Master Thesis

Xylan as Strength Enhancing Additive

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Abstract

The effect of xylan from different plant species on tensile properties of spruce pulp was studied. Xylans from spruce, birch, wheat straw and rice husks were mixed with the fresh white liquor and added at the later stages of separate kraft cooks, in exchange of the black liquor removed from the system at that time.

Results show that xylans, from rice husk, wheat straw and birch, gave stronger pulps. However it was only possible to attach small quantities of xylans onto the fibers. Moreover, pulps containing birch and rice xylan were easier to beat than the other pulps in the study.

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Abbreviations

4-O-Me-GlcA	4-*O*-Methyl-D-glucuronic acid
AGX	(L-Arabino)-4-*O*-methyl-D-glucurono-D-xylan
Ara*f*	L-Arabinofuranose
BL	Black liquor
g/l	Grams per liter
GAX	(4-*O*-Methyl-D-glucurono)-L-arabino-D-xylan
MeGlcA	4-*O*-Methyl-D-glucuronic acid
mol/l	Moles per liter
Na_2S	Sodium Sulphide
NaCl	Sodium chloride
NAF	Nordiska Armaturfabriken
NaOH	Sodium hydroxide
°SR	Schopper Riegler
V/V	Volume/Volume
WL	White liquor
X_3	β-(1→3)-D-Xylan
X_m	β-(1→3, 1→4)-D-Xylan
Xylp	D-Xylopyranose

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1 Introduction

1.1 Wood Constituents

Plants, from any source, consist mainly of cellulose, hemicellulose, lignin and small amounts of extractives such as terpenoids, fatty acids, pectin, resin acids and inorganic constituent materials. Their relative composition in the plants is largely dependent upon plant species and to some extent its growth location.

1.1.1 Cellulose

Cellulose is the most common organic polymer. It has almost 1.5×10^{12} tons of total annual biomass production (Klemm et al., 2002). In 1920, Hermann Staudinger explained the cellulose structure for the first time as polymeric structure. He discovered that cellulosic structure consists of D-glucose units which are covalently bonded to each other (Staudinger, 1920).

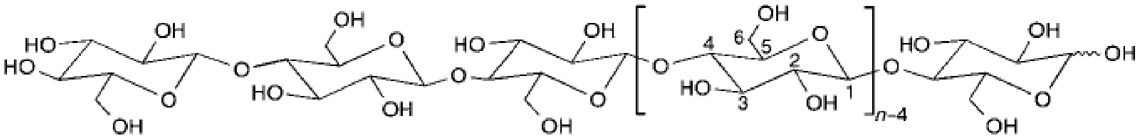

Figure 1: Molecular structure of Cellulose (Klemm, 2005)

Figure 1 shows the molecular structure of cellulose which is composed of linear chains of D-glucose connected with β-1, 4-glucosidic bonds. Each glucose unit has hydroxyl groups attached at 2, 3 and 6 position on the ring. Its degree of polymerization in plant fibers varies from 800 to 10000 whereas as in wood pulp it is usually in the range of 300 to 1700 repeating units (Klemm et al., 2005).

1.1.2 Hemicellulose

Hemicelluloses are amorphous in nature having a degree of polymerization much lower than that of cellulose, in the range of 50-300. There are mainly two types of hemicelluloses in wood i.e. glucomannan and xylan. Table 1 summarizes the percentages of wood components in pine (softwood) and birch (hardwood). It can be seen from the table that the main hemicellulose of softwood is glucomannan whereas in the case of hardwood it is xylan.

Table 1: Percentage of wood components in pine and birch (Brännvall, 2004)

	Pine	Birch
Cellulose	41	40
Glucomannan	17	3
Xylan	8	30
Other carbohydrates	5	4
Lignin	27	20
Extractives	2	3
Total	100	100

During kraft pulping, xylan is much more resistant to dissolution than glucomannan. Glucomannan dissolves/degrades very early in the cook – in fact its large amount degrades during the heating up period (Wigell et al., 2007; Wågberg and Annergren, 1997).

1.1.3 Lignin

Lignin acts as glue for the fibers in the wood. It can be explained as three-dimensional cross-linked structure which is mainly composed of phenolic hydroxyphenyl propane units.

1.1.4 Extractives

These are the low molecular weight organic compounds present in wood in small quantities. These include fatty acids, pectin, resin acids, terpenes and waxes.

1.2 Wood Cell Wall Structure

Figure 2 shows the structure of the wood cell wall with different cell wall layers (Côté, 1967). P, S1, S2 and T represents primary, secondary 1, secondary 2 and tertiary cell wall layers respectively. Middle lamella, ML, is the outer most layer of the cell wall and mostly consists of lignin and dead cells. Secondary wall is subdivided into two further categories. S2 is the most important layer in the cell wall. It is thicker than the S1 and accounts for the physical properties of the cell wall. It also has the main quantity of cellulose in it. The fibril directions in these layers are important as they affect the mechanical properties of the fibers.

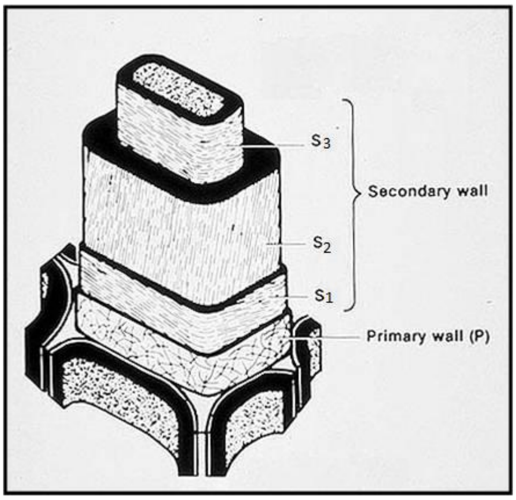

Figure 2: Wood cell wall structure (Côté, 1967)

1.3 Chemical Pulping

As described earlier; lignin holds the fibers together in the wood matrix, so the main purpose of the pulping is to separate the fibers from each other or the delignification of the wood. It involves the degradation and dissolution of the lignin molecules. There are different types of chemical pulping depending upon the cooking chemicals used in these different processes. Some of these processes are discussed here.

