The Significance of Liquor-to-Wood Ratio on the Reaction Kinetics of Spruce Sulphate Pulping

Vätske/ved förhållandets inverkan på kinetiken vid sulfatkokning av gran

Master thesis 20 points
Master of Science in Chemical Engineering

Date/Term: 26th of April 2007
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Abstract

In 1957 Vroom presented an article that dealt with the kinetics of the sulphate cook. He showed that the lignin dissolution exhibited a temperature/time dependency that could be explained by the Arrhenius equation and that the reaction was of first order with respect to lignin. However, even before Vroom introduced the H-factor all wood components were assumed to react according to a first order reaction. In recent years progresses in this area have been made. Lignin for example is nowadays considered to dissolve during three parallel first order reactions, all with differences in activation energies.

When the kinetics are evaluated, several cooking series at different temperatures and concentrations of active cooking chemicals are needed. The data points obtained are then fitted into some equation. If the concentration of the active cooking chemicals is constant, the activation energies and the chemical dependency for the dissolution of wood components can easily be found. In order to simplify the evaluations of the kinetics, very high liquor-to-wood ratios are sometimes used, often as high as 50:1 or even 75:1. In this manner, the chemical concentrations are almost constant during the cook. The problem is that in the normal industrial cook where the liquor-to-wood ratio is about 4:1, the chemical concentration is not constant. This is due mostly to the alkali consumption that takes place in the cook for example when neutralising the acidic groups in the hemicelluloses.

A disadvantage with high liquor-to-wood ratios is the high dilution of the dissolved organic matter. A high concentration of dissolved lignin boosts the dissolution of the remaining lignin in the wood residue and xylan can redeposit on the fibres when its concentration in the cooking liquor is high.

The aim of this project was to describe how different liquor-to-wood ratios influence the kinetics during sulphate cooking of spruce.
Preface
The present study was carried out in the autoclave laboratory at Karlstad’s University and the laboratory at Metso Fibre, the former Kvaerner Pulping, during the autumn term in 2006.

My warmest thanks are due to my supervisor Dan Johansson for his support, helpfulness and good advices. I would also like to thank Professor Ulf Germgård for giving useful tips and constructive criticism. Pia Eriksson and Göran Walan are acknowledged for being most helpful with troubleshooting in the autoclave laboratory. I would also like to thank the personnel at Kvaerner Pulping for being helpful and for the loan of the analysis equipment. I would also give a special thanks to Mats Strandberg at Canfor Pulp, for supplying useful information.
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1. Introduction

In industrial kraft pulping applications it is of vital importance to be able to foresee the quality of the pulp with the intention to produce pulps tailored for each customer’s demand. Softwood pulp contains three carbohydrates i.e. cellulose and the hemicelluloses arabino-glucuronoxylan and O-acetyl-galactoglucomannan, often denoted xylan and glucomannan. The hemicelluloses are degraded to a large extent during kraft cooking, but it is of great interest to keep as much as possible of the hemicelluloses in the pulp as the yield increases. The pulp is also easier to beat and paper properties are to a certain extent improved when the amount of hemicelluloses is increased.

A loss of carbohydrates from the pulp has however also an influence on the evaporation plant and the recovery boiler. Today it is crucial to run mills at optimized operations from an economical point of view and this demands good model-based optimisation and control.

One of the most used models in pulp prediction is the H-factor developed by K.E. Vroom (1957). The model, involving time and temperature, describes how the lignin content in the wood residue is reduced as the cooking proceeds. In much the same way the G-factor describes the cellulose degradation (Theliander et. al., 2002).

In recent years the models have been more and more sophisticated, and researchers have found that the dissolution of different components in the pulp follows different kinetics. The kinetic model for each component also varies throughout the cook. Establishing kinetic expressions involves laboratory work where pulp fractions are produced in several time series. To eliminate variations of chemical composition in the cooking liquor, a high liquor-to-wood ratio is sometimes used, also designated as constant composition cooks or homogenous cooks. The denomination indicates an insignificant change of the cooking chemicals and thus more or less constant concentrations. It is common to carry out the laboratory cooks at a ratio between 50 and 75 times as much liquor as wood chips, whereas for industrial application the ratio usually is between 3.5 and 5.

The purpose with this thesis is to investigate and describe how the liquor-to-wood ratio affects the kinetics of different wood components during kraft cooking of spruce chips.
2. Background

The active cooking chemicals in kraft pulping are hydroxide- and hydrogen sulphide ions, OH⁻ and HS⁻ respectively. For simplicity, it can be assumed that the ionic strength is only built up by the concentration of the cations in the cooking liquor. In industrial white liquor sodium ions Na⁺, but also calcium ions Ca²⁺ and potassium ions K⁺ normally exist among the positively charged ions. When the kinetics of pulping is studied it is common to carry out the cooking process at high liquor-to-wood ratio as the ions then easily can diffuse and the concentrations of chemicals are fairly constant.

Throughout a cook the dissolution of carbohydrates and lignin are simultaneous but it is the relative rate of the dissolution for each component that determines the selectivity. Lignin is according to the literature dissolved in three parallel phases (Lindgren and Lindström, 1996). They all exist at the same time but there is always one of them dominating the reaction at any given time (Andersson et.al., 2003 and Teder, 2004). During the initial phase, which is short and the pulping rate high, nearly 20% of the lignin content is dissolved (Brännvall, 2004 and Danielsson, 2006). In the following bulk phase the pulping rate is lower. When this phase has come to an end almost 90% of the lignin has been dissolved. The last phase is the residual phase where the delignification rate is very low and may even completely stop (Danielsson, 2006). The selectivity in this phase is very poor.

Carbohydrate dissolution differs from lignin dissolution and the opinion diversts if there are two or three phases in the carbohydrate reactions. Lindgren (1997) has reported two kinetic phases where the first is rapid and the second is slower. In the first part of the second carbohydrate phase and the bulk delignification phase, the selectivity with respect to carbohydrates is high. The activation energy is lower for lignin than for the carbohydrates in this phase so a low temperature in the cook is preferred. Andersson (2003) defined in his study four wood components with three subspecies each to capture the diversity in reaction rates. Johansson (2006) denoted the three carbohydrate phases as the initial, the intermediate and the final phase and that is also the way which the carbohydrate dissolution is referred to in this thesis.

During the kraft cook dissolved glucomannan is largely degraded to smaller parts while xylan is more stable toward degradation in the liquid phase. It has been shown that xylan can precipitate back onto the fibres later on in the cook. When this occur the pulp yield is increased and the load on the recovery boiler decreases. A pulp with higher xylan content is also easier to beat and the tensile properties of pulp and paper can be enhanced. This fact is not yet fully understood but Danielsson (2006) asserts that the pulp strength improvement is associated with the location of xylan on the fibres surface. The theory suggests that xylan acts like a glue between cellulose fibres and that it contributes to the cellulose swelling capacity. However, xylan located in the inner part of the fibres does not contribute to the strength improvement.

