures. As less alkali is expended, this should correspond to less alkali consumed due to carbohydrate degradation. That the screened pulp yield is increased with impregnation at a lower temperature for a longer time can be seen in Figure 21, which confirms that the alkali consumption is linked to the yield.

![Figure 19. Alkali expended during a cook as a function of alkali expended during impregnation. The thick line indicates the reaching of a kappa number of 35 at the two impregnation temperatures (Paper I).](image)

**Cooking Effect**

There can be large differences apparent effect between cooking systems, even though the conditions applied in the systems are exactly the same. For example, the two systems available at the Pulping Technology Department at KTH differ greatly in apparent cooking effect, as one system achieves only 67% of the kappa number reduction of the other system under identical conditions. Reaching the same kappa number with the less effective system therefore requires a substantially larger H-factor. This larger H-factor can be achieved by increasing cooking time or temperature.
After impregnation, cooking proceeded under standardized conditions, and the results indicate a difference in cooking effect, expressed as the kappa number related to the H-factor (Figure 20). Concerning the temperature, it is clear that a higher impregnation temperature can increase the cooking effect, as a lower kappa number is reached with an impregnation stage for 30 min at 130°C compared to 60 min at 105°C, with the same total H-factor. In addition, Figure 20 shows that a longer impregnation stage at a relatively low temperature can give a more effective cooking stage, as a lower kappa number is reached at the same H-factor in a sample in 120 min at 105°C than in 60 or 90 min at 105°C. This shows that the impregnation procedure is an important factor in determining system behaviour and effectiveness.

![Figure 20](image-url)

Figure 20. Kappa number reached compared to H-factor, with varying impregnation stages and standardized cooking stages. Error bars are shown for the kappa number, but most are too small to be visible behind the data points (Paper I).

Reaching the same kappa number at a lower overall H-factor, and a lower alkali charge, could benefit a pulp mill by opening up several possibilities: decreased retention time in the digester, decreased cooking temperature, or decreased alkali charge.

Reducing the retention time in the digester might increase the product flow, though whether this can lead to a higher production rate depends on
where the bottleneck is situated. It is also possible to change the pulp parameters by reducing the temperature or alkali charge, which could result in a less degraded pulp at the same kappa number. Another possibility is to leave everything the same, but reach a lower kappa number than before. This would reduce the amount of bleaching chemicals needed, though if the recovery boiler is the bottleneck, and the load on it is already high, this might cause problems as more biomaterial will be dissolved in the BL.

Yield and Shives

Earlier studies demonstrate that increased impregnation time will reduce the shives content (Hart et al. 2011; Wedin 2012: Paper II), as can a longer impregnation stage with a relatively high liquor-to-wood ratio of 7:1 L kg⁻¹ (Karlström 2009; Wedin et al. 2010). However, the effect of the impregnation stage on the product varies depending on the product, as the product determines the methods and parameters used during production. If a high-kappa pulp is desired, there is a huge increase in screened yield at a kappa number of approximately 75 when using a low-temperature impregnation stage for a longer time (i.e., 120 min/105°C). This difference in kappa number decreases as the cook continues, but is still apparent at a kappa number of 45. At lower kappa numbers, below 40, the impregnation time does not appear to make much difference, as the samples impregnated at 105°C all give higher yields at a certain kappa number, compared with impregnation at 130°C for 30 min. However, at a kappa number closer to 30, the significant differences are much smaller, indicating that the effect of the impregnation stage is no longer significant for the system used (see Figure 21).
The shives content Figure 22 plots the shives content at given kappa numbers) displays trends similar to the yield trends. At high kappa numbers, in this case around 75, longer impregnation at a lower temperature results in a substantial decrease in shives content. For impregnation stages carried out at 105°C, the time allotted for impregnation is important, as the 60-min stage results in far higher shives contents at kappa numbers close to 50, though this difference decreases and is not significant at somewhat lower kappa numbers. The results indicate a critical point for impregnation between 60 and 90 min for the system used, at which the impregnation stage causes a substantial decrease in shives content.