1.3.1 Soda Cooking

This is an old pulping process. Sodium hydroxide is used as cooking chemical.

1.3.2 Sulphite Cooking

Active chemicals used for the degradation and dissolution of lignin molecules are sulphurous acid and bisulphate ions. It can be performed in acidic (pH in the range of 1-2) or neutral (pH 7-9) conditions.

1.3.3 Kraft Cooking

Kraft, or sulphate, cooking is the most widely used chemical pulping process at this time. Wood chips are subjected to a high temperature (150-170^{0}C) treatment, in the presence of cooking chemicals - sodium hydroxide (NaOH) and sodium sulphide (Na_2S). Hydroxide (OH^-) and hydrogen sulphide (HS^-) act as the active cooking species in the delignification process. The task of hydrogen sulphide is to delignify the pulp whereas hydroxide keeps the lignin fragments in the solution.

The shortcoming of using chemicals to delignify the pulp is that they also can dissolve carbohydrates, or partially degrade them into low molecular weight species. No chemical is entirely selective towards lignin, so there is always a compromise. In kraft cooking almost half of the wood are also dissolved during delignification process.

There are three different phases in the delignification of pulp (Wilder and Daleski, 1965; Kleinert, 1966; Lemon and Teder, 1973) – the initial, bulk and residual phase. These three phases are overlapping during kraft cooking. The delignification rate during the initial phase is high and almost 20% of the lignin is removed. It is mostly dissolution of low molecular weight lignin molecules and there are not so much of degradation reactions during this phase. The rate during the bulk phase is somewhat slow and it continues until almost 90% lignin is removed from the pulp. The rate during the residual phase is very slow.

1.4 Different Xylan Structures

As described earlier in Table 1 that xylan constitutes up to almost 30% in hardwood whereas it is present as 8% of the total mass of softwood trees. But the structure of the xylan is different in different type of trees and other plant materials. All the structures are based on the *β*-(1→4)-D-xylopyranose backbone chain. Side chains on these molecules separate different types of structures from others. Following are some of the structures of xylan commonly found in the trees (Ebringerová et al., 2005).

1.4.1 Homoxylans

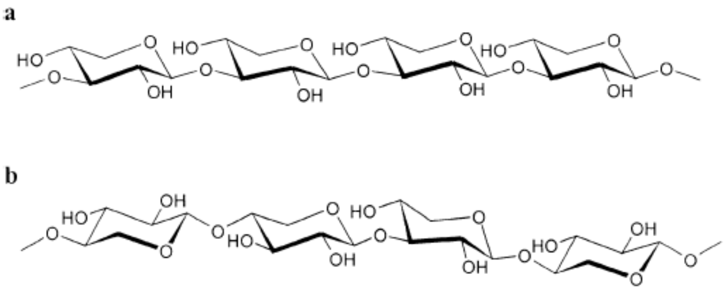

Figure 3: Primary structure of X_3, β-(1→3) (fig. a), and Type X_m, mixed β-(1→3, 1→4)-glycosidic linkages (fig. b) (Ebringerová et al., 2005)

As it is obvious from its name that these type of molecules are pure homopolymers. Their Xylp-backbone either have β-(1→3) (Type X_3, Figure 3a) or mixed β-(1→3, 1→4)-glycosidic linkages (Type X_m, Figure 3b). These structures are commonly found in seaweeds of Palmariales and Nemaliales (Ebringerová et al., 2005).

1.4.2 Glucuronoxylans

These structures are commonly found in hardwoods. They have single 4-*O*-methyl-α-D-glucopyranosyl uronic acid residues (MeGlcA) always attached at position 2 of the main Xyl*p*-backbone chain (Figure 4). These structures are usually referred to as 4-*O*-methyl-D-glucurono-D-xylan. The ratio of Xyl : MeGlcA in hardwoods is usually from 4:1 to 16:1, while mostly being around 10:1 (Ebringerová et al., 2005).

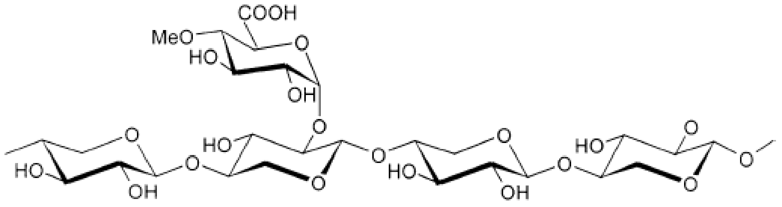

Figure 4: Primary structure of 4-O-methyl-D-glucurono-D-xylan (Ebringerová et al., 2005)

1.4.3 (Arabino)glucuronoxylan and (Glucurono)arabinoxylan

Both of these structures have solitary MeGlcA and α-L-Araf group attached to position 2 and 3, respectively, of β-(1→4)-D-xylopyranose backbone chain (Figure 5). However, the difference in their structures lies in the fact that the backbone chain of (arabino)glucuronoxylan (AGX) structure is heavily substituted with MeGlcA whereas (glucurono)arabinoxylan (GAX) is more substituted with *a*-L-Ara*f* groups. AGX is commonly found in coniferous species, grasses and cereals whereas GAX can be found in softwood trees, wheat, corn and rice bran (Ebringerová et al., 2005).