2.1. Wood composition

The structure of the wood cell wall is constructed in layers where the micro fibrils are oriented in diverting directions. This gives strength to the tree which has to resist strain and stress. The layers within the cell wall are the primary wall (P), the outer secondary wall (S1), the middle secondary wall (S2), the inner secondary wall (S3), and lumen (L). Between the fibres there is a middle lamella (ML). The middle lamella has the highest concentration of lignin, 60-80%, and the rest is mainly hemicelluloses. The thin primary wall consists of
cellulose, hemicelluloses and pectin embedded in lignin. The secondary wall, S2 is the thickest layer, where most of the cellulose and hemicelluloses are found (figure 1).

![Figure 1. A schematic picture of the wood cell wall on fibre level. The cell wall consists of different layers where P is the primary wall, S1, S2 and S3 are outer, middle and inner secondary wall respectively. L is the lumen inside the fibre and ML the middle lamella between the fibres (from Theliander, 2002).](image)

### 2.1.1. Cellulose
Cellulose is a linear polysaccharide that could be seen in figure 2. Cellulose consists of β-1-4 linked glucose units, with a DP of approximately 10,000 units in native wood. The molecules are organised in bundles, so called micro fibrils, which partly are structured in crystalline and partly in amorphous sections. Softwood contains 42±3% and hardwood 45±4% cellulose. Macro fibrils or fibres are threads made by micro fibrils entwining themselves building up the wood cell wall (figure 1). The fibrils are embedded in hemicelluloses and lignin.

![Figure 2. Cellulose molecule (from Theliander et. al., 2002).](image)

### 2.1.2. Hemicelluloses
Hemicelluloses is the generic term for different types of amorphous, branched sugar polymers built up by glucose, mannose, galactose, xylos and arabinose along with acetyl groups (CH$_3$CO) (figure 3). These chains are not polymerized at such high degree as cellulose and commonly not higher than 300 units in native wood. Softwood contains about 27±2% and hardwood 30±5% hemicelluloses. In hardwoods the most common hemicellulose is xylan while glucomannan is the most common in softwood. The polymers glucomannan and xylan could be seen in figure 4.
In the kraft cook hemicelluloses are degraded through endwise peeling, alkaline hydrolysis and secondary peeling. In alkaline environment the acetate groups in xylan are immediately hydrolysed and the backbone side group methylglucuronic acid (MeGlcA) is partly removed. It also participates in the formation of hexenuronic acid (HexA) during pulping, species involved in brightness reversion of pulp and paper (figure 5). Compared to other carbohydrates HexA is much more chemical reactive since it contains a carbon-carbon double bond and is negatively charged. It reacts with bleaching chemicals such as chlorine, chlorine dioxide, ozone and peracetic acid. It also reacts by complex binding metal ions. Beside this HexA contributes to the kappa number as it consumes potassium permanganate in the analysis method (www.medact.se). Another way of determining the kappa number of the lignin has therefore been developed where the content of HexA is firstly removed from the pulp (Vourinen et. al., 1999).

Xylan is initially dissolved in the cooking liquor, but after a brief cooking time it starts to redeposit back on to the fibres. This mechanism is not yet fully understood and whether it is an adsorption or precipitation/crystallisation process has been discussed. But it seems that when the hydroxide ion concentration is low, it is mainly a precipitation process which involves a loss of solubility (Danielsson, 2006).

Xylan redeposition on the pulp has not only proven to increase the pulp yield but also to increase the strength properties. The amount of alkali added in a mill is only slightly larger than that consumed and the concentration of alkali therefore decreases to almost zero at the end of the cook. This was verified by Ylner and Enström (1957) who showed that adsorption from a xylan containing cooking liquor on cellulose fibres made from purified cotton linters
was increased when the initial alkali concentration was between 0 and 2.0 %. They also found that the adsorption increased with increased temperature.

2.1.3. Lignin
Native lignin is a large amorphous polymer containing an enormous number of inter unit linkages, some of them could be seen in figure 6. It is a complex structure with different compositions in different wood species. Hardwood lignin consists of coniferyl and sinapyl alcohol whereas coniferyl alcohol is the dominating softwood lignin component (Sjödahl, 2004). Lignin acts like glue between the fibres. The highest concentration of lignin in the wood cell wall is found in the middle lamella but the largest amount of the lignin is within the S2-layer. The aim of kraft cooking is to reduce the lignin content in the wood matrix so the fibres easily can be liberated.

![Lignin structure](image)

Figure 6. Lignin structure.

2.1.4. Extractives and ash
Extractives in wood consist of low molecular organic compounds such as fatty acids, resin and sterols. The fraction of inorganic compounds also called ash constitutes of Ca, K, Mg, P, Mn, Fe, Si, Al and Na salts and the actual composition varies between wood species and is also influenced by the local compositions of the soil (Theliander et al., 2002).

2.2. Kraft pulping process
The main purpose with kraft pulping is to degrade the lignin and to liberate the fibres. The process produces strong and flexible fibres which conform better to each other than mechanical pulp fibres do. The main disadvantage with the kraft process is the low yield. The process is a complex procedure which involves several reactions and much work has been made trying to establish the dissolution kinetics of the participating compounds.
2.2.1 Transportation mechanisms

Wood porosity is to a certain extent dependent on the wood specie discussed, but roughly 50-75% constitutes of cavities. To make penetration of active cooking chemicals as even as possible in the chips prior to cooking, the initial steaming step is important. When hot steam diffuses into the pores, air is transported out of the chips. Air transportation is driven by two mechanisms, advective and diffusive transport. The diffusive mass transfer into the chips is to a certain extent dependent on the lower internal steam and higher air concentration than outside. Air is transported outwards and steam and liquid into the chips. Steam inside the pores and lumen condensates and the chips get heated. This creates an internal additional pressure, forcing air and steam out of the chips.

The impregnation step when the active cooking chemicals are added is also driven by advection and diffusion. Due to the addition of white liquor to the heated chips the internal steam condensates. The inside pressure is then lowered causing chemicals to be soaked into the pores, lumen and cell walls. The advective transport occurs at an elevated pressure and when the pressure outside and inside the chips is equalized the chemicals are forced into the chips. The diffusion mechanism is driven by concentration gradients (Theliander et.al., 2002).

The cooking liquor is divided into two categories; free and bond liquor. Bound liquor is incorporated in the lumen, pores and cell wall while the free liquor is found between the chips and fibres. The mechanism determines the transport of chemicals and reaction products from the fibre wall to the surface. This action is in accordance with Fick’s law determined by the participating ions, concentration gradients and diffusion surface available. During the dissolution where material is removed from the wood cell wall it becomes more and more porous. (Brännvall, 2004).
2.2.2. Delignification

The desired reaction is cleavage of $\beta$-aryl ether linkages which degrades the lignin and makes it possible for the lignin to be dissolved. The reaction path is shown in figure 7.