Comparing the higher impregnation temperature (130°C) with the two longer impregnation stages (i.e., 90 min/105°C and 120 min/105°C), there is an obvious difference, with a higher shives content at the higher
temperature. However, as for the yield, the differences are not significant at the lower kappa numbers studied. The amount of alkali expended during the 30-min stage is similar to the amount expended during the 90-min stage, but the shives content is higher for the 30-min stage below a kappa number of 50, suggesting that approximately the same amount of neutralization occurs, but nearer surface during the shorter stage at a higher temperature, leaving more fibres untouched by the impregnation, thus increasing the shives content. However, the same amount of neutralization occurs, independent of impregnation and cooking conditions, during a set cooking time. The reason for the alkali expenditure should not be the same, and as the carbohydrate-degrading reactions occur faster at a higher temperature, more of the neutralization reactions at the higher temperature should occur due to carbohydrate-degrading reactions that negatively affect the carbohydrate yield.

Figure 22. Shives content at varying kappa numbers with varying impregnation stages and standardized cooking stages. Inserted plot zooms into kappa numbers 25 to 55. Error bars are included, but many are too small to be visible behind the data points (Paper I).
Spruce Xylan in Spruce Kraft Cook

Spruce, which is one of the wood species most commonly used for pulp production in Sweden, has many good properties. Compared with hardwoods, spruce has longer fibres (3–5 mm long), making spruce a good raw material for papers with high strength properties. Though pine also has long fibres, there is an important difference between pine and spruce, and that is the extractives content. Spruce has a lower extractives content than does pine, which is most important for mechanical pulping, as extractives can cause problems throughout the mechanical pulping process. For kraft cooking, the extractives content mostly affects tall oil production, which is only viable with enough pine in the process.

One negative aspect of using softwood in the kraft process is its low xylan content. This low availability makes it especially important to conserve this scarce xylan, and not waste any of its potential during processing.

To determine how best to utilize spruce xylan in the kraft process, spruce xylans with different chemical structures were added towards the end of a kraft cook of spruce. Jansson and Brännvall (2011) had earlier determined how the chemical structure of xylan varies with cooking conditions, and their findings were used in constructing the present experiments. The parameters that could be varied were the uronic acid content and the molecular weight of the spruce xylan, though these factors could not be varied independently, as both parameters are determined by a combination of several factors during the cook. The uronic acid content is high in the xylan released into solution at an early stage, but decreases with time. The molecular weight distribution is low at first, but increases with time, as larger spruce xylan molecules are dissolved. The molecular weight decreases after reaching a peak, likely due to xylan degradation. As large a diversity as possible was used, as shown in Table 5.
Table 5. Xylan specifications (i.e., uronic acid content and molecular weight) of xylan precipitated from black liquor under differing cooking conditions (Jansson and Brännvall 2011) (Paper II).

<table>
<thead>
<tr>
<th>Uronic acid [µmol g⁻¹ xylan]</th>
<th>Molecular weight [kDa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>6.3</td>
</tr>
<tr>
<td>66</td>
<td>10.6</td>
</tr>
<tr>
<td>188</td>
<td>9.2</td>
</tr>
<tr>
<td>517</td>
<td>8.6</td>
</tr>
</tbody>
</table>

To ensure that these xylans were present at the end of the cook, when xylan precipitates back onto the fibres, half the BL from a standardized cook was replaced with BL containing one of the previously mentioned spruce xylans (Figure 17). This procedure removed half the dissolved native xylan, but added xylan with specified properties.

This procedure of course resulted in differing xylan concentrations in the cooks, as different amounts of xylan can be found in the BL at different points in the process used to produce the xylan with specified chemical structures (Table 6).

Table 6. Concentration of xylan in black liquor after black liquor exchange (A) and at termination of cook (B). Calculations show maximum amount of precipitated xylan (C = A – B), assuming no degradation occurs. Before the liquor exchange, all cooks were identical. UA stands for Uronic Acid content [µmol g⁻¹ xylan]. Mw stands for molecular weight [kDa]. Total charge was determined by conductometric titration of pulp (Paper II).