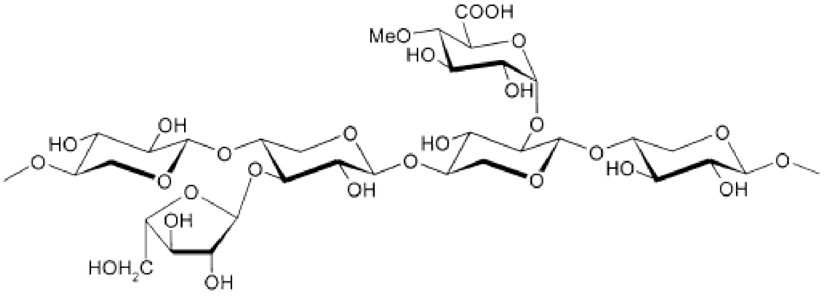

Figure 5: Primary structure of (L-arabino)-4-O-methyl-D-glucurono-D-xylan (AGX) (Ebringerová et al., 2005)

1.4.4 Arabinoxylans

The Xylp-backbone chain of the arabinoxylans is substituted by *a*-L-Ara*f* groups either on O-2 or on O-3 position or on both positions (Figure 6). These structures are commonly found in cereals of wheat, rice, rye and oat (Ebringerová et al., 2005).

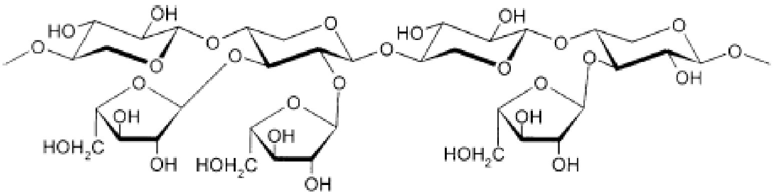

Figure 6: Primary structure of water-soluble L-arabino-D-xylan (Ebringerová et al., 2005)

1.4.5 Complex Heteroxylans

Complex heteroxylans have the backbone chain which is heavily substituted with *β*-D-Xyl*p*, *β*-L-Ara*f* , *a*-D-Glc*p*A groups on position 2 and 3. They are usually a part of seeds, gum exudates and cereals (Ebringerová et al., 2005).

1.5 Xylan Dissolution during Kraft Pulping

As discussed earlier, beside lignin, carbohydrates residues are also dissolved in the cooking liquor. But xylan dissolves as whole molecule during the pulping (Axelsson et al., 1962). This stability of xylan comes from its end group configuration (Johansson and Samuelson, 1977). In 1961 Croon found in a study on hardwood xylans that xylan molecules having high uronic acid contents on its backbone have high solubility in water or weak alkaline solution. The rate of dissolution of birch xylan is high at the start of the cook and decreases as the cook proceeds (Danielsson and Lindström, 2005). In a different study, for softwood hemicelluloses, it was shown that the xylan removal follows a linear trend with lignin removal whereas a large part of the glucomannan is already degraded/dissolved even when very few lignin molecules are removed (Wigell et al., 2007). In the same study it was shown that the xylan solubility increases at higher cooking temperature and at high alkali concentration.

On the other hand Danielsson found that the molecular weight of dissolved birch xylan can reduce due to peeling reactions and alkaline hydrolysis (Danielsson and Lindström, 2005). Especially as substituent group - methylglucuronic acid - on the xylan backbone can transform into hexenuronic acid and eventually separate from the xylan chain (Lisboa et al., 2005, Danielsson et al., 2006).

Arabinose units on the backbone chain of softwood xylan also have an effect on xylan dissolution. Andrewartha (1979) showed in a study that more arabinose units results in a higher solubility of xylan.

1.6 Xylan Adsorption on the Fibers

It has long been suggested that part of the xylan which is dissolved in the cooking liquor is reattached to the cellulosic fibers during the pulping (Yllner and Enström, 1956; 1957; Clayton and Stone, 1963).

1.6.1 Effect of Xylan Structure

Xylan adsorption is dependent on many factors. Uronic acid content in the backbone chain of the xylan molecule seems to be an important factor. It has been a topic of discussion in many studies. These studies conclude that low uronic acid contents of xylan chain favor the adsorption (Hartler, 1962; Hansson and Hartler, 1969; Silva et al., 2011; Danielsson et al., 2007).

Beside uronic acid contents, **arabinose contents** present on the backbone chain of softwood xylan also had an effect on the adsorbed quantity. Xylan samples having lower quantities of arabinose units on its chain had a pronounced adsorption on the cellulose as compared to samples having higher arabinose contents (Kabel et al., 2007).

It was observed that birch xylan with a low **degree of polymerization** have high adsorption on cotton substrate (Hartler and Lund, 1962) and on cellulose substrate (Hansson and Hartler, 1969). While, on the other hand, in case of oat spelt xylan it was shown that the lower xylan molar mass results in lower adsorption (Kabel et al., 2007). It was also shown in the same study that xylan with minimum 15 xylose groups in the backbone chain are needed for the adsorption.

It was also found that amount of **bound lignin** in xylan increases adsorption of xylan (Danielsson et al., 2007). It may be due to the higher degree of aggregation of xylan with more bound lignin. It will be discussed in more detail in the following sections.

According to Danielsson, the radius of gyration for individual chains of birch and eucalyptus xylan is around 10 nm. While for aggregates, it is 40-130 nm for eucalypt and over 300 nm for birch xylan (Danielsson, 2007). Whereas the average pore radius for unbleached kraft pulp is 22 nm (Maloney and Paulapuro, 1998). So from this we can propose that the individual chains of the xylan – having high uronic acid contents - can penetrate inside the fiber wall and when the pores of the fiber wall are closed during the washing of pulp, these chains will be trapped inside and, after beating of the pulp, will increase the contact area between the fibers.

Dahlman et. al. (2003) showed that there is more xylan attached to the surface layer of the pulp than in the inner layer. They also found that the xylan in the surface layer has higher molecular weight and lower uronic acid contents (Dahlman et al., 2003). These results are in agreement with our supposition. Surface xylan has high molecular weight because aggregates of the xylan are attached to the surface.

1.6.2 Effect of Cooking Conditions

High cooking **temperature** also found to be favoring the xylan adsorption (Hartler, 1962; Silva et al., 2011, Yllner and Enström, 1957; Clayton and Phelps, 1965; Henriksson and Gatenholm, 2001). Likewise, Eriksson et al found that adsorption of hemicelluloses on cotton increases with a higher temperature (Eriksson et al., 1963).