As could be seen in figure 8 the delignification process is often dealt with in three different phases where the rates differ from each other. In the initial phase the dissolution is very fast. It is the extractable lignin; the smaller parts of the lignin molecules, which are dissolved in this phase. In the bulk phase most of the lignin is degraded and dissolved. The rate is not as fast as the initial phase and it is more selective where the carbohydrate dissolution is relatively small. The selectivity of degradation and dissolution of residual lignin is poor and is characterized by a much lower delignification rate (Gustavsson et. al., 1997 and Brännvall, 2004). The lignin fraction called residual phase lignin has earlier been thought of as being created during the cook. But Lindgren and Lindström (1996) have shown through their research that this lignin exists already at the beginning. After degradation the lignin fraction is dissolved in the black liquor. Depending on the sodium hydroxide concentration and other parameters affecting the solubility, lignin can precipitate back onto the fibres.
The delignification rate is strongly temperature dependent. Below 140°C the rate is very low but increases rapidly as the temperature rises. The temperature in a digester varies during the cook as the cooking cycle consists of an initial time period where temperature is raised from just beneath the boiling point of water to the effective cooking temperature and a following period where the temperature is kept constant. In earlier days it was hard to know exactly when the cook was completed. The solution of this issue was invented by Vroom in 1957. He found an expression from which the cooking time could be estimated according to the temperature used throughout the process. The equation is a rate expression similar to the Arrhenius equation, and after integration it gives the H-factor, equation (1).

$$H = \int_{t_0}^{t} Ae^{\frac{E}{RT}} dt$$  \hspace{1cm} (1)

Which H-factor that is required in a certain case depends on the pulp properties requested. When the chemical charge is kept constant; the H-factor can predict the kappa number of the pulp regardless of the combination of times and temperatures (Vroom, 1957).

If the bulk delignification phase is prolonged the selectivity of the cook is improved. Previous studies have concluded that an increased amount of OH\(^-\) or HS\(^-\) in the initial phase decreases the amount of residual lignin. Also an increment of HS\(^-\) or the temperature in the bulk phase reduces the amount of residual lignin. This mode of procedure moves the transition point between bulk and residual phases toward lower lignin content in the wood residue. When the reaction rates for the three phases are to be investigated, the remaining lignin content in the pulp at a certain time \(t\) has to be related to the amount present from the start. In this project a method for the lignin analysis has been used where the amount of hexenuronic acid firstly has been removed. Other analysis methods exist such as Klasson lignin or the chlorine number. All methods measure the total amount of lignin i.e. initial, bulk and residual lignin.

The lignin content follows equation (2) according to Lindström and Lindgren (1996).
\[ L = e^{\ln I^2 - k_{h,t}} + e^{\ln I^2 - k_{r,t}} + e^{\ln I^2 - k_{r,t}} \]  \hspace{1cm} (2)

Where:
\[ k_{h} = 0.029 \cdot [\text{HS}]^{0.32} + 0.067 \cdot [\text{OH}^-] \cdot [\text{HS}]^{0.32} \]
\[ k_{r} = 0.0032 + 0.0020 \cdot [\text{OH}^-] \]

### 2.2.3. Carbohydrate degradation and dissolution

The main content in wood is carbohydrates consisting of the polymers cellulose, xylan and glucomannan. During the pulping process not only the lignin is degraded and dissolved, but also the carbohydrates are attacked. The acetyl groups in the hemicelluloses are split off already at low temperatures and at about 100°C the primary peeling reaction starts. This is an attack towards the reducing end group in the carbohydrate chain where a sugar unit is split off (figure 9). The peeling cease when a stopping reaction manages to convert the end group to a more alkali resistant structure. According to Brännvall (2004) the peeling reaction is preferably favoured where the material is amorphous while the crystalline structure is more steric hindered. Primary peeling occurs in the beginning of the cook.

![Figure 9](image-url)  \hspace{1cm} Figure 9. The mechanisms of the peeling reaction where the end units are split off and dissolved (from Brännvall, 2004).

When the cooking temperature has reached about 130°C the alkaline hydrolysis becomes important and the attacking speed increases as the temperature increases. This kind of attack occurs randomly in the chain (figure 10).

![Figure 10](image-url)  \hspace{1cm} Figure 10. The action of alkaline hydrolysis produces shorter chains and new reducing end groups are formed (from Brännvall, 2004).

Alkaline hydrolysis creates new and shorter chains with new reducing end groups where secondary peeling can take place. Peeling reactions results in lower yield, while alkaline hydrolysis results in viscosity reduction (Brännvall, 2004).

Other way to determine the attack on the carbohydrates is to calculate the G-factor (equation 3) which describes to which extent the carbohydrate chains are cleaved. Pulps produced at the same G-factor are supposed to have equal viscosities and strength properties (Theliander, 2002).

\[ G = \int_{0}^{t} \exp \left( \frac{57.7 - \frac{21530}{T}}{t} \right) \, dt \]  \hspace{1cm} (3)

The activation energy was determined to 179 kJ/mole.
2.3. Influence of cooking parameters

The main variables dealt with in kraft cooking are: the hydroxide ion concentration, the hydrogen sulphide ion concentration and the ionic strength. Temperature and liquor-to-wood ratio are also important parameters. The hydroxide ions are consumed during the cooking operation mainly when neutralising acidic groups in carbohydrates. Hydrogen sulphide ions facilitate the lignin degradation. The ionic strength is detrimental to the pulping reaction rate when it reaches too high concentrations.

2.3.1. Hydroxide ion concentration

According to Lindgren and Lindström (1996) the bulk delignification rate is increased when the hydroxide ion concentration is increased but the rate in the residual phase is left unaffected. Although a higher concentration of hydroxide ions results in a pulp with less residual lignin.

The dissolution rates of the carbohydrates also increases when the alkali concentration increases, but the hemicelluloses are more sensitive towards alkaline degradation than the cellulose. About 70% of the glucomannan content is lost during pulping. Below 100°C the soluble glucomannan fraction is lost. Between 100°C and 130°C the peeling reactions dominate the dissolution of the remaining glucomannan content. Higher temperatures however, seems to have no or only a minor impact on the remaining content of glucomannan (Brännvall, 2004).