<table>
<thead>
<tr>
<th>Black liquor xylan</th>
<th>A Xylan after BL exchange [g xylan kg⁻¹ wood]</th>
<th>B Xylan at end of cook [g xylan kg⁻¹ wood]</th>
<th>C Max. redeposited [g xylan kg⁻¹ wood]</th>
<th>Total charge [µekv g⁻¹ pulp]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UA12 / Mw6.3</td>
<td>9.6</td>
<td>6.8</td>
<td>2.4</td>
<td>91</td>
</tr>
<tr>
<td>UA66 / Mw10.6</td>
<td>10.7</td>
<td>7.3</td>
<td>3.4</td>
<td>92</td>
</tr>
<tr>
<td>UA188 / Mw9.2</td>
<td>12.1</td>
<td>8.5</td>
<td>3.6</td>
<td>92</td>
</tr>
<tr>
<td>UA517 / Mw8.6</td>
<td>7.2</td>
<td>6.5</td>
<td>0.7</td>
<td>113</td>
</tr>
<tr>
<td>RefWL</td>
<td>4.4</td>
<td>5.3</td>
<td>-0.91</td>
<td>80</td>
</tr>
<tr>
<td>RefWL NO EXCH.</td>
<td>8.9</td>
<td>6.3</td>
<td>2.6</td>
<td>78</td>
</tr>
<tr>
<td>RefWL, BIRCH XYLAN</td>
<td>21.4</td>
<td>12.7</td>
<td>8.7</td>
<td>90</td>
</tr>
</tbody>
</table>
The resulting pulps display differences that can only be related to differences between the added xylans. The yield as a function of kappa number is presented in Figure 23. From these results, it can be seen that the reference in which BL was replaced with WL, which significantly reduced the xylan concentration versus in the other cooks, has a yield approximately one percentage point lower than that of the other pulps. This is in accordance with Hansson and Hartler (1969), who found that the xylan concentration affects the amount of precipitated xylan, though this must be considered per specific xylan structure, as they also found large differences in behaviour between spruce and birch xylan. Figure 23 shows the slight tendency for higher-molecular-weight xylan to result in higher yield, which agrees with the findings of Westbye et al. (2006). Although the yields should in some way relate to the xylan precipitation, carbohydrate analysis indicated no significant differences between the pulps. There are numerous possible sources of agro-waste xylan, and one not used in this study is oat spelt (Puls et al. 2006).

![Figure 23. Screened yields of pulps with various xylans present at the end of the cook (Paper II).](image)

Regarding the total charge of the pulps, there were clear differences, a very high uronic acid content resulting in a significant increase in charge (Table 6). Where these charges can be found is another matter, and
considering the z-potential, which is related to the surface charge (see Figure 24, showing z-potential versus total charge), no correlation is found between z-potential and total charge. This indicates that xylans differ in behaviour depending on their chemical structure. It is plausible that a more highly charged xylan with a lower molecular weight could penetrate the fibre wall and precipitate inside the fibre wall. That the higher charge makes the xylan less likely to agglomerate with other xylan molecules is supported by the findings of Westbye et al. (2006), indicating that xylan with a higher degree of uronic acid groups has a lower tendency to agglomerate. The pores in unbleached softwood kraft pulp have a radius of 22 nm (Maloney and Paulapuro 1998), while free xylan molecules have a gyration radius of less than 10 nm, which indicates the possibility of whole xylan molecules penetrating the fibre wall during the kraft process.

![Figure 24. Z-potential versus total charge, differences due to differing xylan structures (Paper II).](image)

Further indications that xylans with certain chemical structures penetrate the fibre wall can be found in Figure 25, where the tensile strength index (TSI) is plotted versus the sheet density of sheets made from the pulps produced in this study. At low densities, the pulp with added birch xylan clearly has a higher TSI, though this advantage disappears as beating continues and higher densities are reached. What is
remarkable are the results for the pulp with added high-uronic-acid xylan, as the TSI of that pulp is initially rather low, but increases rapidly with beating to surpass the effect of any other xylan structure studied here. This behaviour suggests that the high-uronic-acid xylan precipitates inside the fibre wall, increasing the TSI as beating puts it in contact with other fibres.

The addition of the high-uronic-acid xylan also increases the TSI development versus drainage resistance (Figure 26), although all pulps display similar behaviour at low degrees of beating.
Figure 26. Tensile Strength development of spruce pulps with addition of differing xylan structures compared to drainage resistance (Paper II).

To ensure that these effects are indeed related to the xylan structures, and not to the number of fibres found in each sheet, the TSI at a certain density (700 kg m\(^{-3}\)) was plotted against the yield, indicating no correlation (Figure 27).

Figure 27. Tensile strength index extrapolated at 700 kg m\(^{-3}\) versus screened pulp yield (Paper II).
Agro-Waste Xylan in Spruce Kraft Cook

Mills using both hardwoods and softwoods in the same system, either singly or in parallel in two different lines, can exploit the strength-enhancing properties of birch xylan (Danielsson et al. 2005, 2009) in spruce pulp by simply adding birch BL to the spruce line. A single continuous kraft line switching to spruce from birch will see a strength loss as cooking continues, as the amount of birch xylan in the system decreases.