There is very little effect of pH on the adsorption of hemicelluloses onto the cellulose fibers during the pH range of 2 to 11 (Eriksson et al., 1963; Henriksson and Gatenholm, 2001). Hansson and Hartler, in 1969, showed that when the pH is higher than the 11, higher pH results in low sorption of birch xylan. Sorption of xylan also increased with low hydroxyl ion concentration (Danielsson and Lindström, 2005; Yllner and Enström, 1957).

It was also shown that in case of birch xylan sorption increases enormously with increase in the xylan concentration where the sorption in case of pine xylan was only slightly influenced (Hansson and Hartler, 1969; Yllner and Enström, 1956).

Higher ionic strength also resulted in increased xylan sorption (Ström et al., 1982, Mitikka-Eklund, 1996).

1.7 Xylan as Strength Enhancer

Some studies have shown that reattached xylan may contribute to the strength of the fiber network (Rydholm, 1965; Sjöberg et al., 2004; Danielsson et al., 2005; Danielsson and Lindström, 2009). Molecular properties of the adsorbed xylan are found to be more important than the adsorbed quantity. It was observed by Molin and Teder (2002) that there was no change in fiber strength when it was cooked under cooking condition to get different amounts of hemicelluloses on the fibers.

Sjöberg et al (2004) noted that only the hemicelluloses present on the surface of fibers contributed to increase in the pulp tensile strength and there was not a pronounced correlation between the sheet strength and xylan present in the inner part of the fibers.

Higher molecular weight birch xylan proved to be more effective in improving the strength of softwood pulp as compared to low molecular weight xylan (Danielsson et al., 2005). But then it was shown in case of kraft cooking of eucalyptus that higher molecular weight of xylan is not the only factor which increases the pulp strength. Degree of substitution (amount of uronic acid attached) of xylan and lignin bound to that xylan also matters (Danielsson and Lindström, 2009). In that study it was shown that attached xylan having low uronic acid contents increases strength the most.

1.8 Xylan Aggregation in Solution

In solution xylan is present as an independent molecule as well as an aggregated structure. However, a study shows that a majority of xylan is present in an aggregated form rather than as individual molecules (Linder et al., 2003). This xylan can be adsorbed on the surface of the cellulose. Again, according to this study, most of the adsorbed xylan is in the form of aggregates (Figure 7).

There are three types of interactions between xylan chains (Linder et al., 2003). Hydrophobic interactions are found between lignin molecules which are covalently bonded to xylan. Then there are interactions between the un-substituted linear segments of the xylan chains. These both types of interaction favors the adsorption but the third type of interaction causes the repulsion between the chains and favors dissolution. This interaction is caused by the presence of negatively charged 4-O-Me-GlcA as the side groups on the xylan chains (Hannuksela et al., 2002; Westbye et al., 2006).

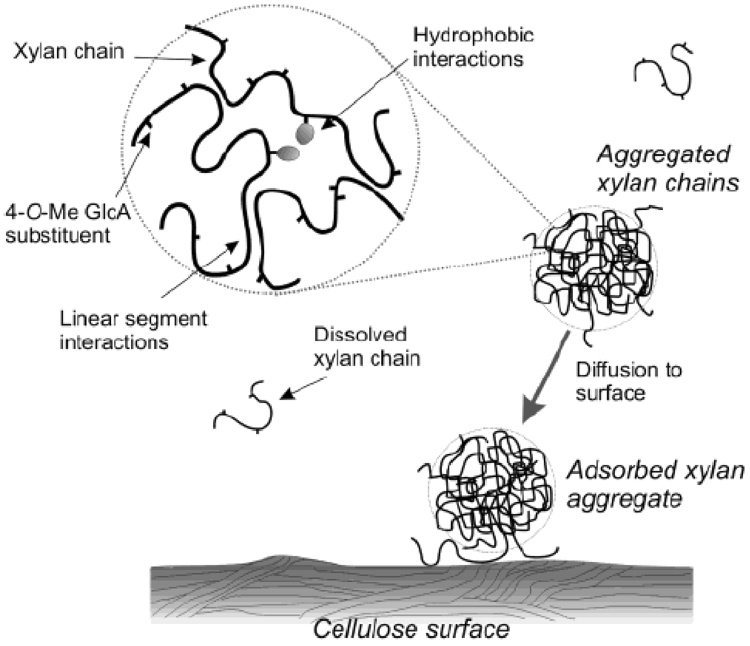

Figure 7: Schematic illustration of xylan aggregation in solution and adsorption on cellulose surface (Linder et al., 2003)

High temperature autoclave treatment decreases the amount of these side groups, as a result aggregation of the xylan chains can be increased. Then these large aggregates also have lower solubility in the solution and therefore they will tend to adsorb more on the cellulose surface (Linder et al., 2003; Westbye et al., 2006; Kabel et al., 2007; Silva et al., 2011).

If there is more lignin attached with the xylan chains, they will tend to aggregate more (Danielsson, 2007; Westbye et al., 2006).

1.9 Xylan in Rice Husks and Wheat Straw

Previous studies show that rice husks has 34-36 % cellulose, 16-18% xylan, 21-24% lignin and 11-18% ash contents (Li, 2011; Vegas et al., 2004; Parajo et al., 2004) whereas wheat straw has around 35-43% cellulose, 30-38% hemicelluloses (most of which is xylan) and 14-22% lignin contents (Sun, 2004; Alemdar, 2008). There has not been a lot of work done to study the structure of xylan in rice husks and wheat straw.

According to Watanabe rice hull has very low arabinose contents having xylose and arabinose in the ratio of almost 19:1 (Watanabe et al., 1983). However, more recent studies show that xylose:arabinose ratio in rice hull is around 12:1 (Vegas, 2004) and 9:1 (Parajo, 2004).

1.10 Purpose of the Study

The aim of this study was to investigate the effects of different xylan structures - obtained from rice husk, wheat straw, birch and spruce - on the strength properties of spruce pulp.