Xylan is mostly dissolved by peeling reactions above 130°C. At lower temperatures it is only the soluble xylan that is dissolved. Some xylan is dissolved without being degraded and this amount may later in the process, when the alkali charge has decreased, readsorb onto the fibres. A high alkali charge increases the dissolution of xylan (Danielsson, 2006). An important parameter in pulping is the effective alkali measured as % on wood, equation (4).

\[
EA(\%) = \frac{m_{NaOH}}{m_{wood}}
\]  

(4)

2.3.2 Hydrogen sulphide ion concentration

The hydrogen sulphide ion, which is a strong nucleophil, is mainly a delignifying agent. An increment of the hydrogen sulphide ion concentration increases the delignification rate in the bulk phase, but leaves the residual phase lignin unaffected. Hydrogen sulphide ions do not react with carbohydrates, but their presence protects the carbohydrates compared at a given lignin content. As a higher hydrogen sulphide concentration increases the delignification rate, the cooking time becomes shorter and the attack on carbohydrates will be reduced (Brännvall 2004). The sulphidity (S) is calculated according to equation (5). The sulphidity influences the delignification rate greatly when increased up to 15-20%, but after that an increment has a lower impact (Theliander et.al., 2002)

\[
S(\%) = 100 \cdot \frac{2[HS^-]}{[OH^-]+[HS^-]}
\]  

(5)
2.3.3 Ionic strength

A high ionic strength has a negatively impact on the selectivity and the brightness. A high ionic strength increases the H-factor demand to a given kappa number which is due to a lower delignification rate in the bulk phase. It also lowers the activity of the hydroxide ions (Sjödahl, 2004).

2.3.4 Additives

Ameliorations of the kraft cook can be made to increase the carbohydrate content. Two well known additives are anthraquinone and polysulphide which both protect the reducing end groups by oxidizing reactions where aldonic acids are formed. Anthraquinone can preferably be used when the sulphidity is low, but can not be generated in the mill while polysulphide can. In the reaction anthraquinone is reduced to anthrahydroquinone which cleaves β-O-4 linkages in the lignin complex resulting in an increment of the delignification rates (Sjödahl, 2004). Polysulphide generation can be realized in three different ways. One way is to add elementary sulphur to the white liquor. Hydrogen sulphide ions are then being consumed and different polysulphide ions are formed with $n$ between 1 and 5, reaction (I) (Hakanen and Teder, 1997). This process has been developed by Pulp and Paper Research Institute of Canada (Paprican).

$$n S + HS^- + OH^- \rightarrow S_nS^{2-} + H_2O$$

(I)

Internal sulphide oxidation in the caustization plant is another useful method according to reaction (I). A third option is to expose white liquor to direct catalytic oxidation (an active coal catalyst and air) according to reaction (II).

$$\left( n + 1 \right) HS^- + \frac{n}{2} O_2 \rightarrow (n-1)OH^- + S_nS^{2+} + H_2O$$

(II)

The last option is the MOXY (Mead Oxidation) process developed in 1974 at Mead Corporation. In this process the white liquor is partial oxidized. As a side reaction also thiosulphate is produced according to reaction (III).

$$2 HS^- + 2 O_2 \rightarrow S_2O_3^{2-} + H_2O$$

(III)

2.3.5 Black liquor

Industrial black liquor contains degraded lignin and carbohydrate fragments as well as unconsumed inorganic active cooking chemicals. By adding a certain amount of black liquor to the wood chips in the impregnation step a positive effect is seen on the delignification rate in the bulk phase. It has been discussed whether the increment originates from the extra added amount of chemicals, mainly the hydrogen sulphide ions, or if it is the dissolved organic matter boosting the reactivity. Sjödahl (2004) used ultra and nano filtrated black liquor fractions as additives in his cooks. The filtrated fractions corresponded to 15, 5 and 1 kDa. The cooks with the smallest molecules were responsible for the highest delignification rate. By exchanging 25% of the white liquor to industrial black liquor, kappa number 26 was reached instead of 34.5 at H-factor 2000 (figure 11). He also tried to replace a larger volume of white liquor to DWC but this did not lower the kappa number any further.
2.3.6. Liquor-to-wood ratio

For industrial purposes it is common to run the cooking process at a liquor-to-wood ratio (L/W) between 3-5 l/kg. A higher ratio, sometimes used in the laboratories, keeps the cooking liquor less affected by the chemical reactions. According to Mortimer (1989) the delignification decreases when the L/W is increased without increasing the EA or the H-factor. In order to maintain a constant kappa number at an increased L/W ratio either the H-factor or the EA has to be increased to counterbalance the lower pulping rate that is due to the lower alkali concentration. If the alkali concentration is increased rather than the H-factor, the total yield decreases at a constant kappa number. In one of Mortimer’s experiments a series were done at a constant H-factor (1600) and constant sulphidity (30%) but with varied EA charge (16-41%) at L/W ratios of 4, 6 and 8. This showed that the selectivity was influenced by the interplay between alkali charge and liquor-to-wood ratio. The yield at a specific kappa number was reduced at higher liquor-to-wood ratios which were due to the observed increased alkali consumption. As for an example; at L/W=4 and EA=18%, kappa number 31.1 was reached. In order to reach similar kappa number at L/W=8 the EA was increased to 26% (figure 12). The alkali consumption then increased from 12.8 to 13.2%. Because of the higher dilution at high L/W, the alkali concentration was lower even though the EA was higher.
2.3.7. Temperature

An ordinary kraft cooking temperature is typically 140-160°C. If the temperature is lowered the transition point between bulk and residual delignification is delayed and it occurs at higher lignin content. Although when extrapolating the residual phase for different temperatures the same value for the amount of residual phase lignin is obtained at \( t=0 \) (figure 13). This means that the initial distribution of lignin reacting as bulk phase and residual phase lignin is independent of the temperature. This was found by Lindgren and Lindström (1996). The apparent decrease of residual lignin during cooking by increasing the temperature is due to the differences in activation energies between the bulk and residual delignification phases.

![Figure 13](image.png)

Figure 13. When extrapolating the residual phase to \( t=0 \) the same amount of residual phase lignin appear weather the cooks have been carried out at 150°C, 160°C, 170°C or 180°C (from Lindgren and Lindström, 1996).

The temperature is also important during the impregnation step since the white liquor has a lower viscosity at higher temperatures and thus a higher flow rate (Theliander et. al., 2002).

2.4. Reaction kinetics

There are methods, more or less applicable depending on the system analysed, to use when reaction rates are measured and evaluated. Examples of such methods are chemical, physical, static and flow methods. When the reaction rates of pulping are evaluated the most appropriate method to use is the chemical.

To measure the reaction rate the concentration of a reactant or a product has to be followed as a function of time. In the chemical method several reaction vessels with identical initial compositions are placed in a constant temperature bath and withdrawn at different times and the reaction is rapidly slowed down or stopped.

