RESEARCH REPORT

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High yield nucleophile cooking of wood chips

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Report's title

High yield nucleophile cooking of wood chips

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Summary

The objective of Thesis was to study the effect of the sulphite cooking at pH 6-8 on the total pulp yield. The idea was that in neutral cooking conditions strong nucleophiles like sulphite ion are able to dissolve lignin while the carbohydrates are preserved in a high extent. In neutral conditions the acid-base- catalyzed degradation of carbohydrates is significantly slowed down, which leads to a high pulping yield.

The cooking experiments produced high kappa pulps with high yield. The target kappa number 50 was reached by cooking pine chips at 180°C during 240 minutes using 30% Na_2SO_3-charge and 0.1% AQ-charge, and the initial pH 8. Lower kappa number was possible to obtain by using higher chemical charge, higher temperature or longer cooking time. The advantages of these pulps are the high cooking yield, which was 55% at kappa number 50, and also the high brightness, over 60% ISO. However, the pulp viscosity was decreased considerably during the cooking. The pulp cooked to kappa number 59 was delignified further with one and multiple oxygen delignification stages. This decreased the brightness of the pulp under 40% ISO, but the yield and the viscosity were maintained. The bleaching sequences tested DEDED, DE$_p$DP, and DED resulted in pulps with brightness of 89% ISO and 87% ISO. The disadvantage of the bleaching was the high chemical consumption, though the pulp properties were maintained. The total yields of the bleached pulps calculated on wood were between 48-53%.

The chemical composition analysis made from the selected pulp samples confirmed that the yield increase was mainly due to high retention of glucomannans. The sulphonic acid groups content measured from the cooked pulps were 250-300 mmol/kg, which indicates that the sulphonic acid groups are also attached to the carbohydrates. However, further experiments are needed to confirm this. Also deeper analyses are needed to find out the application possibilities of the fibres and the dissolved lignin fragments relative to the possible neutral sulphite biorefinery concept.

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Preface

This Master's Thesis was conducted at VTT, Technical Research Centre of Finland during the period of 1.2-30.11.2012. The work was part of EffFibre research program run by Finnish Bioeconomy Cluster.

The goals of the EffFibre program are to increase availability and supply of high quality raw material from Finnish forests in a sustainable and cost-efficient manner, to increase the utility value of domestic raw material and to improve the competitiveness on the whole forest cluster by developing radically new energy and resource efficient chemical pulping technologies and by fining means to reduce the capital intensiveness of the cluster.

The aim of thesis was to increase cooking yield by using strong nucleophiles in neutral conditions. The main target was to study the effect of sulphite cooking at neutral pH on cooking yield and other pulp properties. In this report the literature review and experiments related to this study are presented.

The authors would like to acknowledge the financers of the project (Finnish Bioeconomy Cluster FIBIC Oy), the Management Group of EffFibre –program, and the Steering group of WP6 Future pulp mill concept. Especially the author would like to acknowledge the supervisor of this work Professor Tapani Vuorinen (Aalto University), and the instructors Antero Varhimo (VTT) and Elina Warsta (UNECE/ Food and Agriculture Organization). The author express appreciation to the personnel of VTT and Aalto University involved in the experimental part of the project and for their professional contribution: Marjo Määttänen, Sari Asikainen, Marjatta Erkkilä, Jarna Teikari, Jari Leino, Markku Suikka and Juha Haakana from VTT, and Markus Paananen, Karoliina Junka and Rita Hatakka from Aalto University.

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LITERATURE PART

ABBREVIATIONS

SO_3^{2-}	sulphite ion
HS^-	hydrogen sulphide ion
OH^-	hydroxyl ion
HSO_3^-	hydrogen sulphite ion
$-OCH_3$	methoxyl group
CMP	chemi-mechanical pulp
CTMP	chemi-thermo mechanical pulp
TMP	thermo mechanical pulp
LCC	lignin-carbohydrate complex
SO_2	sulphur dioxide
Na_2SO_3	sodium sulphite
Na_2CO_3	sodium carbonate
NaOH	sodium hydroxide
NSSC	neutral sulphite semi-chemical
AQ	anthraquinone
NS-AQ	neutral sulphite-anthraquinone
$MgSO_4 \cdot 7H_2O$	Magnesium sulphate (Epsom salt)
H_2SO_4	Sulphuric acid
O	oxygen delignification stage
C	elemental chlorine bleaching stage
D	chlorine dioxide bleaching stage
E	alkaline extraction stage
P	hydrogen peroxide bleaching stage

1 Introduction

The availability and the price of the wood raw material are the key factors for the success of the pulping industry. The share of wood material cost of the total manufacturing cost in chemical pulps is significant in Finland covering 60-70% (manufacturing cost=total cost at mill excluding capital cost) (Diesen 2007, p. 56). The domestic wood consumption and the price are affected by several factors. The Russian round wood export tax has continued to decline the utilization of the imported wood, which has increased the domestic pulpwood consumption. The concern of the climate change has increased the interest in utilization of forests and wood not only for pulp, paper and timber production but also for the source of the carbon dioxide -neutral biofuel. (Hetemäki & Hänninen 2009). Though, it seems likely that these factors will affect both the wood consumption and the prices in Finland (Diesen 2007, p. 16).

In export markets the Finnish pulping industry is competing against the modern and high production rate pulp mills built close to the fast-growing wood plantations (Diesen 2007, p. 58). Generally, the production of pulp is heavily connected to the paper and board production, which is more dependent on the global market factors. The structural change in the communication paper (printing and writing papers and newsprint) markets and the increasing competition and supply of the paper products from Asia are weakening the competitiveness of the Finnish forest industry. Also the global economic slump is decreasing the demand and the prices of the pulp and paper products. (Hetemäki & Hänninen 2009).

The on-going structural change in the forest industry in Finland requires innovative and creative actions in order to the sector survive and prosper in the future (Hetemäki & Hänninen 2009). EffFibre –research programme (*Value through Intensive and Efficient Fiber Supply*) run by Finnish Bioeconomy Cluster is a three-year programme (2010-2013), which focuses on improving the efficient use of the high-quality raw material from Finnish forests and developing completely new types of production technologies for chemical pulping. One of the goals is to improve the efficiency by increasing yield in pulp production. (Finnish Bioeconomy Cluster 2013). This thesis is based on the idea to increase the yield by using strong nucleophiles in neutral cooking conditions.

2 Strong nucleophiles in pulping

In general all the major pulping processes are based on the reactions between nucleophiles and lignin structures, which results in lignin fragmentation by cleaving linkages between lignin units and by increasing lignin hydrophilicity (Sixta, Potthast et al. 2005, p. 165). Sulphite ion (SO_3^{2-}), hydrogen sulphide ion (HS^-), hydroxyl ion (OH^-), and the reduced form of anthraquinone, anthrahydroquinone, are all strong nucleophiles that are able to degrade lignin (Sixta, Potthast et al. 2005, p. 165; Dahlblom, Olm et al. 1989).

The aim of delignification is to remove lignin with the least amount of degradation and depolymerisation of carbohydrates, mainly cellulose and hemicelluloses (Sjöström 1981, p. 110). The damage of carbohydrates cannot be totally avoided but the nature and the extent of the reactions can be affected by cooking pH and temperature (Ingruper, Kocurek et al. 1985, p. 35). In strong alkaline conditions carbohydrates are degraded to monomeric hydroxycarboxylic acids through mechanism known as a peeling reaction and by the cleavage of glycosidic bonds. In acidic conditions the hydrolysis of glycosidic bonds is the most important reaction cutting carbohydrate chains. (Sjöström 1981, pp. 41-46). In neutral pH area these alkali and acid catalysed reactions are significantly slower, and depending on the other conditions the carbohydrates are preserved to a large extent.

In kraft pulping HS^- facilitates delignification but at the same time the alkali catalyzed peeling reaction of carbohydrates cannot be avoided. This results in low pulp yield from the wood feedstock, which is reckoned to be the most severe shortcoming of kraft pulping. There are three realistic alternatives, how the cooking yield for the paper grade pulps can be increased. These methods are delignification to a higher kappa number, accelerating delignification and reducing the carbohydrate degradation. (Stenius 2000, p. 77). The sulphite pulping process can meet all these requirements. The sulphite pulping, using sulphite and bisulphite ions as delignification agents is divided to different processes according to pH. Covering the whole pH range makes sulphite cooking a flexible process to produce pulps with alternative qualities. (Ingruber 1985).

The first sulphite process operating at pH 1-1.5, the calcium acid bisulphite process, was invented already 1860's, well before the kraft process (Ingruber 1985). However, it was not until 1950's when the sulphite process began to extend to the neutral pH area and finally the alkaline sulphite process was developed in the late sixties (Ingruper, Kocurek et al. 1985, p. VIII). During the 1960's sulphite pulping was gradually replaced by kraft pulping, which led to decreasing research work in the area of the sulphite pulping (Beatson, Heitner et al. 1984).

The quality of sulphite pulp has been considered to be the main reason for the almost disappearance of this process (Kettunen, Laine et al. 1982). The development of the recovery boiler and chlorine dioxide as a bleaching chemical in the mid-1940's also speeded up this change. Today kraft pulping is the predominant pulping process comprising more than 90% of the world pulp production. (Sixta, Potthast et al. 2005, pp. 394-395). Although, the sulphite process is not a very common pulping method today, it still has several advantages over the kraft process. It has higher initial brightness, good bleachability and higher carbohydrate yield at a given kappa number. Odour problems and the investment costs are also smaller compared to the kraft process. (Fardim 2011, p. 203).

3 Interaction of wood main components with sulphite

All wood species consist mainly of three substances, which are physically and chemically attached to each other: cellulose, hemicelluloses and lignin (Stenius 2000, p. 28). Cellulose and hemicelluloses are polysaccharides that are built up of simple sugar monomers (Sjöström 1981, p. 37). Lignin consists of aromatic phenylpropane-units (Sjöström 1981, p. 70). Besides of these three main components smaller amounts of extractives and other substances are found in wood. Its relative composition depends on the tree species, the growth zone and the wood morphology. (Stenius 2000, pp. 28-31). Figure 1 presents the average chemical compositions of Scots pine and Silver birch.

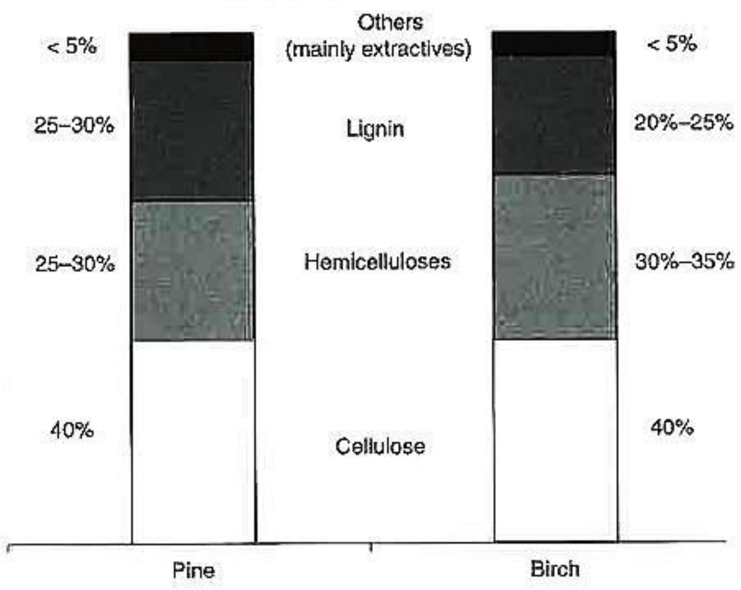
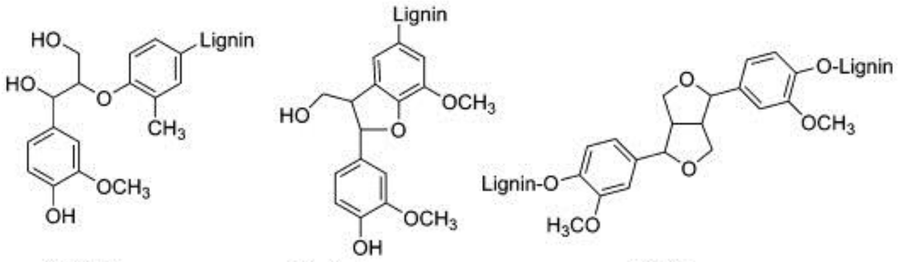


Figure 1. The average chemical compositions of Scots pine (Pinus sylvestris) and Silver birch (Betula pendula) given as % of the wood dry solids (Stenius 2000, p. 29).