2 Materials and Methods

2.1 Materials

Spruce chips used in this study were obtained from Södra mill Värö. Dryness of chips was 92.6%. The chips were sorted manually to have a fraction of 2-8 mm thickness. During the sorting knots and bark were removed.

The stock solution of NaOH, used for kraft cooking, was prepared from pastilles of puriss grade and stock solution of Na_2S was prepared from technical grade flakes of sodium sulphide. NaCl used in the cooking was of puriss grade and obtained from VWR international AB. Acetic acid, used in precipitation of xylan, was of 99.83% purity and was obtained from Fisher Scientific. Acetone, used for washing of xylan, was of 99.9% whereas ethanol was of 96.3% V/V. Both acetone and ethanol were obtained from VWR Internationals AB.

Rice husks (94% dryness) were taken from Tanzania whereas wheat straw (94% dryness) was taken from Sweden. Birch xylan was precipitated from industrial BL obtained from Smurfit Kappa Piteå.

2.2 Cooking

Kraft cooking was done in a forced circulation digester whereas autoclaves were used for extraction of xylan from straw and rice husks.

2.2.1 Xylan Extraction

Three autoclaves were used for this purpose, in each case having 100 g o.d. mass of rice husks and straw. The autoclaves were put under vacuum for 30 minutes. Then cooking liquor was added in the autoclaves using a funnel so as to have 4:1 l/kg liquor-to-wood ratio. Cooking liquor was prepared from stock solutions of NaOH and Na_2S. $[OH^-]$ in cooking liquor was 1.2 [mol/l], sulfidity was 0.26 [mol/l]. No additional Na^+ was added in the cooking liquor.

Autoclaves were put, slightly inclined, into a preheated glycol bath and rotated during cooking. It took 10 minutes for autoclaves to reach cooking temperature of 157^0C. After cooking for 30 minutes, the autoclaves were taken out and put into a water bath for 20 minutes to cool down. BL was squeezed out from the rice husks and straw. Then xylan was extracted from this BL to be used in the forced circulation digester.

2.2.2 Forced Circulation Digester for Kraft Cooking

Spruce chips were subjected to a conventional kraft cooking in a laboratory scale batch digester with forced liquor circulation. The chips were steamed for 5 minutes before the cook. Cooking temperature was 157^0C. Temperature was quickly taken to 100^0C and then ramping rate was set at 1^0C per min. Total cooking time at cooking temperature was 168 minutes in each cook. 1 liter of liquor was exchanged in some of the experiments after 120 minutes. Liquor to wood ration was 4:1. 500 g dried chips were used in each cook. Cooking liquor was prepared from stock solutions of NaOH and Na_2S. $[OH^-]$ in cooking liquor was 1.25 [mol/l], sulfidity was 0.26 [mol/l] and $[Na^+]$ was 2.57 mol/l. In exchange liquor $[OH^-]$ was 0.3 [mol/l].

Pulp obtained after the cook was washed over night with de-ionized water. Then it was defibrated using a water jet NAF defibrator with water pressure of 1.8-2 bars. Afterwards pulp was centrifuged and weighed. Pulp was kept in the fridge for 12-14 hours in order to get uniform moisture content. Then moisture contents of this pulp were determined after putting it into an oven at 105^0C overnight.

Shives were separated from the pulp and weighed separately after being held in an oven at 105^0C over night.

2.3 Analysis of BL

Hydrogen sulphide and hydroxide ion concentration was determined using SCAN N 31:94 and SCAN N 33-94 method respectively.

2.4 Xylan Extraction

Xylan was extracted from BL using the method described by Axelsson et al. (1962). The only difference was that acetone was used in the last washing step rather than ethyl ether. The whole procedure was done in the two following steps.

2.4.1 Xylan Precipitation

In the first step xylan was precipitated from the BL. To achieve this 500 ml acetic acid was slowly poured into the 500 ml BL sample. The pH of the solution was determined. Then this acetic acid-BL solution was added into 3000 ml ethanol. This solution was kept in the refrigerator for 35-40 hours.

2.4.2 Xylan Washing

After keeping the solution in the refrigerator, xylan was precipitated from the solution. The supernatant was skimmed off and the xylan was washed two times with 2:1 ethanol-water solution. Then it was washed for three times with 96.3% ethanol solution and for three more times with acetone. After each washing step the solution was centrifuged using a Potofix 32A centrifuge at 4000 rpm for 20 minutes.

Xylan obtained after these washing steps was dried to remove acetone by keeping in a desiccator under the vacuum for 16-18 hours.

2.5 Kappa Number

Kappa number was determined according to ISO 302:2004 standard. A known quantity of the dry pulp was fed to the apparatus. It was, first, defibrated using water. Then titration was carried out by adding acidified permanganate. It oxidized the aromatic structure.

$$\text{Lignin} + \text{MnO}^{-4} \rightarrow \text{Lignin (Oxidized)} + \ \text{Mn}^{+2}$$

Then potassium iodide was added to the solution. It reacted with remaining permanganate in the solution.

$$2\text{MnO}^{-4} + \ 10\ \text{I}^{-} \ \rightarrow 2\ \text{Mn}^{+2} \ + 5\ \text{I}_2$$

Iodine was liberated from this reaction. It was titrated against standard sodium thiosulphate solution.

$$\text{I}_2 + \ 2\ \text{S}_2\text{O}_3^{-2} \rightarrow 2\ \text{I}^{-} \ + \ \text{S}_4\text{O}_6^{-2}$$

Titrations used in this experiment were Iodometric. Equipment performed the calculation by itself and displayed the kappa number values.

2.6 Physical Testing of Pulps

Pulps were wet disintegrated at 10000 revolutions using ISO 5263 and beaten in a PFI mill (ISO 5264) at 500, 1000, 2000 and 5000 revolutions. °SR number was determined using ISO 5267-1:1999/Cor 1:2001. Rapid-Köthen method was used to make the hand sheets (ISO 5269-2:2004). ISO 5270:1999 was used to evaluate the tensile strength properties of the sheets. Sheet thickness was determined using SCAN P88:2001 method.