For many reactions the rate \( r \) at time \( t \) is experimentally found to be related to the concentrations of the participant species. The expression is then on the form

\[
r = k[A]^\alpha[B]^\beta \cdots [L]^i
\]  

Where \( k \) is the rate constant, \([A]\), \([B]\) and \([L]\) are the concentrations of specie A, B and L and the exponents \( \alpha, \beta \ldots \lambda \) usually are integers or half integers. The sum of \( \alpha, \beta \ldots \lambda \) gives the overall order of the reaction.
To be sure that the rate law has been correctly determined, it is best to make several series of runs. The concentrations should be varied and the reaction should be followed as far to completion as possible according to Levine (2002). The rate constant, \(k\), is strongly dependent on temperature, rapidly increasing with \(T\). In the late 19th century Arrhenius noted that many chemical reactions followed the expression seen in equation (7), where \(A\), the pre-exponential factor, and \(E_a\), i.e. the Arrhenius activation energy, are typical constants for the actual reaction. \(R\) is the gas constant and \(T\) is the temperature in Kelvin.

\[
k = Ae^{\frac{E_a}{RT}}
\]  

(7)

The logarithm of the equation (7) gives equation (8).

\[
\ln k = \ln A - \frac{E_a}{RT}
\]

(8)

By plotting \(\ln k\) versus \(1/T\) a straight line with slope \(E_a/R\) appears which makes it possible to calculate the activation energy. The intercept at \(1/T=0\) gives \(\ln A\).

To find \(k\) for a certain reaction the logarithm for the formation or degradation of the observed species is plotted versus time. The straight line has the slope \(k\).

In the field of kraft cooking there has been various suggestions of how to model the pulping reactions. Some propose consecutive reactions, other parallel reactions. The components participating, i.e. lignin, cellulose, xylan and glucomannan each react in three phases, all with diversity in reactivity and dissolution according to Andersson et al. (2003). For the lignin degradation a general model was developed that described the kinetics, equation (9). It is valid for kraft cooking conditions when \([HS^-]\) > 0.

\[
\frac{dL_j}{dt} = -k_j[OH^-][HS^-]^p L_j
\]

(9)

For \(j=\) species 1, 2 and 3.

Such kinetics have been studied and determined by lots of researchers through the years. In Lindgren and Lindström (1996) the residual delignification rate has been summarized according to equation (10).

\[
\frac{dL_j}{dt} = \left(0.0032 + 0.0020 \cdot [OH^-] \right) \cdot \frac{-146000}{8.314} \cdot \left(\frac{1}{7443.15} \right) \cdot L_j
\]

(10)

The carbohydrates also degrades but at different extents. Xylan for example has a rapid initial degradation at low temperatures which levels out. When the temperature is increased a new rapid degradation takes place. Toward the end of the cook the reaction rate is low. The model structure for carbohydrate kinetics proposed by Andersson et al. (2003) is shown in equation (11).
\[
\frac{dW_i}{dt} = -k_1 \left( [OH^-]^n + k_2 \right) W_i
\]  \hspace{1cm} (11)

For the three components \(i\) = cellulose, xylan or glucomannan each with three species = \(j\).

The model implies that the reactions occur without any hydrosulphide and that degradation proceeds even at very low alkali concentrations. By combining equations (9) and (11) the generic model structure for all components and species becomes equation (12).

\[
\frac{dW_i}{dt} = -k_1 \left( [OH^-]^n [HS^-]^m + k_2 \right) W_i
\]  \hspace{1cm} (12)

3. Method and materials

The pulping method used in these experiments was in compliance with the study of Johansson (2006) described in the article “A Kinetic Study of Softwood Kraft Cooking – Carbohydrate dissolution as a Function of the Cooking Conditions”.

3.1. Experimental

Several cooks have been carried out in time series in order to estimate the kinetics of kraft pulping. Industrial wood chips from Norwegian spruce (Picea abies) were used which firstly were laboratory screened. The fraction that passed 45 mm holes and 8 mm slots but not 7 mm holes were collected. Knots and bark were hand sorted. Air-dried chips were added to stainless steel autoclaves and pre-treated by forcing air out from cavities in the chips with steam at a pressure of 2 bars for 10 minutes. The cooking liquor, prepared from technical grade NaOH, Na₂S and NaCl, was then mixed and added. The autoclaves were pressurised with nitrogen at 9 bars, attached to the rotating shaft in a polyethylene glycol bath (PEG) and treated for 30 minutes at 90°C in order to impregnate the chips further. The pressure was then released and the temperature was increased during a 60 minutes period to the effective cooking temperature. To stop the reactions the autoclaves were taken from the PEG bath and rapidly cooled in a cold water bath. Black liquor was collected from each fraction and analysed according to SCAN-N 31:94 for hydrogen sulphide ion concentration and SCAN-N 33:94 for hydroxide ion concentration. The wood residue fractions were left over night in beakers filled with deionised water. In the following treatment the fractions were defibrated, washed, screened and air dried at room temperature. The pulp containments were analysed for detection of the carbohydrate composition where the pre-treatment was according to Tappi T 249 cm-00 for sample preparation and the samples were analysed in a HPLC. Hexenuronic acid content in the pulps were analysed according to a procedure based on the article “Selective Hydrolysis of Hexenuronic Acid Groups and its Application in ECF and TCF Bleaching of Kraft Pulps” (Vourinen et. al., 1999). Kappa number was analysed according to ISO 302:2004.

Since the carbohydrate analyses are very time consuming only half of the pulps produced were analysed, namely those called 4:1(160), 4:1(170), 50:1(160) and 50:1(170).

The cooking set-ups were varied with respect to liquor-to-wood ratios, effective cooking temperature, sulphidity, EA and ionic strength. All data are given in appendices I-VIII.
3.2. Calculations

Carbohydrate content in softwood:

Cellulose = G - \( \frac{M}{3.5} \)

Glucomannan = M + \( \frac{M}{3.5} \)

Galactan + Arabinan = Gal + Ara

Xylan = X

Where:

G= glucose
M= mannose
Gal= galactose
Ara= arabinose
X= xylose

Hexenuronic Acid:

\[ n_{HexA} = \frac{A_{245 \text{ nm}} \cdot V}{\varepsilon \cdot l \cdot m} \]

Where:

\( n_{HexA} \)= mol HexA/ g bone dry pulp

\( A_{245 \text{ nm}} \)= absorbance of the solution at 245 nm

\( V \)= volume of the solution (1000 ml according to standard)

\( \varepsilon \)= molar extinction coefficient for 2-furoic acid corrected for the 90% yield of it in HexA degrading reaction, 8700 l.mol\(^{-1}\).cm\(^{-1}\)

\( l \)= 1 cm

\( m \)= pulp mass (5 g according to standard)

H-factor:

\[ H = \int_{t_0}^{t} \frac{E}{e^{\left(\frac{43.2 \cdot 16113}{T}\right)}} dt \]

Every cooking set began with pre-treatment and a one hour heating up period. This was transformed and related to the effective cooking temperature using Vroom’s H-factor eq. (1). For the set ups ran at 170°C the calculations corresponded to 9.2 minutes and for 160°C to 10 minutes.
4. Results and discussion

The profiles in figure 14 exhibit a rapid initial alkali reduction for low L/W ratios but only a moderate decrease for high L/W ratios. In the pulping experiments carried out at high L/W ratios the alkali concentration was relatively constant during the kraft cook, while the final alkali concentration in the low L/W ratio cooks was close to zero.