Sulphite (SO_3^{2-}) and bisulphite (HSO_3^-) ions are strong nucleophiles, which are able to degrade lignin by the cleavage of the ether bonds (Sixta, Potthast et al. 2005, p. 412). It has to be kept in mind that the pH area of the various types of the reactions partly overlaps, which makes the prediction of the results of the sulphite treatment extremely difficult. Following chapter represents the more detailed structures of the main wood components and their behaviour under the sulphite pulping conditions at the neutral pH area.

3.1 Lignin

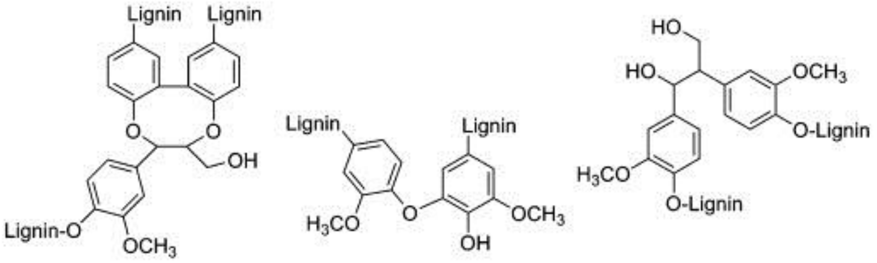
Lignin can be divided into three groups according to their chemical structure and botanical origin: guaiacyl, syringyl and p-hydroxyphenyl lignins. Guaiacyl lignin carrying one methoxyl group (-OCH_3) is the most common type of lignin in softwoods (>90%). Roughly estimated half of the hardwood lignin also consists of the guaiacyl and the other half of the syringyl lignin. (Stenius 2000, pp. 39-40). Figure 2 shows the most common linkages between these lignin phenylpropane units. Predominantly lignin is linked by ether bonds, and the other part consists of carbon-carbon –bonds (Sjöström 1981, p. 77). The β-aryl ether structure (Figure 2, a) is the most common linkage between the phenyl propane units in both hardwoods and softwoods covering 40-60% of the total linkages (Stenius 2000, pp. 40-41). Consequently its reaction must play a key role in fragmentation and dissolution of lignin (Gellerstedt 1976).



a. β-O-4
(β–ether)

b. β-5
(phenylcoumaran)

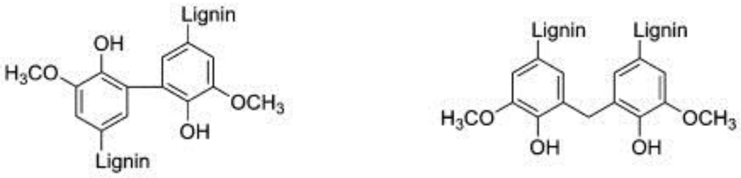
c. β–β'
(pinoresinol)



d. 5-5'–α,β-O-4'
(dibenzodioxocine)

e. 5-O-4'
(biphenyl ether)

f. β-1'
(diphenyl ethane)



g. 5-5'
(biphenyl)

h. diphenylmethane

Figure 2. The molecular structures of the lignin interunit bondings (Crestini, Crucianelli et al. 2010).

3.1.1 Lignin reactions

Under neutral sulphite pulping conditions the lignin reactions are mainly occurring in the phenolic lignin units, sulphonation being the most important reaction (Gellerstedt 1976). The reaction begins by elimination of the hydroxyl group in the α-carbon, which leads to the formation of a quinone methide structure (Ingruper, Kocurek et al. 1985, p. 32). This enables the negatively charged sulphite (SO_3^{2-}) or bisulphite (HSO_3^{-}) ions to attach to the α-carbon. The sulphonation of the α-carbon enables a nucleophile attack of the sulphite ion also to the β-carbon. (Stenius 2000, p. 83). This leads to the sulphitolytic cleavage of the β-aryl ether bond as is shown in Figure 3. However, the reaction step is strongly dependent on the pH (Gellerstedt 1976). The main reaction product formed from the extensive cleavage of the β-aryl ether bonds is styrene sulphonic acid (Gellerstedt & Gierer 1968A).

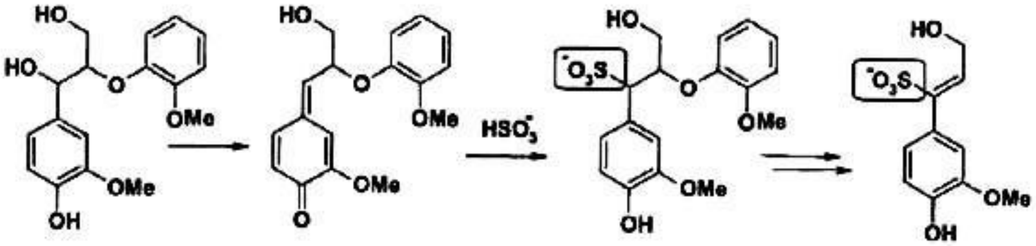


Figure 3. Sulphonation of the α-carbon leads to the sulphitolytic cleavage reaction of the β-aryl ether bond (Sixta, Potthast et al. 2005, p. 413).

Similar to kraft pulping demethylation of lignin occurs in the neutral sulphite conditions (Sixta, Potthast et al. 2005, p. 414). Methyl groups are cleaved from both the phenolic and the non-phenolic phenylpropane units. Demethylation leads to the conversion of the non-phenolic lignin into the phenolic lignin thus resulting in formation of new phenolic hydroxyl groups. (Gellerstedt & Gierer 1968A). In average even 30% increase in the phenolic hydroxyl group content is measured for softwoods after the neutral sulphite treatment (Lai & Guo 1992).

The reaction of the phenylcoumaran structure (β-5) in Figure 4 is also relevant since it covers ~10% of all the linkages in softwood lignin (Sjöström 1981, p. 77). As in the case of the β-aryl ether structure, also only the phenolic type of the β-5-structure is reacting under the neutral pH. The formation of the new phenolic hydroxyl groups and the sulphonation of the α-carbon facilitate the dissolution of lignin but do not contribute to its degradation. (Gellerstedt & Gierer 1968B). The reactions of the other linkage types are not fully known but it is thought that those reactions are unimportant because of the rareness of these structures in lignin (Gellerstedt 1976).

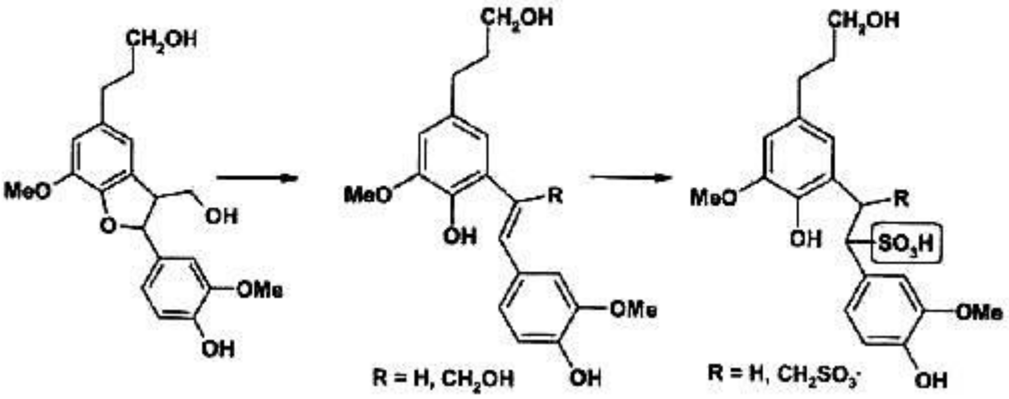


Figure 4. Sulphonation of the lignin phenylcoumaran structure (Sixta, Potthast et al. 2005, p. 413).

In theory the sulphonation should proceed as long as the lignin units having free or liberated phenolic hydroxyl groups linked by the β-aryl ether bond exist (Gellerstedt & Gierer 1968A). However, if cooking pH is decreased the benzylium ions may react with weakly nucleophilic positions of other phenylpropane units. Some extractives in softwood can also generate harmful cross-links under the sulphite pulping conditions. These condensation reactions are unwanted, since they retard or inhibit the delignification process. (Stenius 2000, p. 83). In general, hardwood lignin has lower tendency for condensation and sulphonation than softwood lignin due to the higher content of the syringyl-type lignin (Sixta, Potthast et al. 2005, p. 414).

3.1.2 The effect of sulphonation

The acidic groups in different pulp types affect the flexibility and swelling properties of the separated fibres and thus influence the pulp physical properties (Zhang, Sjögren et al. 1994). Many pulp grades contain only carboxylic acid groups but including those, sulphite pulps, CMP, and CTMP pulps contain also sulphonic acid groups (SCAN-CM 65:02; Heitner & Hattula 1988). The acidic groups in fibres are capable of ionization, which causes negative charge in the pulp fibre wall (Scallan 1983). According to the Donnan theory this negative charge attracts soluble cations but repel anions, which lead to a higher concentration of cations in the fibre wall than in the external solution. To overcome the osmotic pressure difference between the fibre wall and the external solution more water is brought to the fibre wall, which causes the fibre swelling. (Towers 1996). The Donnan theory is illustrated in Figure 5.

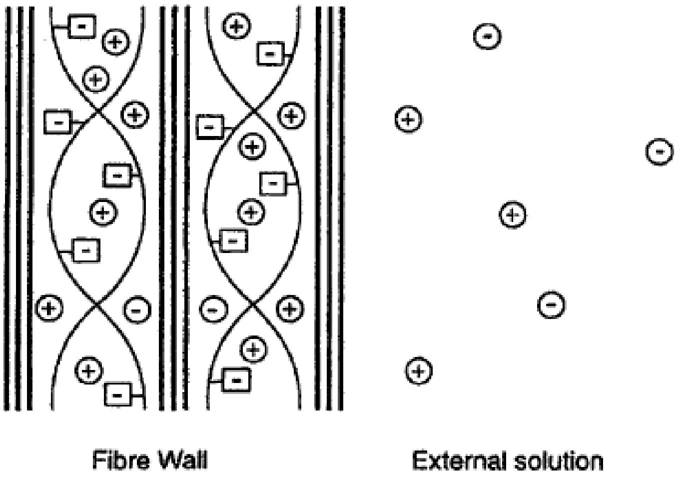


Figure 5. The higher concentration of ions in the fibre wall relative to the external solution causes swelling of the fibre wall, which continues until the osmotic pressure in the fibre wall is reduced by dilution (Towers 1996).

Untreated wood material contains only little acidic groups, 60 mmol/kg or less. Chemical treatments may cause a rapid increase in acidic group content by the hydrolysis of esters and in the case of the sulphite treatment formation of the sulphonic acid groups. (Scallan 1983). Unbleached softwood kraft pulp contains approximately 110 mmol/kg of carboxylic acids, CTMP, which is only moderately sulphonated contains 50-100 mmol/kg of sulphonic acid groups, whereas their content in almost completely sulphonated CMP is 250-300 mmol/kg (Heitner & Hattula 1988; SCAN-CM 65:02).

The sulphite treatment (pH 7.5, 140ºC, 1 h) of different softwoods species resulted in an average sulphonation of 88.0 mmol/100 g lignin. On the contrary, hardwood lignins showed more variation in degree of sulphonation ranging from 427 to 581 mmol/kg lignin for white birch and red oak, respectively. The sulphonation seemed to be hindered by the increased of methoxyl group content in lignin. (Lai & Guo 1992). The study of Lindgren showed that a rapid sulphonation of spruce sawdust occurred during the first hour at temperature 135ºC. The maximum molar ratio of sulphur to methoxyl group was 0.25-0.28 during 24 hours treatment of wood. (Lindgren 1951).