3 Results and Discussions

In this study, five cooks were carried out. In all cooks spruce chips were used. One of the five cooks was carried out without any exchange of liqour. However it was stopped for five minutes after 2 hours of cooking time to simulate the exchange. In other words it contained the spruce xylan in it. This cook is being represented by “Spruce – No exchange”.

In the other four cooks, liquor was exchanged after 120 minutes of cooking time. One liter of black liquor was removed and fresh white liquor was added into the system. This procedure is shown in Figure 8. Out of these four, in three cooks xylan from different sources – rice husks, wheat straw and birch - was mixed with WL before adding it to the system. While in the 5th cook nothing was mixed with the WL. This cook is being represented by “Ref – WL”.

Residual hydroxide [OH^-] in all the cooks was in the range of 8-10 [g/l] (0.20-0.25 [mol/l]).

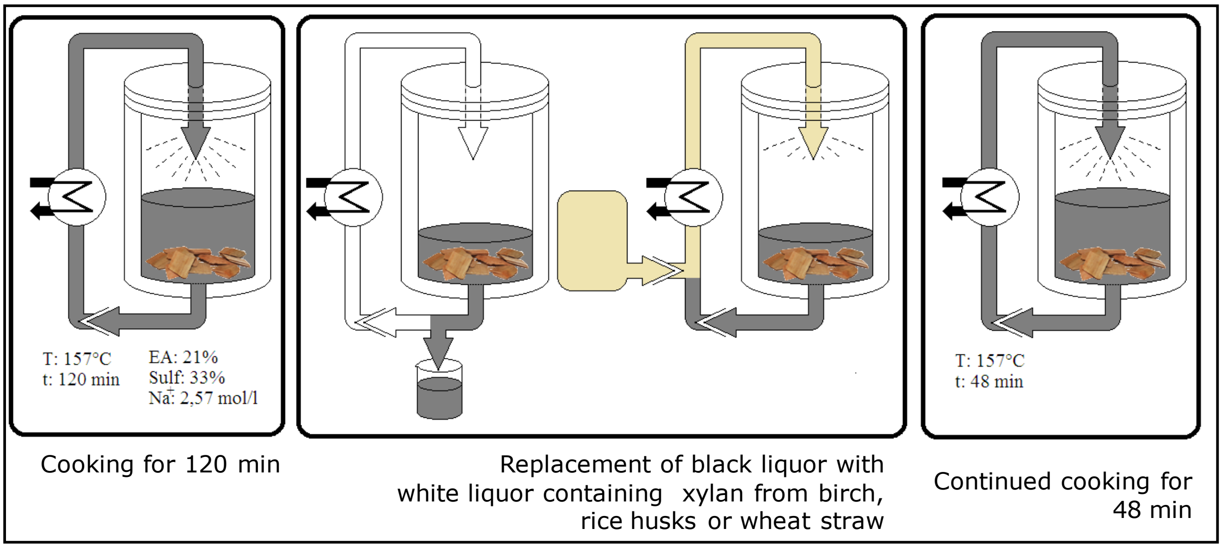

Figure 8: Summary of the cooking procedure (Illustration by Daniel Tavast)

3.1 Xylan Precipitated from Cooking of Rice Husks and Wheat Straw

Figure 9 shows the amount of xylan precipitated from the black liquor collected after the autoclave cooking of the rice husks and wheat straw. The value for birch is taken from a previous study (Li Jansson, 2011). It shows that a lot more xylan can be obtained from rice husks and wheat straw as compared to birch. Wheat straw gave two and three times more xylan as compared to rice husks and birch respectively. Liquor to wood ratio in all the cooks was 4 l/kg.

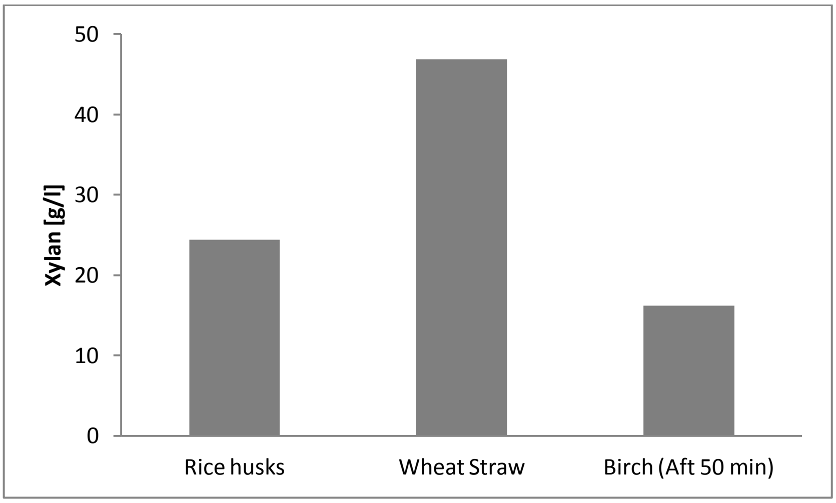

Figure 9: Xylan precipitated [g/l] from black liquor of rice husks, wheat straw and birch

3.2 Xylan Concentration Profile

Figure 10 shows the xylan concentration profile in the black liquor during the cook. Values at cooking time of 50 and 100 minutes are taken from a previous study by Li Jansson (2011) on the same spruce chips at the same cooking conditions. The xylan concentration increased as more xylan dissolved into the cooking liquor during pulping. At some point, in this case after around 100 minutes of cooking, the xylan concentration decreased, probably as a result of re-adsorption of xylan onto the fibers. At the exchange point (cooking time: 120 min), more xylan was added in three of the cooks. One cook was carried out without exchange of the liquor, so xylan concentration is not effected at that point. While in the last cook, half of the xylan was removed, as we took out half of the black liquor and added fresh WL without any xylan in it.