Figure 14. Alkali profiles versus cooking time at different L/W ratios and temperatures.
To be able to compare the alkali consumption in the pulping experiments the values had to be standardised as the ratio between consumed alkali and dissolved wood components (OH-/DWC). As could be seen in figure 15 the alkali consumption during the cooks carried out at L/W ratio 8:1 was lower than at 4:1 during the lignin residual phase compared at a given kappa number. At the highest L/W ratio, i.e. 50:1, the alkali consumption at 170°C followed the same pattern as those in the 4:1 cooks, but as the temperature was lowered the alkali consumption increased, especially in the later part of the bulk phase. The appearance could not be easily explained by a longer cooking time, as this pattern could not be seen in the lower L/W ratio cooks. But the disparity could be an analysing error. However, the mechanisms involved in a kraft cook are complicated and combinations of temperature, alkali charge and L/W ratio all seems to have an influence.

Figure 15. Consumed alkali per amount dissolved wood components vs. kappa number for the pulps produced at high and low L/W ratios and different temperatures.
According to Mortimer (1989) either the H-factor or the EA charge has to be increased in order to maintain a constant kappa number when the L/W ratio is increased, thus compensating for the dilution of the active cooking chemicals and to counterbalance the slower pulping rate. In this case, as could be seen in figure 16, the high EA charge measured as percentage on wood resulted in a higher pulping rate at high L/W ratio than at low L/W ratio where the EA charge had been lower, 200% and 21% respectively. So the EA charge increment was nearly tenfold at the high L/W ratio cooks to compensate for the dilution of the active cooking chemicals. The charged hydroxide ion concentration was 1 mol/l in the high L/W ratio cooks but 1.3 mol/l in the low L/W ratio cooks.

Figure 16. Development of the kappa number versus cooking time at high, 50:1, L/W ratio and low, 4:1, L/W ratio. The EA charge at high L/W ratio was 200% and 21% at low L/W ratio.
During the initial part of the kraft cook a large and rapid yield loss was seen (figure 17), while in the following phases the vital importance of EA charge and L/W ratio became more pronounced in the dissolution pattern. In the high L/W ratio cooks wood components could easily diffuse and remain in the liquor, while in the low L/W ratio cooks a certain fraction of dissolved components reabsorbed on the fibers.

![Figure 17. The initial yield loss in kraft cooking is large.](image-url)
4.1. Glucomannan dissolution

According to Johansson (2006) glucomannan dissolves in three phases, an initial, an intermediate and a final phase. During the initial cooking phase which involved a heating up period to the effective cooking temperature, a rapid decrease in the alkali concentration was seen. This was probably due to peeling reactions especially toward glucomannan.

As could be seen in figure 18 no significant difference in the glucomannan content was seen between the two temperatures or the L/W ratios. This study did not show any major difference between the activation energy for the glucomannan dissolution than the corresponding lignin dissolution reaction. This was in agreement with Andersson (2003) who reported activation energies for glucomannan dissolution to be 50 kJ/mol for specie 1 and 144 kJ/mol for species 2 and 3. Lignin has the activation energies: 50 kJ/mol for specie 1 and 127 kJ/mol for lignin species 2 and 3. Johansson (2006) found in his study that the glucomannan dissolution had the activation energies 70 kJ/mol in the initial phase, 121 kJ/mol in the intermediate phase and 139 kJ/mol in the final phase.

![Figure 18. Glucomannan percentage on wood vs. kappa number.](image-url)
Lignin dissolution during cooking is known to have a very rapid initial phase. The constant initial ratio between glucomannan and lignin content, encircled in figure 19, indicated that the initial reaction rate for glucomannan dissolution was about the same as for the initial lignin dissolution. Figure 19 also indicates that the amount of initial dissolved glucomannan was as extractable as lignin and not dependent on the EA charge (% ow) as the ratio for all cooks had equal value.

![Graph showing ratios between glucomannan and lignin content](image)

Figure 19. The ratios between glucomannan and lignin content in the pulp versus cooking time. During the initial phase the ratio was constant in all cooks.
When considering the reaction rates for glucomannan dissolution in the intermediate and final phases it could be seen that the rate increased with increasing L/W ratio, EA charged and increasing temperature, figure 20.

Figure 20. The glucomannan content in pulp versus cooking time.
4.2. Xylan dissolution

When the xylan content was compared to the lignin content as could be seen in figure 21, it was seen that the xylan amount was about twice as high in the pulps produced at low L/W ratio than in the pulps produced at high L/W ratio. During cooking xylan fragments of various sizes dissolved. According to the theory larger xylan fragments can redeposit onto the fibres if the alkali concentration is low. During cooking when the L/W ratio was low the amount of alkali consumed early in the cook was high and the alkali concentration then markedly decreased. The xylan content in the pulp thereby increased. At high L/W ratio only a minor amount of the hydroxide ions was consumed and the alkali concentration was therefore preserved. The action of xylan redeposition in the highly alkaline environment was then not favoured.

The appearance of the lines in figure 21 does not show any specific tendency about the activation energy for xylan dissolution but Johansson (2006) reported two xylan phases were sufficient to capture the xylan dissolution reaction, 158 kJ/mol for the initial xylan phase and 160 kJ/mol for the final xylan phase. Andersson (2003) reported three species of xylan where the activation energies were 50 kJ/mol for specie 1 and 144 kJ/mol for specie 2 and 3.

![Figure 21. Xylan percentage on wood vs. kappa number.](image-url)
When the cook was run at low L/W ratio the initial rate of xylan redeposition exceeded the initial rate of xylan dissolution and as could be seen in figure 22 the xylan content increased in the first part of the cook. Yllner and Enström (1957) also saw this happen during their experiments, but only when the alkali concentration had decreased to a very low level and at high temperatures. In the existing circumstances at high L/W ratios the xylan content continued to decrease throughout the cook.

Figure 22. Xylan percentage on wood vs. cooking time.
In alkaline environment hexenuronic acid, HexA, is formed from the methylglucoronic acid on the xylan backbone. This study showed no significant difference in the ratio of HexA to xylan content between the pulps at a certain kappa number (figure 23). However, comparisons between the cooks indicated a somewhat lower HexA to xylan ratio during the lignin bulk phase when cooking was performed at high L/W ratio, containing a very high EA charge (% ow).