The fact that a non-native xylan can be used as a strength-enhancing agent raises interesting questions regarding alternative xylan sources. Immense amounts of plant material could be utilized much more efficiently than they are today, materials such as rice hulls and many kinds of straw, which are agricultural industry wastes. This prospect is even more interesting as there is now ongoing research into the extraction of hemicelluloses from various agro-waste sources for the purpose of producing “green” plastics (Albertsson and Edlund 2009; Ibn Yaich et al. 2012; Mikkonen et al. 2012; Ibn Yaich et al. 2014, 2015). If this research proves viable, future biorefineries might be another possible xylan source for the pulp and paper industry.

To investigate the effect of adding agro-waste xylan to a spruce kraft cook, xylan was extracted from rice husks and wheat straw, precipitated, and added at a late stage of the cook (Figure 17).

The chemical structure varies depending on the source of the xylan, and the amount of available xylan also varies greatly with species. Wheat straw was a good source of xylan, producing a far higher yield than either rice husk or birch wood (Table 7). Xylan from cereals, such as wheat and rice, contains arabinose groups, as does spruce xylan (Erbringerová et al. 2005).
Table 7. Amount of precipitated xylan after kraft cooking rice husks, wheat straw, and birch, with corresponding contents of lignin and lignin-free xylan (Paper III).

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Precipitate in black liquor [g precipitate kg–1 raw material]</th>
<th>Bound lignin [%]</th>
<th>Xylan in precipitate [g xylan kg–1 raw material]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husks</td>
<td>98</td>
<td>33</td>
<td>65</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>188</td>
<td>11</td>
<td>167</td>
</tr>
<tr>
<td>Birch wood</td>
<td>59</td>
<td>15</td>
<td>50</td>
</tr>
</tbody>
</table>

According to Figure 28, the pulps obtained displayed a rather small spread in kappa number (28.5 ± 0.7) but a larger difference in yield. The lowest yield corresponds to the reference pulp from which xylan was removed, but not replaced, which indicates that removing xylan negatively affects yield. The yields with the addition of either wheat straw xylan or rice husk xylan were also rather low compared with those of the cooks without liquor exchange or the addition of birch xylan (Figure 28). As any increase in yield compared with that of the cook from which xylan was only removed should be related to precipitation of the added xylans, this indicates that only small amounts of those xylans precipitated on the fibre surfaces. A carbohydrate analysis found only very small differences in pulp composition and no significant differences in xylan content (calculated as Ara and Xyl) content. That the structures of the added xylans differ can also be seen when analysing the total charge, as adding a small amount of wheat straw or rice husk xylan increases the total charge at least as much as does adding a greater amount of birch xylan (Table 8).
Figure 28. Screened yield of pulps with xylan from differing sources added (Paper III).
Table 8. Carbohydrate and Klason lignin analysis of produced pulps, as percentage of bone dry pulp, as well as total charge. Xylan content is calculated as xylose and arabinose together (Paper III).

<table>
<thead>
<tr>
<th></th>
<th>Rice Husks</th>
<th>Wheat Straw</th>
<th>Birch Wood</th>
<th>Ref-WL</th>
<th>Ref-No-Exch.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ara [% of pulp]</td>
<td>0.6 ± 0.01</td>
<td>0.6 ± 0.01</td>
<td>0.5 ± 0.02</td>
<td>0.5 ± 0.03</td>
<td>0.5 ± 0.02</td>
</tr>
<tr>
<td>Gal [% of pulp]</td>
<td>0.4 ± 0.01</td>
<td>0.4 ± 0.00</td>
<td>0.4 ± 0.00</td>
<td>0.4 ± 0.00</td>
<td>0.4 ± 0.01</td>
</tr>
<tr>
<td>Glc [% of pulp]</td>
<td>78.1 ± 1.36</td>
<td>76.1 ± 1.57</td>
<td>77.6 ± 1.43</td>
<td>78.8 ± 2.43</td>
<td>78.5 ± 0.63</td>
</tr>
<tr>
<td>Man [% of pulp]</td>
<td>7.0 ± 0.08</td>
<td>6.9 ± 0.16</td>
<td>7.0 ± 0.07</td>
<td>6.8 ± 0.02</td>
<td>7.0 ± 0.04</td>
</tr>
<tr>
<td>Xyl [% of pulp]</td>
<td>8.0 ± 0.06</td>
<td>7.9 ± 0.19</td>
<td>8.4 ± 0.95</td>
<td>7.9 ± 0.80</td>
<td>7.9 ± 0.07</td>
</tr>
<tr>
<td>Lignin [% of pulp]</td>
<td>5.7</td>
<td>6.2</td>
<td>6.2</td>
<td>5.6</td>
<td>5.7</td>
</tr>
<tr>
<td>Total charge [µekv g⁻¹ pulp]</td>
<td>91</td>
<td>93</td>
<td>90</td>
<td>80</td>
<td>78</td>
</tr>
</tbody>
</table>