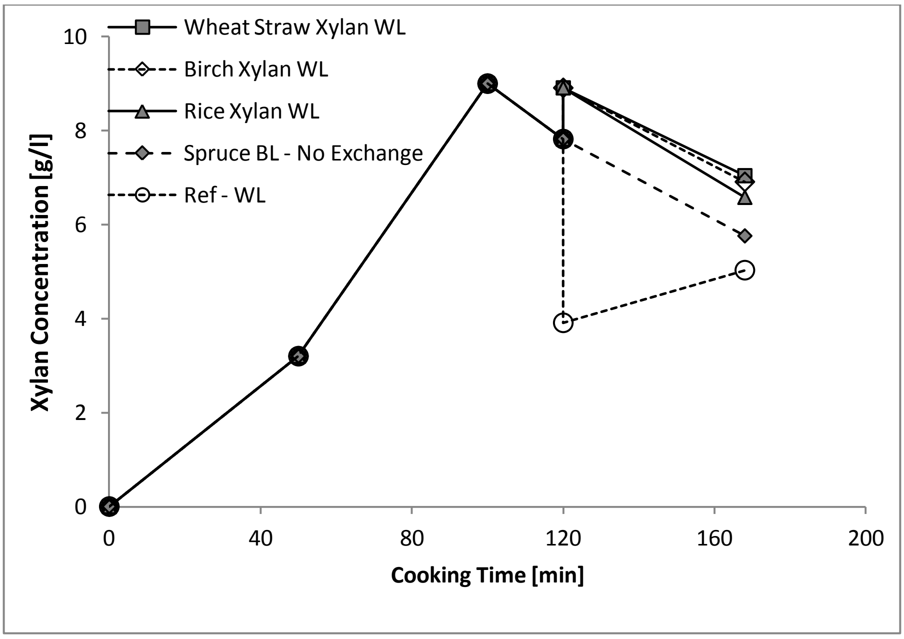

Figure 10: Xylan concentration profile in the black liquor throughout the cook

Cooking was resumed after the exchange. Xylan concentration in the BL keeps on decreasing for the cook in which no exchange was done. This result is in agreement to the previous studies (Li Jansson, 2011; Danielsson and Lindström, 2005).

The cook, in which the exchange was done with WL, shows an increase in the xylan concentration in the BL again. This tells us that added fresh WL keeps on extracting xylan from the pulp so at the end of the cook there should be very little xylan remained in the fibers.

The other three cooks – with added wheat straw, rice husk and birch xylan – followed a similar trend i.e. xylan concentration decreased after the exchange. It indicates that xylan precipitated onto the fibers. In case of cook with the rice xylan, a little more xylan (almost 5%) was precipitated onto the fibers as compared to other two cooks.

3.3 Yields of the Cooks

In Figure 11 kappa number and yield for types of cooks are compared. Kappa number values for all of the cooks are fairly close. The "No exchange cook" has highest yield. This may be because of more lignin attached to spruce xylan than other xylans. The cook with added birch xylan also has a higher yield than wheat straw and rice husk xylan cooks. It is most probably because of the difference in xylan structures. Birch xylan has much lower uronic acid contents so it may have precipitated more onto the fibers than the straw and rice xylan.

On the other hand, in "Ref – WL" cook, BL was removed and there was no xylan in added WL. This can explain why it had the lowest yield. From this we can say that we were able to precipitate a lot more birch and spruce xylan onto the spruce pulp than rice and wheat straw xylan.

Shives' contents for all of the cooks were close to 1g or less than that.

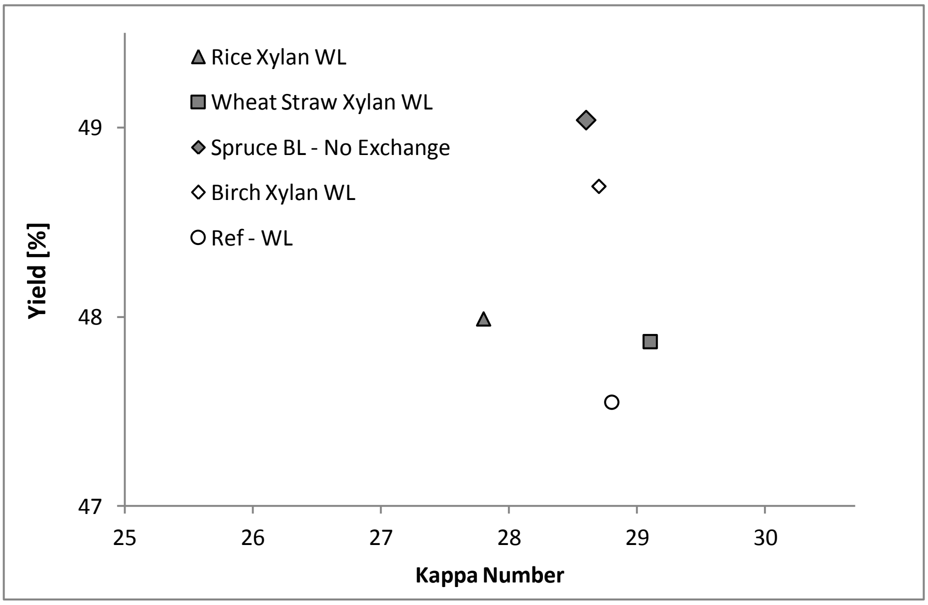

Figure 11: Comparison of kappa number and yield for different types of cooks

3.4 Tensile Strength

The pulps were beaten in PFI mill at different revolutions. Tensile strengths of the sheets made from these pulps were determined. The results are plotted in Figure 12. The pulp with the birch xylan gives the strongest pulp – measured in terms of tensile index. Birch xylan has a more linear structure as compared to softwood xylans. So it would have higher bonding strength with the pulp and, as a result, stronger pulp.