The swelling of the fibres increases their flexibility and conformability, and thus bonding between the fibres. Though, no unambiguous correlation between the total acidic groups and the tensile strength of TMP and CTMP has been found, since the effect of the other factors may also be notable. (Zhang, Sjögren et al. 1994). However, the breaking length of the high yield pulps is known to depend on the fibre quality and length. High degree of long fibres usually produces paper with low breaking length but the sulphonic acid content above 160 mmol/kg has shown significantly improved breaking length, which is shown in Figure 6. (Heitner & Hattula 1988).

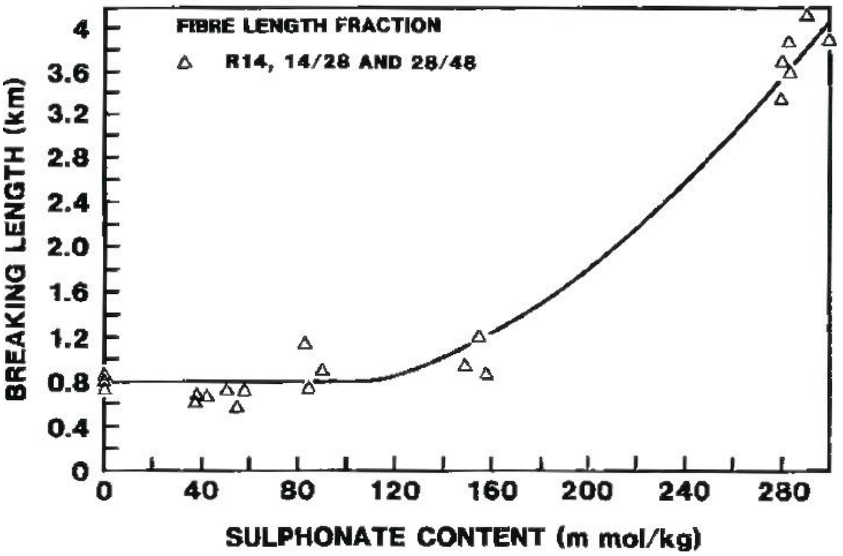


Figure 6. The breaking length of the handsheets made from the different fibre fractions of spruce CMP increases significantly after the sulphonation content of the fibres exceeds 160 mmol/kg (Heitner & Hattula 1988).

A high level of sulphonation decreases the specific scattering and opacity of the pulp, which has been attributed to the lower fine fractions content and the increased interfibre bonding. This may restrict the use of the pulp in printing papers, since refining does not improve this phenomenon. (Heitner & Hattula 1988). Figure 7 shows, how the specific scattering of the different fibre fractions behave when the degree of sulphonation increases.

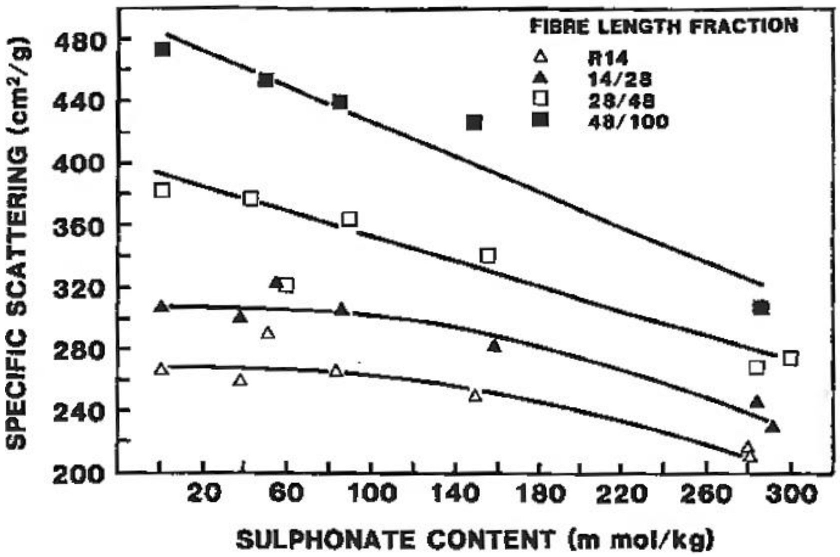


Figure 7. The specific scattering of spruce CMP fibre fractions, R14 and 14/28, decrease throughout the sulphonation range. However, the specific scattering of fibre fractions, 28/48

and 48/100 decreases only moderately until around sulphonation content 160 mmol/kg. (Heitner & Hattula 1988).

3.1.3 The effect of LCC

The physical and chemical interaction occurring between lignin and carbohydrates, generally termed lignin-carbohydrate complexes, prevents the selective delignification of the chemical pulps (Karlsson, Pettersson et al. 2001). The most part of the linkages exist between hemicelluloses and lignin though the actual type and the amount of these chemical linkages is under debate (Stenius 2000, p. 42). Only few studies report the existence of these bonds during the sulphite pulping but the difficulties in removal of the carbohydrates from lignosulphonates, the sulphonated lignin compounds, strongly support their occurrence (Karlsson 1997).

The lignin-carbohydrate complexes isolated from the unbleached spruce acid sulphite pulp showed that approximately 20% of the original lignin was chemically linked to the carbohydrates. The three major fractions were glucan-lignin, glucomannan-lignin and xylan-lignin-glucomannan complex. (Lawoko, Henriksson et al. 2006). Dialkyl ether linkages, which are formed between lignin and carbohydrates as well as internally in lignin, result in a less hydrophilic, more densely cross-linked, less soluble lignin attached to the carbohydrate. The residual lignin bounds more firmly to cellulose with increasing duration of the cooking and decreasing pulp yield. (Glasser 1981).

Both the softwood kraft pulp and the softwood bisulphite pulp contain considerable more bonds between residual lignin and cellulose than the corresponding hardwood pulps. However, the amount and the type of the bonds depend not only on the wood species but also on the pulping process. (Karlsson 1997). The different types of the LCC in sulphite and kraft pulps may explain the better bleachability of the sulphite pulps, since the LCC rich in xylan is known to degrade fast (Lawoko, Henriksson et al. 2006).

3.2 Cellulose

The main chemical component existing in wood is cellulose. It consists of β-D-glucopyranose units interconnected by 1-4-glycosidic bonds, which form a linear structure as shown in Figure 8. (Sjöström 1981, pp. 51-52). The long polymer chain in native wood can contain approximately 10 000 glucopyranose units (Stenius 2000, p. 34). The bundles of the aggregated cellulose molecules form microfibrils, which contain ordered crystallized regions, derive from the high tendency of cellulose to form inter- and intramolecular hydrogen bonds (Sjöström 1981, p. 52). These properties cause the low solubility of cellulose in most of solvents and its relative stability during chemical treatments (Stenius 2000, p. 35).

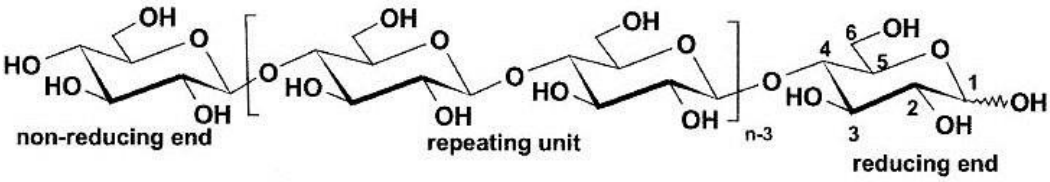
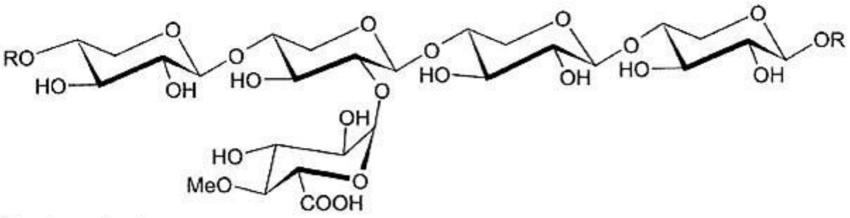


Figure 8. The molecular structure of the cellulose including the reducing and the non-reducing end-groups (Sixta, Potthast et al. 2005, p. 25).

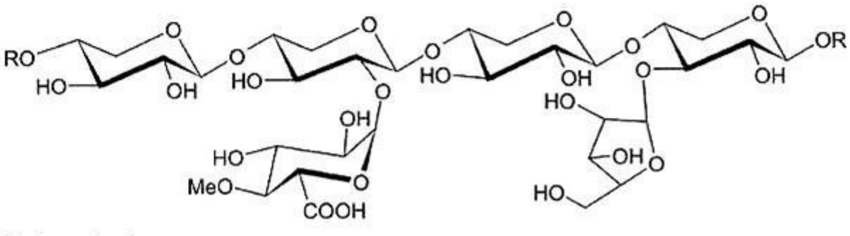
In acid and bisulphite pulping, low pH and high temperature cause hydrolysis of the 1-4-glycosidic bonds. Cellulose is degraded by the peeling reaction in the alkaline environment whereas in the acid environment the acid hydrolysis occurs. In the peeling reaction single sugar units start to cleave from the reducing end of the cellulose chain, and this proceeds until it is terminated by the stopping reaction. (Ingruper, Kocurek et al. 1985, pp. 35-36). Contrary to the carbohydrate hydrolysis in acid sulphite and the alkaline peeling reactions in alkaline sulphite pulping, at neutral pH the carbohydrate material is significantly retained (Ingruper, Kocurek et al. 1985, p. 31). Cellulose is degraded during sulphite pulping practically only when delignification is proceeded to a very low lignin content and the cooking conditions are severe enough (Stenius 2000, p. 83). Singh et al. have suggested that sulphonation of some carbohydrates could be possible (Singh, Bharati et al. 1982).

3.3 Hemicelluloses

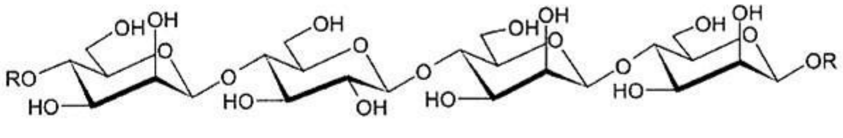
The structure and the content of hemicelluloses are different between softwoods and hardwoods covering approximately 20-30% of wood dry weight (Sjöström 1981, p. 60). In softwood the main hemicellulose components are galactoglucomannan and arabinoglucuronoxylan whereas glucomannan and glucuronoxylan are the major building blocks of hardwood hemicelluloses (Stenius 2000, pp. 36-37). The chemical structures of these hemicelluloses are presented in Figure 9. Hemicelluloses are more sensitive to the chemical and thermal degradation compared to the celluloses due to their amorphous state and low degree of polymerization (Sjöström 1981, p. 117).



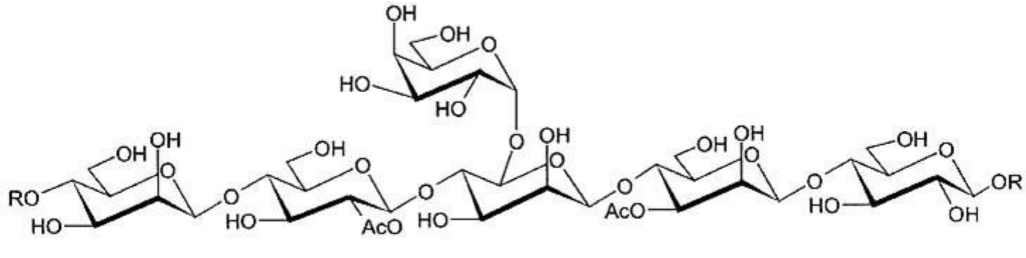
Hardwood xylan



Softwood xylan



Hardwood glucomannan



Softwood glucomannan

Figure 9. The chemical structures of the main hemicelluloses in softwood and hardwood (Sixta, Potthast et al. 2005, p. 28).