The differing xylan species also displayed different stabilities during the cook (see Table 9 for the mass balance of xylan). This analysis indicated that spruce xylan appeared to be the most stable, whereas birch xylan became the most degraded during the cook. Compared with the present findings, Magaton et al. (2013) found that eucalyptus xylan can be even more stable and be retained to a higher degree. It would appear that the xylan structure is very important for stability under kraft conditions, affecting where it would be best to add extra xylan during the kraft process; perhaps adding xylan during the oxygen stage would be beneficial (Ribe et al. 2010).

A certain amount of xylan was added in each case, though as xylan exists as lignin carbohydrate complexes (LCC) and the amount of lignin attached to the xyloans varies the amount of lignin free xylan added differed slightly. However no correlation between amount of added xylan
and amount of reprecipitation could be found. This is unsurprising, as the amount of xylan in wood does not correlate with the amount of reprecipitation (Magaton et al. 2013), and as the chemical structure is important for reprecipitation (Hansson and Hartler 1969; Kabel et al. 2007; Eronen et al. 2011).

Table 9. Mass balance of xylan during cooking, calculated as grams of xylan per kg of wood.
A: xylan in wood.
B: removed xylan.
C: added xylan.
D: xylan in finished pulp.
E: xylan in BL.
F: Degraded xylan, calculated as follows: F = A – B + C – D – E.
G: Degraded xylan as % of added xylan is compared to the behaviour of Ref-WL. Added amount for Ref-No-Exch. is 4.5 g xylan kg⁻¹ wood, calculated as follows: 100 – (F – F(Ref-WL)/C*100 (Paper III).

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husks</td>
<td>80.1</td>
<td>4.5</td>
<td>8.9</td>
<td>41.2</td>
<td>10.9</td>
<td>32.4</td>
<td>77.5</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>80.1</td>
<td>4.5</td>
<td>13.4</td>
<td>40.5</td>
<td>13.4</td>
<td>35.1</td>
<td>64.9</td>
</tr>
<tr>
<td>Birch wood</td>
<td>80.1</td>
<td>4.5</td>
<td>12.5</td>
<td>43.2</td>
<td>12.7</td>
<td>32.2</td>
<td>85.8</td>
</tr>
<tr>
<td>Ref-WL</td>
<td>80.1</td>
<td>4.5</td>
<td>0.0</td>
<td>39.9</td>
<td>5.3</td>
<td>30.4</td>
<td>-</td>
</tr>
<tr>
<td>Ref-No-Exch.</td>
<td>80.1</td>
<td>0.0</td>
<td>0.0</td>
<td>41.0</td>
<td>6.3</td>
<td>32.8</td>
<td>46.7</td>
</tr>
</tbody>
</table>

The effect on the tensile strength index of adding the various xylans is shown in Figure 29. It can be seen that the removal of xylan, when BL is replaced with WL, reduces the TSI. In adding xylan, the greatest benefit is obtained by adding birch xylan to the cook. Adding wheat straw xylan or rice husk xylan is beneficial, as a small amount of precipitated agro-waste xylan can increase the strength as much as can a larger amount of spruce xylan.
Figure 29. Tensile strength index versus sheet density for spruce kraft pulp with the addition of different xylans (Paper III).
Conclusions
Although the kraft process has been around since the end of the 19th century, there is still much we do not know about it and even more that could be improved. Based on this work, a few recommendations for how to improve the kraft process are presented.

Impregnation: Impact on Kraft Cooking
The impregnation procedure is an important factor in determining how a system behaves, and how effective it is.