On the other hand the reference pulp, in which exchange was made with WL and no xylan was added, shows, as expected, the lowest tensile strength. It also had the lowest yield (Figure 11) to indicate that it had the lowest amount of xylan adsorbed onto the fibers.

The other three pulps – having rice, wheat straw and spruce xylan – had intermediate tensile strengths. It is shown in Figure 11 that rice and wheat straw pulps have lower yields than the spruce xylan. This suggests that very little quantities of rice and wheat straw xylans were actually precipitated onto the fibers. But even this little quantity is very effective in improving the strength by 5-7 %. That is a significant amount considering the rather low amount of xylan attached to the fibers.

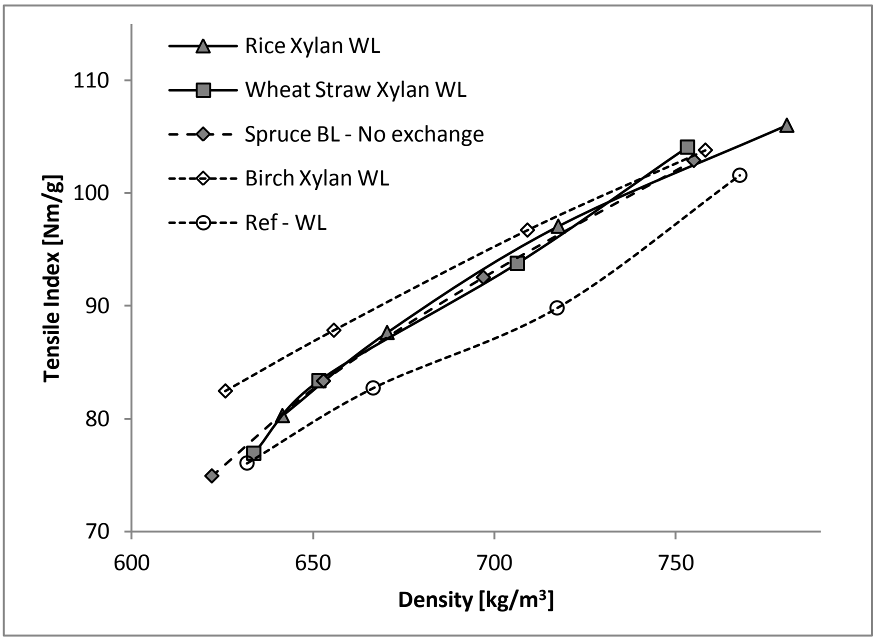

Figure 12: Tensile index at different densities for cooks with differing xylan structure present at the end of the cook

3.5 Revolutions versus Tensile Strength

In Figure 13 tensile index values for these cooks are plotted against number of revolution of the PFI mill. Pulps having rice husks and birch xylan require much less beating energy to get a given tensile index as compared to the reference pulp. The effect was not as significant with wheat straw xylan as it was with rice xylan.

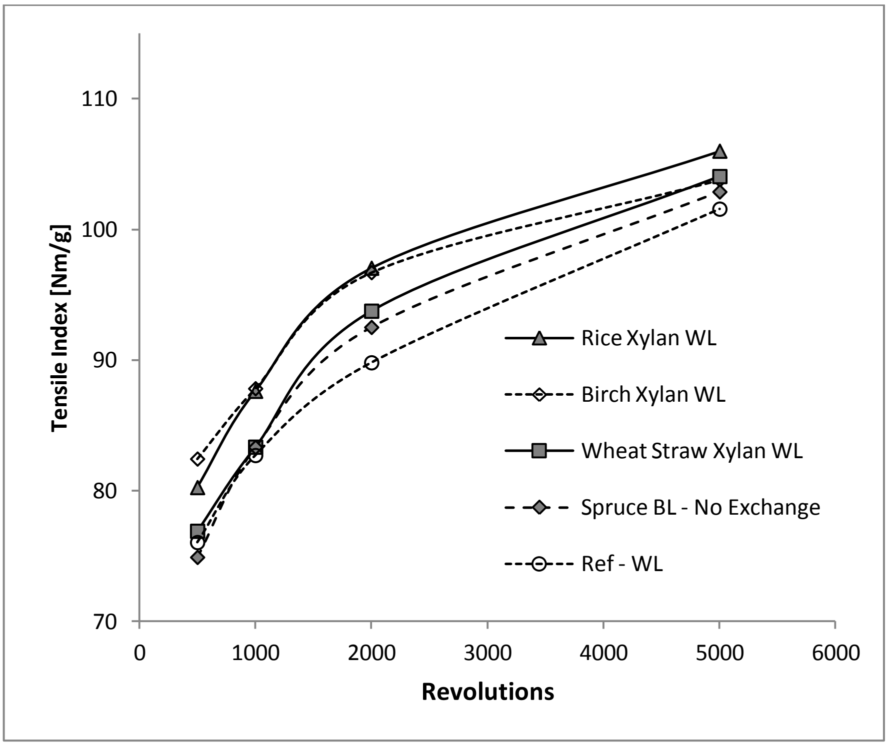

Figure 13: Tensile index values at different revolution of PFI mill for five different types of cooks

3.6 Future Applications

Of the different xylans used in this study, xylan from the rice husks and birch seems to be most effective. In this study this xylan was extracted from the rice husks using the alkaline cooking. However the problem is how we can get it on the industrial scale. Here are some possibilities.

Rice husks are being used in the world to get silica (Yalcin, 2001). If xylan separation can be added as an additional step in that process, then that xylan can be obtained as an additive for the paper production.

Alkaline liquors available in a pulp mill can be used for extraction of xylan from for example agricultural waste products and added to the digester at a later stage of the cook as a means of increasing the amount of xylan attached to the fiber surface and thereby increased pulp strength.

4 Conclusions

Rice husk, wheat straw and birch xylan increased the tensile strength of the pulps when added to the later stage of the cook. It was only possible to attach very little quantities of rice husk and wheat straw xylan onto the fibers. Pulps with the rice husk and birch xylan require less beating energy than the other pulps.

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