In acid medium acid hydrolysis is the main mechanism that degrades carbohydrates. Typically acid bisulphite and bisulphite pulps lose the arabinose side groups of xylan and galactose side groups of glucomannan. In strongly alkaline processes the uronic acid side chains of xylan and the acetyl side groups of glucomannan are lost more rapidly than in the acid cooks. (Kettunen, Laine et al. 1982). Close to neutral conditions are found to be the most useful for preparation pulps with high cellulose and hemicellulose content (Ingruper, Kocurek et al. 1985, p. 36). The neutral sulphite pulping or even a pre-treatment can significantly improve the yield of carbohydrates. The main reason for the high yield is thought to be a consequence of the preserved glucomannan. (Sjöström 1981, p. 118). This phenomenon is important especially for softwoods, since they contain more glucomannan than hardwoods (Annergren & Rydholm 1959).

The hydrolysis of glucomannan is thought to be so slow in neutral media, that the longer polymer chains have time to adsorb on the surface or inside the cellulose microfibrils in sufficient extent, before they are degraded to too small fragments. After this glucomannan is less accessible to acid hydrolysis if the cooking pH is decreased. The hardwood pulps cooked at neutral pH, showed no stabilization against acid hydrolysis. The glucuronic acid side chains are thought to prevent the absorbtion of xylan to cellulose. (Annergren & Rydholm 1959). Comparing pulps produced with different pulping processes it was found that the xylan content of hemicelluloses increased and the glucomannan content decreased when the cooking pH was increased. (Kettunen, Laine et al. 1982).

3.4 Extractives

Extractives are the common name for a large amount of both lipophilic and hydrophilic, low molecular weight substances (Stenius 2000, p. 43). The composition and amount varies between wood species and are also affected by the age of tree, genetic factors and growth conditions (Sjöström 1981, p. 95). Scandinavian wood species contain more extractives than those in a gentler climate. The high extractives content results from a slow growth rate. (Ek, Gellerstedt et al. 2007, pp. 152-153). Typical extractives contents of some wood species are given in Table 1. Extractives cause the specific odour, colour and taste of the wood species. In living trees some of the extractives also serve as energy source and protect the tree against microbiological damages and insects. (Stenius 2000, p. 43).

Table 1. The typical extractive contents of pine, spruce and birch presented as % of wood dry solids (Stenius 2000, p. 44).

Species	**% of dry solids**
Pine *(Pinus sylvestris)*	2.5-4.5
Spruce *(Picea abies)*	1.0-2.0
Birch *(Betula pendula)*	1.0-3.5

Pine wood is not normally used in sulphite pulping due to the high extractive content (Ek, Gellerstedt et al. 2007, p. 171). Under acid sulphite pulping conditions some of the phenolic extractives undergo condensation reactions with lignin and thus inhibit pulping of the heartwood (Sanyer, Keller et al. 1962). However, lipophilic resin components can be dispersed by the lignosulphonic acids formed from lignin (Ek, Gellerstedt et al. 2007, p. 171). Depending on the conditions some resin components may also become sulphonated, which increases their solubility into the cooking liquor (Sjöström 1981, p. 120).

The deresination in sulphite pulping occurs normally during the washing and bleaching stages. At neutral conditions resin is removed easier than in acidic conditions. (Ek, Gellerstedt et al. 2007, p. 171). The harmful condensation reactions can be avoided by cooking at low acidity or neutral pH and low temperature, which favours the sulphonation of the reactive lignin groups over the condensation reactions (Sixta, Potthast et al. 2005, p. 449). This idea was used in the two-stage sulphite pulping process called Stora process, which enabled the use of extractive rich pine wood. The pitch problem occurring in the process was overcome by a separate caustic treatment. (Lagergren 1964).

4 Cooking parameters in sulphite system

The main aims of sulphite pulping are to soften lignin and render it more hydrophilic as required for the high yield chemimechanical pulps, or to remove most part of the lignin from fibres as required for high strength and bleachable chemical pulps (Ingruper, Kocurek et al. 1985, p. 31). Ingruber & Allard have identified the sulphite liquor composition, pH and temperature to be the main factors influencing the lignin and the carbohydrate reactions and thus the delignification. However, these factors are highly interconnected why individual effects are difficult to separate. (Ingruber & Allard 1967). This chapter exposes the effects of the sulphite liquor composition, pH and temperature on delignification in the sulphite system and also their mutual relations. Anthraquinone is also presented more closely since it is an essential chemical when chemically defibrated pulp is produced.

4.1 Sulphite liquor

In a sulphite process the active chemicals are sulphur dioxide (SO_2), hydrogen sulphite ions (HSO_3^-) and sulphite ions (SO_3^{2-}). Their proportions in the cooking liquor depend on pH of the cooking liquor. (Stenius 2000, p. 78). Sulphite cooking liquor is composed of SO_2 gas dissolved in water and the base (Fardim 2011, p. 230). Thus the equilibrium of the sulphite solution is as follows:

$$SO_2(g) \leftrightarrow SO_2 + H_2O \leftrightarrow H_2SO_3$$

$$H_2SO_3 \leftrightarrow H^+ + HSO_3^-$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$$

The four soluble bases that are commonly used in the sulphite process are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and ammonium (NH_4^+) (Fardim 2011, p. 229). The process conditions and the pulp produced set some limitation for the base chosen. Calcium is soluble below pH 2.3 why it is used only in the acid sulphite process (Ingruper, Kocurek et al. 1985, p. 7). Magnesium bisulphite solution is in the soluble form up to pH 5.6 (Ingruper, Kocurek et al. 1985, p. 11). In contrast, sodium and ammonium are soluble in the whole pH range and thus they are possible bases for the alkaline sulphite process (Fardim 2011, p. 229). However, in industrial practise sodium is more commonly used than ammonium because ammonium is thermally less stable (Sixta 1998).

The base is generally needed to neutralize the acids generated during the cook (Husband 1953). Sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) are the commonly used alkalizing agents in neutral sulphite pulping. Sodium carbonate (Na_2CO_3) is used to stabilize the sulphite cooking, without a role in delignification. If the cooking is carried out in alkaline pH scale, where no sodium hydroxide (NaOH) is used sodium carbonate has the major role also in alkalizing the cooking liquor. (Kettunen, Virkola et al. 1979; Ingruber 1985). The cooking with Na_2CO_3 or NaOH enhances the removal of lignin but reduces carbohydrate retention (McDonough, Van Drunen et al. 1985).

The cooking pH decreases along with the formation of acids, which is time and temperature dependent (Husband 1953). If only Na_2SO_3 is used in the cooking liquor, the chemical charge has to be high enough, otherwise the pulp yield is lost by the acid hydrolysis of carbohydrates. The minimum Na_2SO_3 charge to keep the pH high enough was determined to be 16.5% on o.d. wood. (Pereira, Patt et al. 2011). The total chemical charge needed is always dependent on wood species, other cooking conditions, and the targeted degree of delignification. However, an excess of chemical is always required to complete cooking in a reasonable time and to prevent the harmful lignin condensation reactions. (Keskin & Kubes 1994).

McDonough et al. showed that the liquor composition has a significant effect on delignification. Delignification is fastest in the NaOH rich liquor and slowest if liquor contains only Na_2SO_3. The liquor containing 100% Na_2SO_3 removed around $^1/_3$ of glucomannan, ¼ of arabino-xylan and $^2/_3$ of lignin. Replacing 20% of Na_2SO_3 with Na_2CO_3 almost doubled the amount of glucomannan removed and reduced the residual lignin content by 50%. The same replacement with NaOH instead of Na_2CO_3 gave more effective lignin removal but also removed more carbohydrates including cellulose. (McDonough, Van Drunen et al. 1985)

Though the right adjustment of the cooking liquor has a significant importance to the delignification result, the interaction between the wood chips and pulping chemicals has to be proper (Ingruper, Kocurek et al. 1985, p. 24). The impregnation of the cooking liquor in the porous wood structure consists of two distinctive mechanisms, penetration and diffusion (Sharareh, Tessier et al. 1995).

The factors that influence the penetration of liquids into wood chips can be divided in the three main groups relating to structure of the wood chips, the cooking liquor, and the process conditions (Malkov, Tikka et al. 2003). In acidic and weakly alkaline sulphite pulping conditions the liquor penetration rate is fastest in the longitudinal direction, which makes the length of the chip to be the most critical dimension. Since fibres do not swell as in alkaline liquor, which could affect the uniformity of the cook, chips thickness does not have the same importance. (Ingruper, Kocurek et al. 1985, p. 26).

Several techniques are developed to enhance penetration by removing the air present in wood capillaries and by adding of auxiliary substances (Malkov, Tikka et al. 2003). Surfactants can improve penetration by wetting and emulsifying hydrophobic extractives. The benefits are the decreased cooking liquor consumption to achieve the same kappa number and the increased pulp yield due to the decreased amount of reject. (Wei, Ulkem et al. 2005). However, more research is needed to understand the effect of surfactants in sulphite pulping.

4.2 pH of the cooking liquor

The different modifications of the sulphite processes are classified according to their pH (Fardim 2011, p. 229). The first sulphite process invented, the acid calcium bisulphite process, operates at pH 1-1.5. The use of the more soluble bases than calcium enabled the development of the bisulphite process at the pH range of 3.5 to 8, the chemi-mechanical NSSC process at pH 7.5 to 9 and finally the alkaline sulphite process at around pH 13.5. (Ingruber 1985).

The sulphite liquor pH is determined by the proportions of the sulphite (SO_3^{2-}), hydrogen sulphite (HSO_3^-) and hydroxyl ions (OH^-) in the cooking liquor (Ingruber 1962). It has to be kept in mind also that the pH of the cooking liquor is temperature and pressure dependent (Fardim 2011, pp. 230-231). This dependence is noticed as shifts of pH, when the temperature increases or the pressure changes, which is caused by the concentration changes of the ions in the sulphite solution. When temperature is increased, pH of the acid sulphite liquor is increased, whereas in the alkaline sulphite liquors the pH is decreased during the temperature increase. (Ingruber 1962).

The aqueous system containing sulphur dioxide is strongly dependent on concentration, the strength of the cation present, temperature and pressure (Ingruber 1962). The pure sodium sulphite water solution has pH around 9.5 and thus the pH is increased by addition of the alkaline compounds (Ingruber & Allard 1973). An aqueous solution of sodium bicarbonate has pH 8.4 and sodium carbonate solution pH 11.6. To raise the pH over 11, sodium hydroxide needs to be added. (Ingruper, Kocurek et al. 1985, p. 20).

Though the use of Na_2CO_3 and NaOH to buffer pH in alkaline sulphite cooking is justified, they are unnecessary substances in the sodium sulphite pulping occurring at neutral pH. Sodium bisulphite and sodium sulphite ions can create a buffer system when their amount equals. This buffer system neutralizes acids liberated from wood toward pH 7.2 and thus prevents pH to drop considerably. (Husband 1955). Sodium ions provided by sodium sulphite molecules in the cooking liquor neutralizes dissolved lignin products, lignosulphonic acids, and acids formed in side reactions (Sjöström 1981, p. 111). When the maximum buffer capacity of the bisulphite-sulphite system is gained, primarily depends on liberation of wood acids and the amount of sodium sulphite relative to wood (Husband 1955). The relative concentration of ions in sulphite solution at 25°C and its dependence on pH is shown in Figure 10.

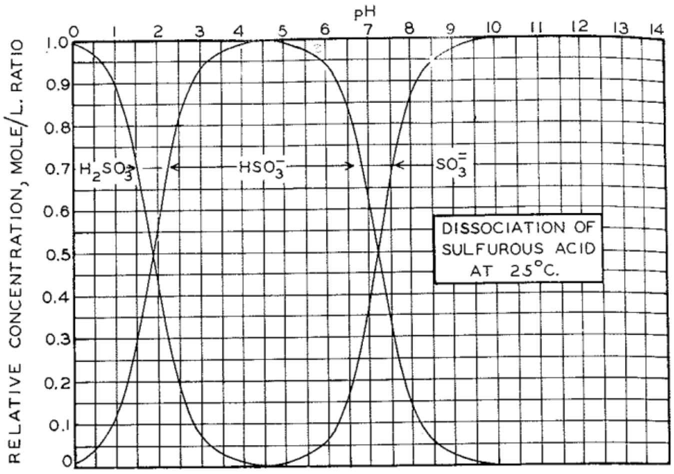


Figure 10. The proportions of sulphur dioxide (SO_2), hydrogen sulphite ions (HSO_3^-), and sulphite ions (SO_3^{2-}) and their dependence on pH (Peckham & Van Drunen 1961).