Compared with the most common impregnation stage in modern mills, impregnation should be performed at a lower temperature for a longer time. This will make the wood chip impregnation more complete before any significant cooking reactions start, ensuring a more homogenous cook. This will also result in a narrower kappa number distribution if measured on single fibres, which would improve the pulp quality.

A longer impregnation time at a lower temperature has the following effects:

- increased screened yield
- decreased shives content
- a certain kappa number reached at a lower H-factor
- a certain kappa number reached with lower alkali consumption

As such an impregnation stage reduces the shives content as well as pushing the defibration point towards higher kappa numbers, it will then be possible to terminate the cook at an even lower H-factor, compared with the old reference system. To counter a higher kappa number coming out of the digester, an increased oxygen delignification stage is suggested, as such a system change can give a pulp with a higher carbohydrate yield (Jamieson and Fossum 1976; Leader et al. 1986; Parsad et al. 1994). With a great enough increase in the oxygen delignification, the kappa number going into the bleaching sequence can be maintained at previous levels, without increasing the need for chemicals in the bleaching plant. The increased yield also allows the mill to increase production, if the current bottleneck is the recovery boiler, as the increased pulp yield reduces the load on the recovery boiler.
The overall consumption of alkali indicates that a certain amount of alkali is expended per kg of wood during a set cooking time, no matter whether it is expended during impregnation or during the cook, and consumption in the impregnation stage is more beneficial for the carbohydrate yield.

Each option has its own benefits, and it would be up to each mill to utilize these benefits as seen fit. It is also important to note that any effects would vary depending on the system. As this new system variation combines several techniques that increase yield, it could provide a very interesting basis for a new pulp mill system.

**Xylan: Spruce and Agro Waste Xylans in the Kraft Process**

As spruce contains only a small amount of xylan, it is important to use that resource to the fullest extent.

It is clear that the chemical structure of the xylan present in pulp is far more important than how much xylan has precipitated on the fibre surfaces. Furthermore, the xylan structure that gives the highest strength increase is not the same structure that gives the highest yield, so the pulp producer must decide which factor is more important. One thing to consider is the possibility of making a paper product with less pulp, while maintaining the same properties as if a stronger pulp were used.

Spruce xylan with a very high uronic acid content has positive effects on pulp strength at high degrees of beating, compared to both density and drainage resistance. Such a spruce xylan can be found at an early stage of the kraft cook of spruce. To utilize this, it could be possible to draw BL from an early stage, possibly during impregnation, depending on the conditions there, and to add that liquor to a late stage of the cook. This would be done to ensure that the intended xylan structure is available when the xylan reprecipitates.

That the xylans display different chemical stabilities under identical kraft conditions can only be due to the differing chemical structures of the studied xylans. Spruce xylan appears to be the most stable during cooking, whereas birch xylan is the least stable of the studied xylans.
Removing xylan negatively affects yield, which is unsurprising as material that could contribute to the yield is removed.

Adding agro-waste-derived xylans to a kraft cook of spruce increases the tensile strength of the pulp. Even though only small amounts of rice husk and wheat straw xylans precipitated onto the fibres, the strength-enhancing effect was the same as that of a greater amount of spruce xylan. However, as the stability of those xylans under kraft conditions is questionable, it might be better to add those xylans during oxygen delignification, as Ribe et al. (2010) suggests.

As the agricultural industry produces immense amounts of agro waste that contain xylan, there exists a possible cheap source of xylan that could be used to increase pulp strength. However, this possibility could hinge on combined production with plastics based on the same hemicelluloses in a future biorefinery.

As xylan’s chemical structure is crucial for its behaviour, and for its effect of on pulp, it is important to specify what kind of xylan is used and what plant species the xylan comes from.

**Suggestion: Modifications to the Kraft Process**

The objective of this thesis was to present suggestions for how to modify the current kraft process, with a view to improving it.

It is suggested that impregnation take place at 105°C, at increased pressure, for 90 min. The retention time in the impregnation vessel would increase, which means that the volume of the vessel would have to be larger than before (Figure 30C). That could be a costly investment, but one that would likely pay for itself quickly. This new impregnation stage will improve chip impregnation, providing a more even cook.