Figure 23. HexA/ xylan content vs. kappa number.
When the HexA content instead was related to the remaining pulp weight as could be seen in figure 24 the HexA content proved to be more pronounced in the pulps produced at 4:1. HexA is known to be formed during pulping in alkaline environment, but this result indicated that there is an optimum in the relationship of HexA and EA charged. The pulps produced at 4:1 (figure 24) exhibited the largest HexA to pulp ratio where the EA charged had been lowest. Within the pulps produced at 4:1 also the sulphidity was varied. It was discovered that the highest HexA to pulp ratio was found in the pulp produced at the highest sulphidity. A high sulphidity is said to be beneficial for the carbohydrates as the delignification rate then increases. The cook would then be terminated earlier (at lower H-factor) and the carbohydrates would then be preserved. This means that the xylan content could have been larger in the pulp produced at L/W ratio 4:1 with 35% sulphidity than in the pulps produced at 4:1 with 24% sulphidity. The increased HexA content could then be explained as being associated with higher xylan content. This could be suspected when comparing figures 23 and 24, where figure 23 showed no significant difference between high L/W ratio cooks and low L/W ratio cooks as the amount of HexA was related to the amount of xylan.

Within the low HexA group in figure 24, pulps were found that were cooked at low L/W ratio, 3.5:1, and pulps cooked at high L/W ratios, 8:1 and 50:1. The difference between these pulps and the pulps produced at 4:1 was the EA charged. In a previous work made by Gustavsson and Wafa Al-Dajani (2000) the main objective was to investigate how cooking parameters affected the dissolution/degradation rate of HexA during the kraft cook of softwood. They concluded that the HexA content at a given corrected kappa number could be reduced by applying high hydroxide ion concentration, high ionic strength, low hydrogen sulphide ion concentration and a low cooking temperature. In another project based on kraft pulping of eucalyptus (Daniel et.al., 2003) it was discovered that also the L/W ratio had an impact on the HexA content. Other cooking parameters as active alkali, sulphidity and temperature were held constant. They found that the HexA content increased from L/W 3.5 to L/W 4, and then decreased for higher L/W ratios at constant kappa number 14±0.3.

Figure 24. The HexA content measured as mmol/g pulp versus kappa number. The initial EA charges measured as $m_{NaOH}/m_{wood}$ were 23% at L/W 3.5:1, 21% at L/W 4:1, 42% at 8:1 and 200% at 50:1. The sulphidities were 19% at L/W 3.5:1, 24% and 35% at L/W 4:1, 24% at L/W 8:1 and 30% at L/W 50:1.
4.3. Cellulose dissolution

It is important to distinguish between degradation and dissolution of wood components since the cellulose degradation contributes to the viscosity loss whereas dissolution is seen as the yield loss.

In the spruce wood chips the cellulose content was 44%. During the initial cooking phase the content was rapidly decreased and this phase is known to be unselective, i.e. carbohydrates are attacked to a high degree versus lignin. As the intermediate phase is reached the selectivity is enhanced. Figure 25 shows a higher cellulose yield versus a given kappa number when the temperature was decreased from 170°C to 160°C in the high L/W ratio cooks. This was in compliance with the theory suggested and thus higher activation energy was indicated for the cellulose dissolution than for lignin dissolution. However, the cellulose dissolution in low L/W ratio cooks appeared differently during the lignin bulk phase. This would probably be due to estimating errors, but as the residual phase was reached the cellulose yield in the low L/W ratio cooks also proved to be enhanced when the temperature was lowered. The activation energies reported by Johansson (2006) were in the case of cellulose dissolution reactions 153 kJ/mol for the initial phase and 151 for the final phase. Andersson (2003) reported 50 kJ/mol for specie 1 and 144 kJ/mol for species 2 and 3.

![Figure 25. Cellulose percentage on wood vs. kappa number.](image-url)
The rate of cellulose degradation is known to have higher activation energy than the delignification, thus to protect the cellulose yield the temperature should be kept as low as possible. The trend in these cooks, as could be seen in figure 26, showed that the cooks also should be processed at an appropriate alkali concentration as the cellulose content in the high L/W ratio cooks, with high initial EA charge, was low compared to the low L/W ratio cooks with lower initial EA charge.

Figure 26. Cellulose percentage on wood vs. cooking time.
4.4. Lignin dissolution

The aim of pulping is to remove the lignin content in the wood chips and to keep as much as possible of the carbohydrates in the pulp; therefore it is interesting to compare the dissolution rates for the different wood components versus lignin dissolution. The initial phase where the extractable lignin is dissolved is very rapid and has low activation energy. According to Teder (2004) the initial lignin phase is probably governed by diffusion of chemicals as the activation energy is low. Andersson et.al. (2003) have suggested that the initial activation energies have about the same value for the lignin and the different carbohydrate reactions. These diffusion controlled degradation reactions stands for a large yield loss early in the cook. During the bulk delignification most of the lignin content was dissolved as could be seen for the experiments in this study (figures 27 and 28).

Comparison between the four pulps produced at low L/W ratio (figure 27) showed a slightly more rapid delignification at ratio 3.5:1 with 19% sulphidity and 23% initial EA charge than 4:1 with 35% sulphidity and 21% initial EA charge. When the black liquor from the cook at 3.5:1 was analysed polysulphide was discovered to have been formed already from the beginning of the cook, whereas in the 4:1 cooks polysulphide was not discovered until very late in the cooks. This may have contributed to the rate improvement when cooking at 3.5:1. But it could also be an effect of the dissolved organic components speeding up the lignin dissolution in the 3.5:1 cook as the concentration presumably was higher. According to Sjödahl (2004) small molecules of dissolved organic matter from industrial black liquor improves the delignification rate when added to the white liquor. The difference in EA charged could also have contributed to the delignification improvement.

The third pulp from the left in figure 27 was cooked at L/W ratio 4:1, 24% sulphidity and 21% EA charge. The only parameter separating the two lines in the middle was hence the sulphidity where the higher value contributed to a slightly more rapid bulk delignification. As the residual phase was reached the two lines converged. All these three pulps were cooked at 170°C. When the temperature was lowered to 160°C, represented by the line to the right, the delignification was delayed (figure 27).
Figure 27. Lignin percentage on wood vs. cooking time at low L/W ratios. The denomination 3.5:1(170) stands for 3.5:1 at L/W, cooking temperature at 170°C, 23% EA and 19% sulphidity. 4:1(35%) stands for 4:1 at L/W, cooking temperature at 170°C, 21% EA and 35% sulphidity. 4:1(170) denotes 4:1 at L/W, cooking temperature at 170°C, 21% EA and 24% sulphidity. 4:1(160) denotes 4:1 at L/W, cooking temperature at 160°C, 21% EA and 24% sulphidity.
In figure 28 pulping at L/W ratios 8:1 and 50:1 are shown. It seems that the bulk delignification (prevailing down to kappa ~20-30, i.e. the first rapid part of the curves in the figure) was almost independent of the L/W ratio, the EA and the sulphidity. For the ratios 8:1 and 50:1, the charged EA were 42% and 200% respectively and the sulphidity were 24% and 30% respectively. The only parameter that separated the cooks was the temperature. One way to interpret the appearance of the bulk delignification at high L/W ratios was that when the liquid volume was large the delignification was affected to a minor extent by the diluted dissolved wood components.