If bisulphite-sulphite buffer capacity is exceeded and the pH continues to decrease, another buffer system created by acetic acid-sodium acetate can be reached at pH around 4.75 when the amounts of these two components equals. The acetic acid liberated from wood at the beginning of the cooking is neutralized by sodium ions while the bisulphite reacts with lignin. When the concentration of acetic acid formed exceeds the concentration of sodium sulphite, this new buffer system is created. (Husband 1955).

4.3 Temperature and time

The temperature used in sulphite pulping ranges from 130ºC to 185ºC (Ingruper, Kocurek et al. 1985, p. 4). Cooking at neutral pH requires higher cooking temperature and/or longer cooking time than the acid cooks to reach the same degree of delignification (Virkola, Pusa et al. 1981). The relatively high temperature (>175 ºC) used in the alkaline and the neutral sulphite cooks is needed to reduce the cooking time closer to the cooking time of the kraft cooks (Wong 1988). It is more practical to use higher temperature than long cooking time, why the neutral sulphite cooks are generally carried out at temperature 170ºC or higher (Virkola, Pusa et al. 1981).

Delignification of softwoods takes more time and requires higher chemical charge than hardwoods, because of the higher content and molecular weight of lignin and the inaccessibility of the cell wall. Also the higher resin content can resist penetration of the cooking liquor. (Ingruper, Kocurek et al. 1985, p. 132). Although the neutral pulping process proceeds slowly, it is more selective than the kraft or the other alkaline pulping processes (Ingruber 1985). The reaction rate increases with increasing total SO_2 content and temperature. Between 120 and 150ºC the rate of the lignin dissolution was increased around 40% for every 10ºC increase in temperature. (Heitner, Beatson et al. 1982).

The rate of lignin removal in the neutral sulphite pulping differs from acid and alkaline sulphite cooking. The rate of delignification in middle lamella and secondary cell wall are equal in neutral cooking whereas in the alkaline and the acid cooks lignin is mainly removed from the cell wall in the early stages of cooks. (Ingruper, Kocurek et al. 1985, p. 29). The more recent studies with light microscopy and UV microspectrophotometry carried out under the neutral sulphite cooking, however, showed that the compound middle lamella appears to decompose while the secondary cell wall is swollen but morphologically unaffected. (Rehbein, Pereira et al. 2010).

4.4 Anthraquinone

The potential of anthraquinone (AQ) as an auxiliary substance in pulping was first noticed in 1972 (Ingruper 1985). Its rapid, generalized use in alkaline pulping industry also increased the interest toward the dying alkaline sulphite pulping process. The benefits over the kraft process in mildly alkaline sulphite pulping were the selective cooking resulting both higher yield and higher viscosity at a given kappa number. (Sixta, Potthast et al. 2005, p. 476).

The effect of AQ in alkaline pulping conditions is based on acceleration of delignification rate and stabilization of carbohydrates against alkaline peeling reactions (Keskin & Kubes 1991). In neutral sulphite cooking, where delignification is significantly retarded, production of chemically defibrated pulp would be almost impossible without AQ. It not just increases delignification rate but also reduces the chemical dose needed in cooking. (Kettunen, Virkola et al. 1979).

Many studies have been made to explain the role of anthraquinone in the delignification process of the sulphite-AQ pulping system (Dimmel 1996; Keskin & Kubes 1991; Suckling 1988). AQ is known to be very effective chemical in strongly alkaline conditions, where pH is increased up to 13-14. However, at the presence of sulphite it can act as a catalyst at pH at least as low as 7. (Suckling 1988). Though, many suggestions have been presented on the role of AQ in neutral sulphite solution, this subject seems to be still unclear.

Anthraquinone as such is insoluble in water but in the presence of wood carbohydrates it is reduced becoming soluble in alkaline aqueous solution (Sixta, Potthast et al. 2005, p. 317). Anthraquinone is believed to act as a redox catalyst, which transfers electrons from carbohydrates to lignin (Keskin & Kubes 1991). During this redox cycle shown in Figure 11 aldehyde end units of carbohydrates are oxidized, which prevents carbohydrate degradation. At the same time AQ is reduced to anthrahydroquinone (AHQ), which reacts with lignin oxidizing itself back to AQ. (Dimmel 1996).

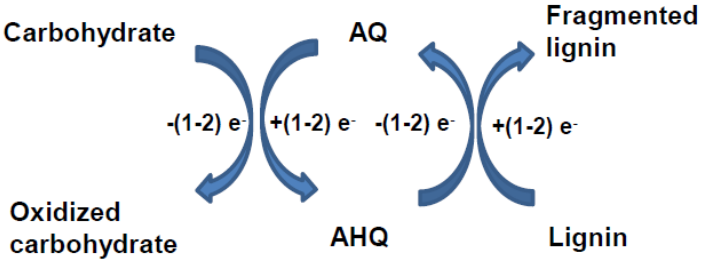


Figure 11. The redox cycle of anthraquinone with the wood components (according to (Dimmel 1996)).

However, the redox cycle presented above only functions in alkaline pH. When alkalinity is decreased, the reaction leads to formation of different type of reduced form, anthrone, and no such a strong oxidising agent exists in pulping, that could reduce anthrone back to anthraquinone. (Suckling 1988). The investigation of Keskin and Kubes showed that dissolution of the carbohydrate-free lignin with anthraquinone was not accelerated when glucose was added. It was concluded that carbohydrates do not reduce anthraquinone in sulfite liquor. (Keskin & Kubes 1991).

Suckling found that sulphite is capable to act as a reducing agent for AQ under sulphite-AQ pulping conditions. The presence of sulphite-AQ cooking side products, anthrone, sodium anthraquinone-2-sulphonate and sodium anthrone-10-sulphonate, seemed not to enhance β-ether cleavage. (Suckling 1989). Keskin and Kubes confirmed the same effect in neutral sulphite-AQ pulping. However, they suggest that the reduced AQ cleaves the β-ether aryl ether bond whereas sulphite does not. (Keskin & Kubes 1991).

Anthraquinone can be used to improve delignification of both chemical and chemi-mechanical pulping processes, which are carried out under neutral or alkaline conditions (Chen, Ghazy et al. 1994). Already small amounts of anthraquinone (0.02-0.05% on wood) were found to accelerate pulping of the softwood NSSC pulps (Fleming, Barbe et al. 1984). In case of neutral sulphite pulping the amount of anthraquinone sufficient to improve delignification is 0.1-0.2% on wood (Virkola, Pusa et al. 1981). The effect of the AQ dose is shown in Figure 12.

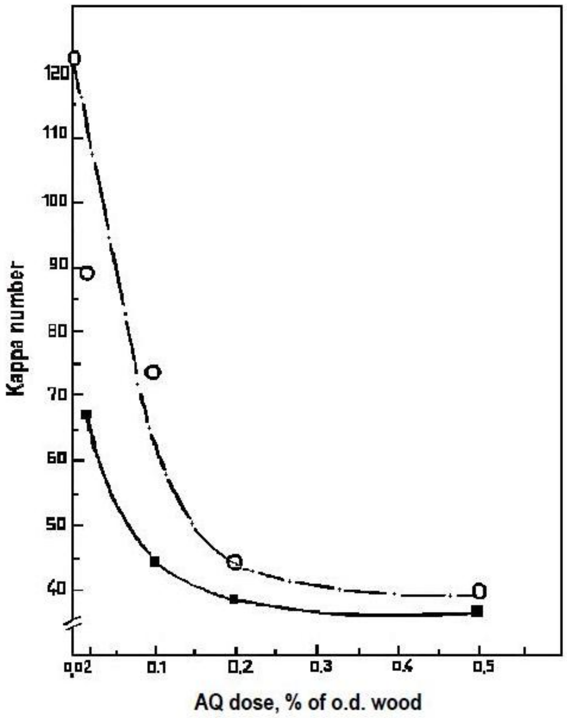


Figure 12. The effect of AQ dose on the delignification in neutral sulphite cooking of spruce. The conditions were for ○ total alkali 19.4% as NaOH, alkali ratio 0.80, for ■ total alkali 21.9%, alkali ratio 0.94. Both cooks were carried out at temperature 160°C during 420 min. Figure modified from (Virkola, Pusa et al. 1981).

5 Sulphite based processes near neutral pH area

Figure 13 presents the different pulping processes classified by the cooking pH. It can be seen that sulphite pulping covers the whole pH range. It is used in the wide range of different pulping processes producing both high yield chemi-mechanical as well as bleachable chemical pulps having comparable properties with kraft pulp. (Ingruber 1985). This versatility of the sulphite process enables a high flexibility in pulp yields and properties (Stenius 2000, p. 78). This chapter presents the sulphite-based processes near neutral pH area, the neutral sulphite-anthraquinone (NS-AQ) and the neutral sulphite semi-chemical (NSSC) processes. The multiple stage sulphite processes containing one neutral stage have been introduced with some insides of the future sulphite-based biorefinery but with a minor attention.

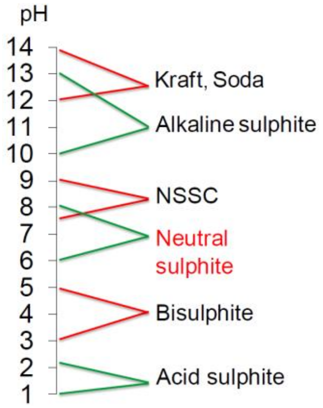


Figure 13. pH scale and the different pulping processes operating in the varying pH areas.

5.1 Neutral sulphite and neutral sulphite anthraquinone cooking

According to Ingruber neutral sulphite process is carried out at cold pH<10 using mainly Na_2SO_3 and Na_2CO_3 as cooking chemicals (Ingruber & Allard 1973). The interest toward NS-AQ process was raised in Finland in 1980's, when also a significant amount of research material has been published. At that time the disadvantages of the kraft process was seen the high investment costs, the low pulp yield, the poor bleachability and beatability of the pulp, and the odour problems. (Kettunen, Virkola et al. 1979).

The characteristics of neutral sulphite process are low rate of delignification and high pulping temperature (Gellerstedt 1976). The most dominant characteristic of NS-AQ pulps is the significantly increased yield, which makes the process more economical (Kettunen, Virkola et al. 1979; Virkola, Pusa et al. 1981). NS-AQ pulp is considered strong enough for many paper grades (Kettunen, Virkola et al. 1979). The mildly alkaline conditions in NS-AQ pulping produce stiff fibres, which have a good bonding ability due to long and branched hemicellulose chains (Kettunen, Laine et al. 1982).

5.1.1 Cooking variables

The main factors influencing the result of NS-AQ cooking are total alkali charge, alkali ratio (Na_2SO_3:(Na_2SO_3+Na_2CO_3)) and AQ charge (Virkola, Pusa et al. 1981). The neutral sulphite cooking liquor consists mainly of Na_2SO_3 containing some parts of Na_2CO_3 (Kettunen, Virkola et al. 1979). To produce chemically defibrated paper pulp anthraquinone is a necessary substance, which both speeds up delignification and enables the delignification further (Tulppala 1984). Only small amount of anthraquinone, 0.1-0.2%, is needed to significantly improve the delignification (Virkola, Pusa et al. 1981).

The optimum sulphite charge to reach the maximum delignification of the pine NS-AQ pulp was determined 80-85% of the total alkali charge (Kettunen, Virkola et al. 1979). Figure 14 shows the development of kappa number in the case of spruce NS-AQ pulping, when the total alkali charge and the alkali ratio have been varied (Virkola, Pusa et al. 1981). The same alkali ratio was found optimal also for the birch NS-AQ cooking (Ojanen, Tulppala et al. 1982). If the liquor contains only Na_2SO_3, the rate of delignification is slow but the most selective one. Using the optimal alkali ratio, 80-85%, lignin removal and viscosity retention are improved yet the pulp yield is lower. If more than 20% of the total alkali consists of Na_2CO_3, the viscosity of pulp is still improved but both delignification and the yield are deteriorated. (McDonough, Van Drunen et al. 1985).