The benefits of this would include:

- reaching the same kappa number at a lower H-factor, possibly reducing retention time in the digester, which would increase production
• reaching the same kappa number with lower alkali consumption
• the longer impregnation stage would increase the pulp yield
• decreased shives content, which pushes the defibration point towards higher kappa numbers, making it possible to terminate the cook at an even higher kappa number

This, in combination with increased oxygen delignification (Figure 30E), would increase the yield even more, while keeping the kappa number going into the bleaching plant the same, so as not to increase the need for bleaching chemicals per tonne of pulp.

To better exploit the strength-enhancing qualities of spruce xylan, it is suggested that BL containing spruce xylan extracted during impregnation be added at the end of the cook (Figure 30C–D). This would improve the strength of the pulp, perhaps making it possible to use less pulp per product, improving the yield of the end product.

Producing xylan from agro waste could be a profitable concept, especially if combined with other uses for the xylan, such as the production of “green” plastics. It is suggested that xylan extracted from agro waste be added towards the end of the cook or during the oxygen delignification stage (Figure 30H–E). This would increase the pulp strength, as did adding spruce xylan, and potentially increase the yield of the end product.
Figure 30. A simplified overview of the kraft process, showing suggested changes in blue. A: The raw material, trees, are felled, de-branched, and transported to the mill. B: The logs are debarked and chipped. C: The chips are steamed to remove air from within them, and impregnated with cooking liquor. Suggestion: Longer impregnation at decreased temperature. D: The impregnated chips are cooked at high temperature under harsh conditions. Suggestion: Spruce xylan from the impregnation or an early part of the cook is added towards the end of the cook to influence the characteristics of spruce xylan present at the end of the cook. E: Delignification continues with the help of oxygen. F: The pulp is bleached to the desired brightness. G: The pulp is converted into paper using a paper machine. H: Extraction of agro-waste xylan, used as strength enhancer or possibly for “green” plastics.
**Abbreviations and Technical Terms**

**Air-dry metric tonnes per year**

ADMT $y^{-1}$ The amount of pulp or paper produced per year at 90% dryness; 1 ADMT is equivalent to 0.9 metric tonnes of b.d. pulp.

**Black Liquor**

BL Cooking liquor after extraction of biological material, mainly lignin; black in colour and opaque.

**Bone Dry**

b.d. Without moisture.

**Cellulose**

Polysaccharide consisting of unbranched $1\rightarrow4$ $\beta$-bound $\beta$-glucopyranoside residues.

**Cooking Liquor**

Liquid containing active cooking chemicals.

**Dry Content**

Percentage of dry matter.

\[
\frac{m_{\text{DRY}}}{m_{\text{WET}}} \times 100\%
\]

**Effective alkali (%)**

EA The load of OH⁻, as kg NaOH ton⁻¹ pulp.

**Fibre**

Wood cell.

**Hemicellulose**

Polysaccharide, often branched; includes xylan and glucomannan, depending on species.

**Hexeurope acid**

HexA 4-deoxy-$\beta$-L-threo-hex-4-enopyranosyluronic acid.
**H-factor**

A function used to estimate delignification; based on relative reaction rate, which is a function of temperature.

**Hornification**

Irreversible reduction of the internal volume of the wood cell wall due to structural changes during drying (Minor 1994).

**ISO**

International Organization for Standardization.

**Kappa Number**

Approximation of the amount of lignin remaining in the pulp; measures remaining oxidizable structures using ISO 302:2004.

**L:W**

Liquor to wood, the ratio of added liquid (WL) [kg] to wood [kg].

**LCC**

Lignin carbohydrate complex.

**Lignin**

Polymer consisting of monolignols (aromatic alcohols); the “glue” that holds the cells together.

**Moisture Content**

Percentage of water in a sample.

**Molecular Weight**

$M_w$

**Oven Dry**

o.d. Without moisture.

**Schopper-Riegler**

$^\circ$SR Determines drainability of pulp suspension.
**Sulphidity (%)**

Hydrogen sulphide ion concentration in WL or BL.

\[
Sulphidity \, (\%) = \frac{2 \times [HS^-]}{[OH^-] + [HS^-]} \times 100
\]

**Tensile Strength Index**

TSI The maximum tensile force developed in a specimen at break during a tensile strength test according to ISO 194-3:2005; indexed by grammage

**White Liquor**

WL Cooking liquor containing fresh chemicals (OH\(^-\) and HS\(^-\)) before addition to cooking system; clear solution, slightly yellow because of addition of Na\(_2\)S

**Uronic Acid**

UA
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