According to Lindgren and Lindström (1996) the residual delignification is almost unaffected by the hydroxide ion concentration but strongly influenced by the temperature. The present experiment showed that when the residual phase was reached the two pulp samples at 170°C gave diverting results which could be interpreting as an alkali dependency also in the residual phase. This contradicts the results of Lindgren and Lindström (1996). The same pattern was also seen for the two pulps produced at 160°C in figure 28.

Figure 28. Lignin percentage on wood vs. cooking time at high L/W ratios. The denomination 50:1(170) stands for 50:1 at L/W, cooking temperature at 170°C, EA at 200% and sulphidity at 30%. 8:1(170) denotes 8:1 at L/W, cooking temperature at 170°C, 42% EA and 24% sulphidity. 50:1(160) denotes 50:1 at L/W, cooking temperature at 160°C, EA at 200% and sulphidity at 30%. 8:1(160) denotes 8:1 at L/W, cooking temperature at 160°C, 42% EA and 24% sulphidity.
5. Conclusions

- A rapid alkali consumption at low L/W ratio resulted in decreased alkali concentration, whereas at high L/W ratio the alkali concentration was nearly constant during the cook.
- In the high L/W ratio cooks dissolved wood components could easier diffuse into the black liquor whereas dissolved wood components in the low L/W ratio cooks were hindered to diffuse by the limited amount of liquor. The dissolved material dwelled by the fibres and could redeposit onto the fibres resulting in an increased yield.
- The dissolution of glucomannan did not show any significant difference between the varied L/W ratios. No differences could either be associated to varied temperature nor varied EA charge.
- Reactions involving xylan acted differently in high and low L/W ratio cooking experiments. The alkali concentration was rapidly decreased in the low L/W ratio cooks which proved to be beneficial for xylan redeposition. This could not be seen in the high L/W ratio cooks as the alkali concentration was rather constant.
- Simultaneously as the amount of xylan increased, the amount of hexenuronic acid increased. No significant difference in the HexA to xylan ratio was seen between the low and high L/W ratio cooks.
- The cellulose yield increased when the temperature and the L/W ratio decreased.
- The delignification rate proved to be more rapid at high L/W ratio. This was due to the higher EA charged in the high L/W ratio cooks and to lignin redeposition in the low L/W ratio cooks.

In the present study differences was seen between the pulps produced but it is difficult to decide whether the differences originate from the difference in L/W ratio or the varied alkali concentration. To be able to distinguish between these two parameters the experimental work should have been concentrated only to two L/W ratios, for example 4:1 and 50:1.
6. References

• Yllner, S.; Enström, B., Studies of the adsorption of xylan on cellulose fibres during the sulphate cook. Svensk Papperstidning 1957, 15, 549-554.
• http://www.medact.se/t_papper/artikel_detalj.asp?Artikel_Kod=245&Sid_kod=papper (2006 01 20)
Appendix I

L/W ratio 3.5:1
Temperature 170°C
Wood 320 g
Liquor 1.12 l
Chemicals charged [OH\(^-\)] 1.65 mol/l  [HS\(^-\)] 0.176 mol/l  [Na\(^+\)] 1.8 mol/l  EA 23%  S 19%

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<th>[OH(^-)] (mol/l)</th>
<th>[HS(^-)] (mol/l)</th>
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**Appendix II**

L/W ratio 4:1  
Temperature 170°C  
Wood 320 g  
Liquor 1.28 l  
Chemicals charged [OH⁻] 1.31 mol/l  
[HS⁻] 0.176 mol/l  
[Na⁺] 1.5 mol/l  
EA 21%  
S 24%  

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## Appendix III

L/W ratio 4:1  
Temperature 160°C  
Wood 320 g  
Liquor 1.28 l  
Chemicals charged  
- [OH\(^-\)] 1.31 mol/l  
- [HS\(^-\)] 0.176 mol/l  
- [Na\(^+\)] 1.5 mol/l  
EA 21%  
S 24%

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<th>Hydrogen sulphide ion consumed/DWC (mol/l)</th>
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<th>Galactan, arabinan (% ow)</th>
<th>HexA (mmol/g pulp)</th>
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Appendix IV

L/W ratio  4:1
Temperature  170°C
Wood  320 g
Liquor  1.28 l
Chemicals charged  [OH⁻] 1.31 mol/l  [HS⁻] 0.278 mol/l  [Na⁺] 1.5 mol/l  EA 21%  S 35%

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<th>[HS⁻] (mol/l)</th>
<th>Alkali consumed/DWC (mol/g)</th>
<th>Hydrogen sulphide ion consumed/DWC (mol/l)</th>
<th>Yield (%)</th>
<th>Kappa number</th>
<th>Yield/kappa number</th>
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Appendix V

L/W ratio 8:1
Temperature 170°C
Wood 150 g
Liquor 1.2 l
Chemicals charged [OH\(^-\)] 1.31 mol/l [HS\(^-\)] 0.176 mol/l [Na\(^+\)] 1.5 mol/l

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Lignin (% ow) | HexA (mmol/g pulp)
---|----------------|
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3.67 | 0.0272
1.80 | 0.0158
1.07 | 0.0078
0.61 | 0.0026
0.49 | 0.0018
0.39 | 0.0014
Appendix VI

L/W ratio  8:1
Temperature  160°C
Wood  150 g
Liquor  1.2 l
Chemicals charged  [OH\(^-\)] 1.31 mol/l  [HS\(^-\)] 0.176 mol/l  [Na\(^+\)] 1.5 mol/l

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EA 42%  S 24%
### Appendix VII

L/W ratio 50:1  
Temperature 170°C  
Wood 40 g  
Liquor 2.0 l  
Chemicals charged  
- $[\text{OH}^-]$ 1.0 mol/l  
- $[\text{HS}^-]$ 0.176 mol/l  
- $[\text{Na}^+]$ 1.5 mol/l  
EA 200%  
S 30%

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### Appendix VIII

L/W ratio 50:1  
Temperature 160°C  
Wood 40 g  
Liquor 2.0 l  
Chemicals charged [OH⁻] 1.0 mol/l  
[HS⁻] 0.176 mol/l  
[Na⁺] 1.5 mol/l  
EA 200%  
S 30%

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<th>Cellulose (% ow)</th>
<th>Glucomannan (% ow)</th>
<th>Xylan (% ow)</th>
<th>Galactan, arabinan (% ow)</th>
<th>HexA (mmol/g pulp)</th>
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