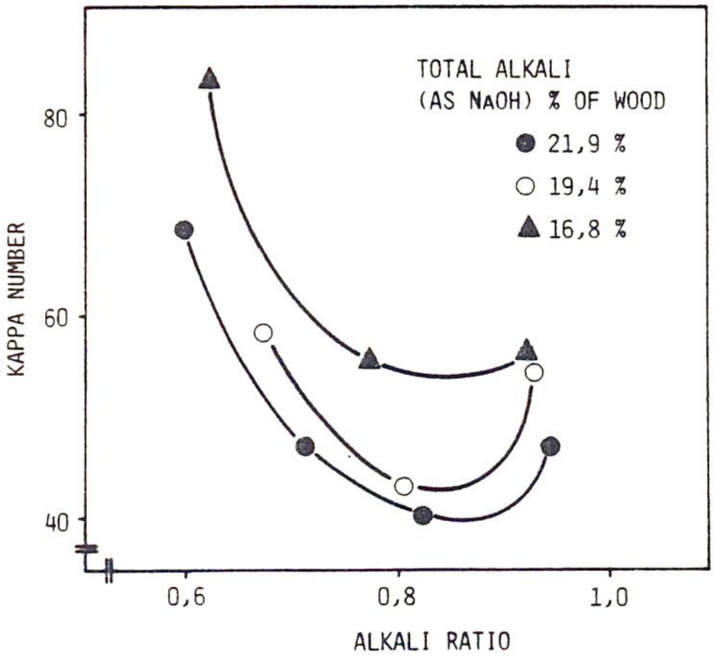


Figure 14. The effect of the total alkali charge and the alkali ratio on spruce NS-AQ pulping. The AQ charge was 0.2 % on o.d. wood. (Virkola, Pusa et al. 1981).

It is possible to use relatively high cooking temperature in NS-AQ process without deteriorating pulp yield or pulp properties considerably (Tulppala 1984). The temperature increase from 170ºC to 180ºC was not noticed to have any effect on the pulp yield-kappa number ratio or the pulp properties, but the cooking time shortened from 240 min to 130 min (Virkola, Pusa et al. 1981). The cooking time in the NS-AQ cook was approximately twice of the cooking time in the kraft cook, when the NS-AQ pulp was cooked to kappa number 40 at 175ºC and the kraft pulp to kappa number 30 at 170ºC. Cooking time was approximately 205 minutes to reach the kappa number between 40 to 45 by using alkali charge 24% (as NaOH) and alkali ratio 83%. (Tulppala 1984).

The proceeding of the delignification in the different stages of cooking, the initial, the bulk and the residual stage is presented in Figure 15. It is clearly seen that the yield advantage of the NS-AQ pulping is gained during the selective bulk delignification stage. At the end of this stage the carbohydrate yield is 10.5%-units higher compared to the kraft cook. In the case of the birch NS-AQ cooks the selectivity of the bulk delignification is not as clear as for pine. (Ojanen, Tulppala et al. 1982). In the residual stage the removal of lignin results in a significant carbohydrate loss, hence cooking to low kappa numbers decreases the total yield (Tulppala 1984). The slow and non-selective delignification in the residual stage is not fully understood (Virkola, Pusa et al. 1981). One reason might be the more specific delignification in the middle lamella than in the fibre wall. The preserved hemicelluloses in their original location may prevent the large lignin fragments from diffusing out through the fibre wall. (Kettunen, Laine et al. 1982).

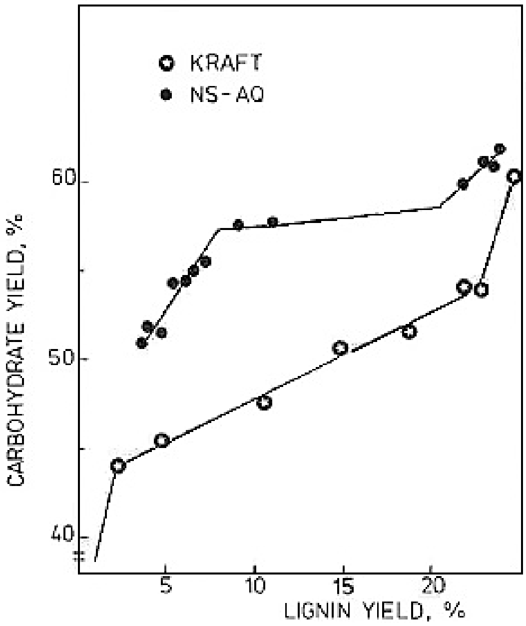
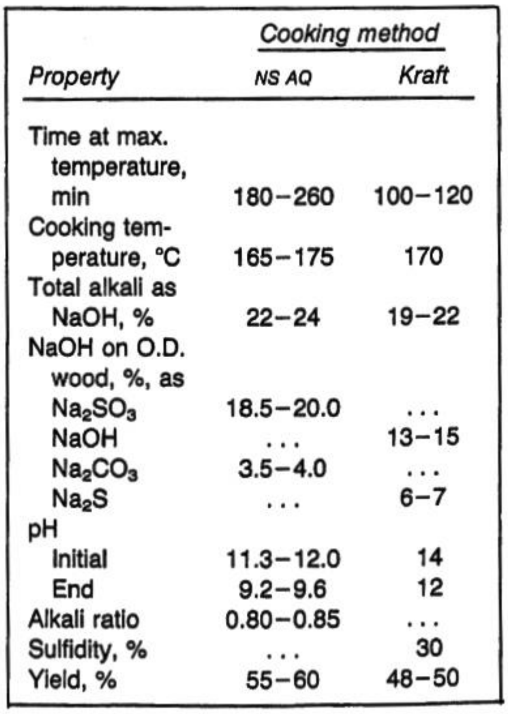


Figure 15. Carbohydrate yield as a function of lignin yield in pine NS-AQ and kraft cooks (Ojanen, Tulppala et al. 1982).

It is possible to produce chemically defibrated pulp with a kappa number of 40-50 under different NS-AQ cooking conditions, which are shown in Table 2 (Virkola, Pusa et al. 1981). Delignification to lower kappa numbers is difficult with reasonable process conditions since the delignification of pine is significantly slowed down at kappa number around 45, or lignin content of about 7%. The retardation of delignification was also seen for birch at kappa number 40. It is suggested that the slowdown of the delignification at a relatively high kappa number is caused by the consumption of the remained sulphite in the reactions with already dissolved lignin or in the reactions with undissolved lignin without making it soluble. (Kettunen, Virkola et al. 1979). According to this increasing the Na_2SO_3 charge and prolonging the cooking time can accelerate the delignification to lower kappa numbers (Virkola, Pusa et al. 1981). Increasing the alkalinity of the liquor or raising the cooking temperature has also suggested but at the same time more carbohydrates are removed resulting lower pulp yield and viscosity (McDonough, Van Drunen et al. 1985).

Table 2. General pulping conditions of NS-AQ and kraft pulping (Virkola, Pusa et al. 1981).



	Cooking method	
Property	*NS AQ*	*Kraft*
Time at max. temperature, min	180–260	100–120
Cooking temperature, °C	165–175	170
Total alkali as NaOH, %	22–24	19–22
NaOH on O.D. wood, %, as		
Na_2SO_3	18.5–20.0	. . .
NaOH	. . .	13–15
Na_2CO_3	3.5–4.0	. . .
Na_2S	. . .	6–7
pH		
Initial	11.3–12.0	14
End	9.2–9.6	12
Alkali ratio	0.80–0.85	. . .
Sulfidity, %	. . .	30
Yield, %	55–60	48–50

5.1.2 Oxygen delignification and bleaching

Oxygen is commonly used in the post-delignification stage ahead of the bleaching sequences in the pulp manufacturing. Since the oxygen stage is more selective than the final cooking phase removing 40-65% of the lignin, it is an attractive option for the high kappa pulps prior the final bleaching. (Fardim 2011, pp. 552-553). It was mentioned earlier that cooking of NS-AQ pulps was significantly retarded around the kappa number 40 (Kovasin, Kettunen et al. 1987). If fully bleached NS-AQ pulp is produced, it is necessary to carry out the oxygen delignification. Otherwise the yield advantage obtained during the cooking may be lost in the post-delignification stage. (Kettunen, Virkola et al. 1979). The lower pulp lignin content is also beneficial considering the chemical consumption and the bleaching effluent load (Kovasin, Kettunen et al. 1987).

The primary process variables affecting oxygen delignification are alkali charge, pH, temperature, retention time, oxygen pressure, and pulp consistency (Fardim 2011, p. 553). The process parameters of softwood kraft pulp and NS-AQ pulps in the single-stage oxygen stage are compared in Table 3. They seem to be quite equal apart from the alkali charge, which is higher for the NS-AQ pulp. However, not only the process variables but also the conditions at the previous cooking stage and the unbleached pulp properties are known to have a significant impact on the oxygen delignification efficiency (Lai, Luo et al. 1998).

Table 3. Comparison of the process conditions of single-stage oxygen delignification systems for softwood kraft and NS-AQ pulps (Fardim 2011, p. 556; Kettunen, Virkola et al. 1979).

	Kraft	NS-AQ
Consistency, %	10-14	11.8
Pressure, bar	7-8	8
Retention time, min	50-60	55 (1
Max. temperature, °C	85-105	100-110
Alkali charge, % on o.d. pulp	2.2-3	3.5-5.8
$MgSO_4 \cdot 7H_2O$, % on o.d. pulp	0.1-0.2	0.5

(1 Time to max. temperature 25 min and time at max. temperature 30 min.

All the alkaline pulps in Figure 16 seem to have a rapid initial phase at the beginning of the oxygen delignification, which is completed within one hour reaction at 100°C (Lai, Luo et al. 1998). The role of the lignin phenolic units is thought to be central for the efficiency of the oxygen delignification stage. Uncondensed phenolic units are known to be responsive to oxidation while the condensed phenolic units are found to react slowly (Argyropoulos & Liu 1998). The content of the phenolic hydroxyl groups in the residual kraft lignin showed to have a direct impact on the delignification efficiency, but the same relation was not valid for NS-AQ pulp, though it contains relatively high amount of the phenolic units. Not only the content but also the chemical nature of the phenolic units seemed to affect the reactivity of the residual lignin (Lai, Luo et al. 1998).

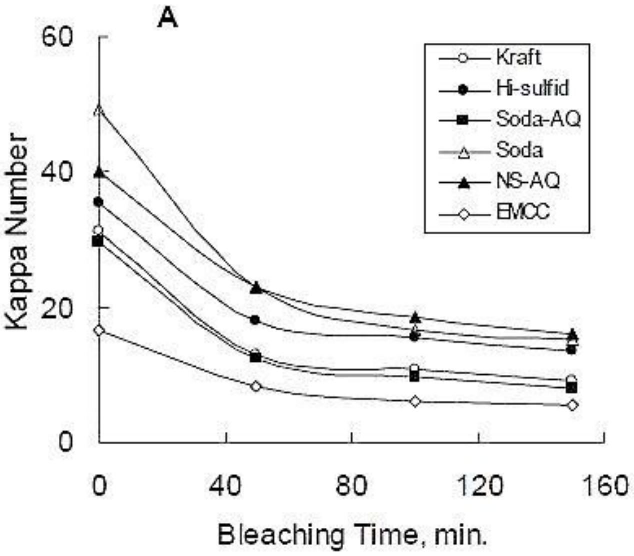


Figure 16. Oxygen delignification rates of different alkaline pulps. The process was carried out using 3% consistency and alkali charge of 5% in the presence of $MgSO_4$ (0.5%) at 100°C for different durations. (Lai, Luo et al. 1998).

Some alternative methods to replace the conventional oxygen delignification have also been presented to continue delignification after cooking. Kovasin et al. have tested hydrostatic oxygen delignification for the NS-AQ pulp, which is a milder process than the normal pressurized method. The oxygen pressure was varied from 4 bar to zero, which resulted in

30% delignification in 60 min and 40% delignification in 120 min. (Kovasin, Kettunen et al. 1987). The ozone-stage is also proposed to be an alternative stage instead of the oxygen delignification. Results showed that ozone affects more the brightness of the sulphite pulps than oxygen increasing it 5-8 units. Only a small charge of ozone is needed to remove 60-70% of lignin. The kappa number was reduced from 30 to about 10 using only 1% ozone charge. However, oxygen and ozone are both aggressive chemicals toward cellulose resulting in decrease of the pulp viscosity. (Låras & Soteland 1982).

It is known that the NS-AQ pulps cannot be cooked to very low kappa numbers under reasonable conditions (Kovasin, Kettunen et al. 1987). The idea of the lignin preserving bleaching of the high yield pulps is to remove the chromophores and the leucochromophores occuring either by oxidation or by reduction. Sodium or zinc dithionite represents the reducing bleaching, which is carried out at 50-60°C for 1-2 hours using 0.5-1% chemical charge. (Sjöström 1981, pp. 165-166). Hydrogen peroxide is almost exclusively used in the oxidative bleaching of the high yield pulps. Peroxide bleaching is carried out at initial pH of 11 at 50-60°C for 3-4 hours. The brightness increase depends on the peroxide charge and can sometimes be even 25% ISO. Figure 17 presents the brightness development of different pulp types as a function of peroxide consumption. (Sjöström 1981, p. 167).

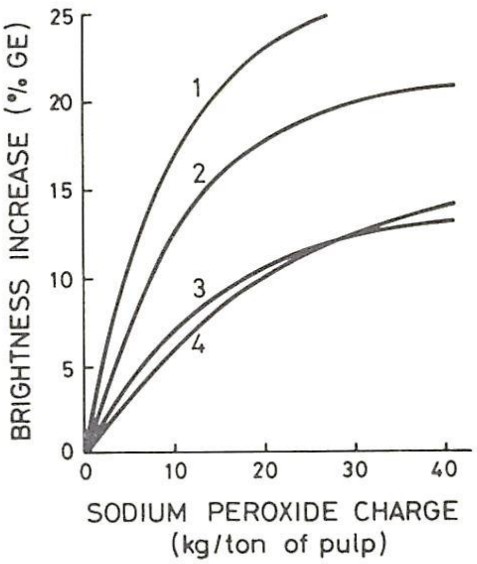


Figure 17. Brightness increase of different pulp types as a function of sodium peroxide charge: 1 semichemical (cold alkali) hardwood, 2 acid sulphite softwood, 3 mechanical spruce, 4 semichemical (neutal sulphite) hardwood pulp (Sjöström 1981, p. 167).

Bleachability of the NS-AQ pulps is known to be good. NS-AQ pulps are easier to bleach than kraft pulps and they also require less bleaching chemicals regardless of the high kappa number in the most cases after cooking. (Kovasin, Kettunen et al. 1987). McDonough et al. have bleached Southern Pine NS-AQ pulp with the three-stage bleaching sequence CED obtaining pulp with 89% ISO brightness (McDonough, Van Drunen et al. 1985). The pine NS-AQ pulps at kappa number 25-39 were bleached with the 5-stage (D30C70)EDED sequence to a target brightness of 89% ISO. The active chlorine consumption was in the level of about 2.1-2.3 kg/kappa unit reduction which was about 20-30% smaller compared to the reference sulphate pulp. (Nikki & Pekkala 1986). Environmental concern in the 1980’s related to the high content of the chlorinated organic compounds (AOX) in the bleaching effluents and the pulp products lead to replacement of the chlorine in the C-stage with chlorine dioxide and development of the totally chlorine-free (TCF) sequences (Fardim 2011, p. 465).

The above-mentioned NS-AQ bleaching cases were performed without any post-delignification stages after cooking. The pine NS-AQ pulps at kappa number 31-38 were further delignified with O-, EO-, or P-stage, after which the pulps were bleached with (D85C15)(EO)D sequence to 85-86% ISO brightness. The active chlorine consumption was 0.29-0.37% depending on the starting kappa number level. However, the active chlorine consumption seemed to be independent of the delignification treatment after cooking. (Nikki & Pekkala 1986). Kettunen et al. (1979) have also studied shorter sequences by bleaching the pine NS-AQ pulp at kappa number around 35 to 84.4% ISO brightness with bleaching sequences of ODP and to brightness of 88% ISO with ODED (Kettunen, Virkola et al. 1979).

5.1.3 Pulp properties

Unbleached pulp

The total yield of the pine NS-AQ pulp was 8-10% higher and the total yield of the birch NS-AQ pulp 6-8% higher than the corresponding kraft cooks (Ojanen, Tulppala et al. 1982). The high yield results from the mild cooking conditions and the selective delignification especially in the bulk stage of the cooking, which preserve hemicelluloses (Virkola, Pusa et al. 1981). The average yields of NS-AQ, alkaline sulphite and kraft pulps are compared in Figure 18, which shows the increasing yield advantage of the NS-AQ pulps with increasing kappa number (Kettunen, Virkola et al. 1979).

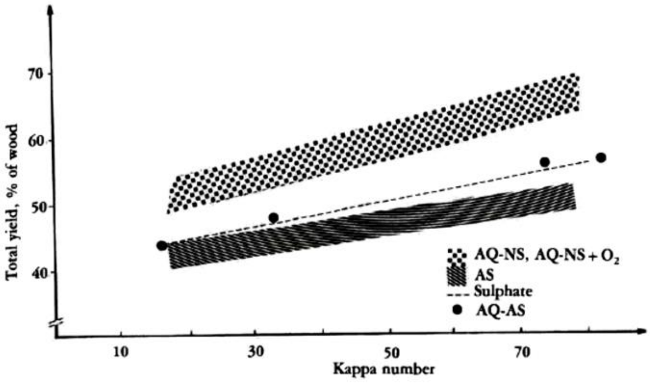
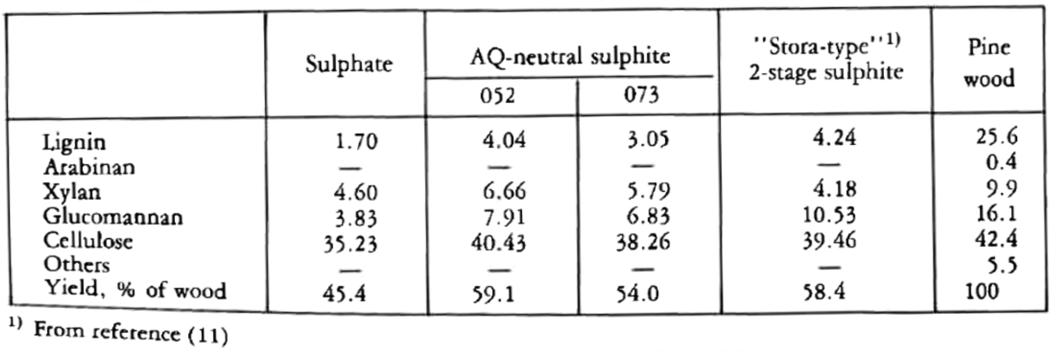


Figure 18. The total cooking yield as a function of kappa number of different pulp types (Kettunen, Virkola et al. 1979).

The paper properties of the chemical pulps are likely to originate from the structure and the composition of the carbohydrates. However, in high yield and mechanical pulps the high lignin content also plays a role being a disadvantage especially when bleached pulps are produced. (Kettunen, Laine et al. 1982; Virkola, Pusa et al. 1981). Table 4 shows the chemical composition of different pulp types. The stabilization of both glucomannan and xylan in the NS-AQ pulps is obvious compared to the two-stage Stora type process in which the high yield is mainly due to the high glucomannan content. The high xylan and glucomannan contents are thought to provide a potential base for developing the special properties of the pulp. (Kettunen, Virkola et al. 1979).

Table 4. The chemical composition of the different pulp types calculated as % of o.d. wood. The NS-AQ pulp number 052 has kappa number 43.4 and the pulp number 073 has kappa number 35.8. (Kettunen, Virkola et al. 1979).



	Sulphate	AQ-neutral sulphite		"Stora-type"[1)] 2-stage sulphite	Pine wood
		052	073		
Lignin	1.70	4.04	3.05	4.24	25.6
Arabinan	—	—	—	—	0.4
Xylan	4.60	6.66	5.79	4.18	9.9
Glucomannan	3.83	7.91	6.83	10.53	16.1
Cellulose	35.23	40.43	38.26	39.46	42.4
Others	—	—	—	—	5.5
Yield, % of wood	45.4	59.1	54.0	58.4	100

[1)] From reference (11)

The amount of reject is dependent on the moisture content of the wood chips, the completeness of the impregnation and the process conditions (Tulppala 1984). However, the effect of the different process variables is not fully understood. The amount of the reject remains in the range of 0.5-4.0% on wood if the moist chips are properly impregnated. The pulps with a high kappa number also contain more reject. Pine NS-AQ pulp contains 4-5% reject at kappa number range 40-50. (Virkola, Pusa et al. 1981). Laboratory experiments have demonstrated that the screenings of the NS-AQ pulp at kappa number 38 are easy to defibrate, and they can be mixed with the original pulp without having any visible effect on the pulp strength or the optical properties (Tulppala 1984).

No significant viscosity loss after pulping has been reported. Virkola et al. (1981) found even higher viscosity values, between 1100 and 1400 dm^3/kg, for the NS-AQ pulps compared to the kraft pulp (Virkola, Pusa et al. 1981). Nikki and Pekkala (1986) have obtained similar results for the pine NS-AQ pulps at kappa number range 25-50. These pulps had viscosity values between 1000-1300 dm^3/kg. (Nikki & Pekkala 1986). Viscosity is strongly affected by the cooking liquor composition. Viscosity is well preserved in the pulps cooked with liquor rich in Na_2CO_3 whereas the lowest viscosity selectivity is noticed in the pure Na_2SO_3 liquors. (McDonough, Van Drunen et al. 1985).

It is generally known that pulps with high hemicellulose content are easily beaten, which also predicts easier dewatering on the paper machine (Kettunen, Virkola et al. 1979). Especially the high glucomannan content in the pine NS-AQ pulp is considered to be a reason for its good beatability (Ojanen, Tulppala et al. 1982). The good beatability of the NS-AQ pulps compared to the kraft pulps is observed as a shorter beating time and as a decrease of the beating energy needed (Kovasin, Kettunen et al. 1987). The unbleached pine NS-AQ pulp needs 25-30% and the bleached pulp 65-70% less beating energy than the kraft pulp to reach a certain tensile index level (Ojanen, Tulppala et al. 1982).

Using the optimum sulphite charge 80-85% of the total alkali charge, temperature 175°C and 0.1% AQ charge resulted in pulp with high yield and comparable papermaking properties with the kraft pulp except for the tearing strength. The tearing strength of the pine NS-AQ pulp was 15-30% lower than the corresponding strength of kraft pulp but it was still better compared toyhe strength of conventional sulphite pulp. (Kettunen, Virkola et al. 1979). The tear-tensile –index relationship of different softwood pulp types are compared in Figure 19. The tear index of birch NS-AQ pulp was 17-25% lower than that of birch kraft pulp (Ojanen, Tulppala et al. 1982). NS-AQ softwood pulps showed good bonding ability so the tensile strength is equal to that of the kraft pulp (Kovasin, Kettunen et al. 1987). In general, tensile strength is considered to be a measure of the bonding ability of the fibres in the pulp. The individual bonds in NS-AQ pulps are thought to be stronger, which is caused by the mild cooking conditions and high hemicellulose content. (Ojanen, Tulppala et al. 1982). The optimum kappa number level for NS-AQ pulps concerning the strength properties is considered to be 50-55 (Kettunen, Virkola et al. 1979).

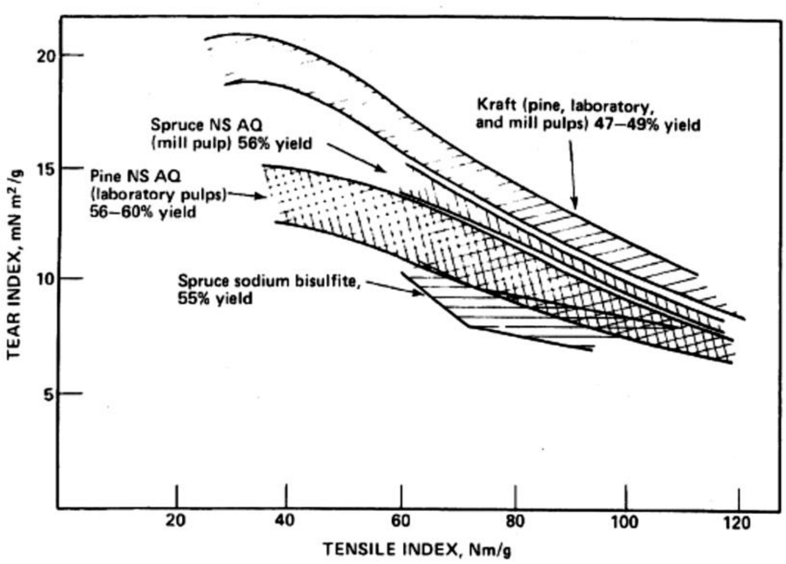


Figure 19. Tear-tensile index relationship of unbleached softwood pulps (Virkola, Pusa et al. 1981).

The good optical properties of sulphite pulps produced in the pH range from acid to neutral are a clear advantage against kraft pulps (Ingruber & Allard 1973). Regardless of the high yield the opacity of NS-AQ pulp is good (Kettunen, Virkola et al. 1979). Depending on the cooking conditions the brightness of softwood NS-AQ pulps varies between 40-53% ISO. Though the pulp is brighter than the pulp produced with the kraft process, it remains lower than the brightness of the conventional acid bisulphite pulp (60-65% ISO). (Virkola, Pusa et al. 1981). Brightness of kraft, NS-AQ, and bisulphite pulps are compared in Figure 20. Pulp brightness can be increased by reducing the lignin content or by increasing the sulphite ratio in the cooking liquor (Kettunen, Virkola et al. 1979). It is also known that pulp brightness decreases with increasing alkalinity (Ingruber & Allard 1973). The light scattering coefficient is still rather high, which is not normally the case with the high yield pulps. The reason may be stiff and uncollapsed fibres, which results in a large optical area. (Virkola, Pusa et al. 1981).

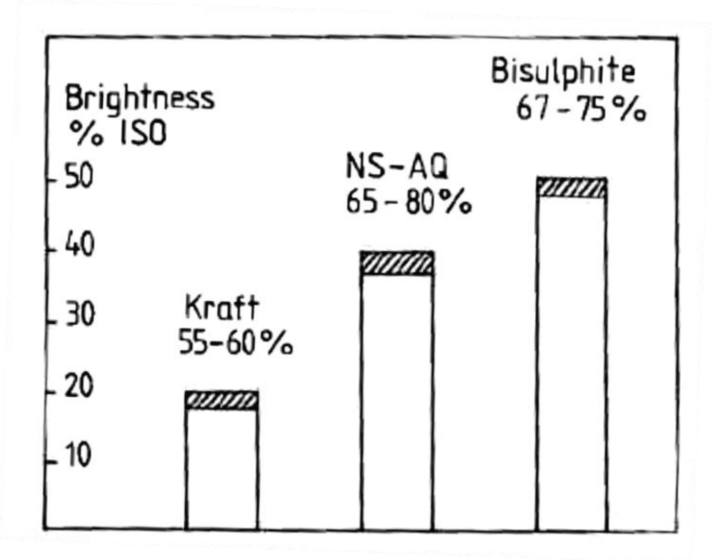


Figure 20. The brightness range of the different pulps after cooking. Hatched areas represent the brightness variation caused by the yield ranged marked above. (Isotalo 1983).

NS-AQ and alkaline sulphite anthraquinone pulps are suggested to be suitable pulps to replace kraft pulps in the production of linerboard (Wong 1988; McDonough & Paulson 1985). Burst strength and stiffness are the crucial parameters characterizing the physical strength properties in the production of linerboard (Wong 1988). Compared to the 54% yield kraft pulp, the 70% yield sulphite-AQ pulp had the same burst strength but 20% lower tensile and 50% lower tear strength. However, decreasing the sulphite-AQ yield the tensile strength disadvantage was removed and the tear strength disadvantage was lowered. (McDonough & Paulson 1985).

Bleached pulp

Due to the high kappa number of the NS-AQ pulp after cooking, oxygen stage is used before bleaching to decrease the kappa number. The high total yield obtained during cooking is maintained. (Virkola, Pusa et al. 1981). The results of some oxygen delignified pine NS-AQ pulps are shown in Table 5. If oxygen is used in the first bleaching step, the kappa number is diminished to a half of the starting level (Kovasin, Kettunen et al. 1987). The disadvantage is the brightness loss of the NS-AQ pulp during the oxygen delignification, which is seen in Table 5 (Kettunen, Virkola et al. 1979).

The alkali charge in the oxygen stage affects the kappa number reduction and the pulp viscosity. Depending on the initial kappa number level kappa number is decreased by 12-20 kappa units. (Ojanen, Tulppala et al. 1982) If the oxygen delignification is carried out under hydrostatic pressure, the yield loss is 4-5% for the NS-AQ pulp at the cooked kappa number 34 (Kovasin, Kettunen et al. 1987). Viscosity of the birch NS-AQ is decreased 10-20% during the oxygen delignification depending on the alkali charge. A similar viscosity drop has also noticed in the case of pine pulp. (Ojanen, Tulppala et al. 1982).

Table 5. Oxygen delignification of pine NS-AQ pulps and one AS-AQ pulp. The starting kappa numbers varied between 35 and 75. (Kettunen, Virkola et al. 1979).

Cooking method	Pulp no.	NaOH		Treatment yield	Total yield	Kappa number		CED-viscosity dm^3/kg		ISO-brigtness % 1)	
		dose %	consump. %	%	%	B	A	B	A	B	A
AQ-NS	043	5.80	5.50	85.7	56.1	75.3	40.4	—	—	39.0	34.6
AQ-NS	045	5.00	4.76	88.8	54.2	59.2	27.9	1 015	975	40.7	36.7
AQ-NS	052	4.00	3.36	90.0	53.7	43.4	21.5	1 113	989	47.8	46.0
AQ-NS	065	5.00	4.42	90.8	56.3	54.1	22.8	1 101	—	53.5	42.1
AQ-NS	073	3.50	3.33	93.4	50.6	35.8	18.3	1 075	911	53.2	49.2
AQ-AS	103	3.30	2.70	96.3	46.3	32.7	12.7	—	837	24.3	40.7

B = before O_2-treatment
A = after O_2-treatment
1) Pulps not washed with SO_2 water

The carbohydrate yield advantage is not lost during oxygen delignification or bleaching. Kovasin et al. compared the properties of pine NS-AQ pulp at kappa number 34 and kraft pulp at kappa number 32 after bleaching with a (DC)EDED sequence to a brightness of 88% ISO. The yield loss of NS-AQ pulp during the bleaching was more significant but the total yield remained 5-6 units higher compared to the kraft pulp. (Kovasin, Kettunen et al. 1987). The yield of NS-AQ pulps at kappa number 25-38, bleached with a (DC)EDED sequence to ISO brightness of 88-89%, was between 45-48%. This was about 2.5% higher than that of the reference kraft pulp. (Nikki & Pekkala 1986). Kettunen et al. have obtained similar results when bleaching NS-AQ pulp with an ODP sequence to 85% ISO brightness and with an ODED sequence to 88% ISO brightness. In both cases the total yield remained 4-5% higher than that of the corresponding kraft pulp. (Kettunen, Virkola et al. 1979). The high glucomannan content of the pulps with a high unbleached kappa number (37-52) was still seen after bleaching (Nikki & Pekkala 1986). Bleaching of the oxygen delignified spruce NS-AQ pulp with a DED sequence resulted in pulp with 88% ISO brightness, 48% yield and 895 dm^3/kg viscosity (Virkola, Pusa et al. 1981).

Table 6. Properties of bleached pine NS-AQ and kraft pulps bleached with a conventional bleaching sequence (CD)EDED (Ojanen, Tulppala et al. 1982).

Code	Kappa number	Consumption of act. Cl % on pulp	Consumption of act. Cl per Kappa number unit	Bleaching yield %	Bleached yield on wood %	ISO-brightness %		Viscosity dm^3/kg bleached
						B	A	
NS-AQ	41,6	13,2	0,32	90,0	49,3	44,6	90,9	1 341
NS-AQ	45,5	14,5	0,32	88,9	48,5	44,3	89,7	1 348
NS-AQ	49,6	14,7	0,30	89,0	47,9	42,1	90,1	1 422
kraft	33,8	11,5	0,34	89,6	42,8	23,3	84,4	959
kraft	38,8	13,4	0,31	88,7	42,6	23,3	84,5	1 008
kraft	45,9	14,8	0,32	89,0	44,0	21,8	83,5	1 051

B = unbleached brightness
A = bleached brightness

Bleaching was not shown to change the papermaking properties of pine NS-AQ pulp markedly (Ojanen, Tulppala et al. 1982). The strength properties of the fully bleached NS-AQ pulp are close to those of the kraft pulp, which is seen in Figure 21. The tear index at a given tensile strength of the fully bleached pulp was somewhat lower than that of fully bleached kraft pulp. (Kovasin, Kettunen et al. 1987). The tensile index of the (DC)EDED bleached NS-AQ pulps did not differ from the tensile index of the reference kraft pulp when the kappa number after cooking was 25-31. Higher cooking kappa number showed better tensile index, but the tear index dropped more compared to the reference kraft pulp. (Nikki & Pekkala 1986).

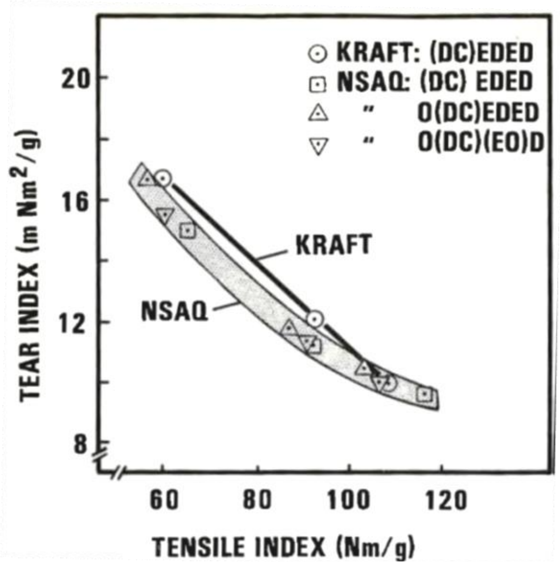


Figure 21. The tear index as a function of the tensile index of the fully bleached kraft and the NS-AQ *pulps (Kovasin, Kettunen et al. 1987).*

5.2 Neutral sulphite semi-chemical process (NSSC)

NSSC was the first process developed for the production of high yield chemi-mechanical pulp covering the pH range from 7.5 to 9 (Ingruper 1985). The process consists of a chemical pre-treatment at high temperature followed by refining of the softened chips at high pressure and temperature. The aim of the chemical pre-treatment is to remove only part of the lignin to enable liberation of the fibres without significant fibre damage or energy consumption in the refining stage. (Fardim 2011, p. 248).

The yield target of the NSSC pulp is normally between 75-85%, which means that the residual lignin content is maintained at the level of 15-20% of the pulp (Fardim 2011, pp. 248-250). During the chemical pre-treatment lignin becomes partly sulphonated increasing its hydrophilicity and swelling (Sjöström 1981, p. 120). The neutral pH of the cooking liquor is intended to minimise the carbohydrate losses. However, hemicelluloses are hydrolyzed along with lignin. (Fardim 2011, p. 248).

5.2.1 NSSC process variables

NSSC process is mainly applied for hardwoods, since softwoods require more chemicals and energy for the defibration. The high resin content may also cause pitch problems in the paper machine. (Ingruper, Kocurek et al. 1985, p. 131). However, the use of the AQ to accelerate the delignification enable the production of lower yield pulps also from softwoods (Keskin & Kubes 1991). By adding catalytic charges of the AQ to the chemical pre-treatment and prolonging the cooking time enable the production of delignified pulp similar as the NS-AQ pulp (Obrocea, Teodorescu et al. 2005).

The pH requirement enables only the use of sodium and ammonium as a base in the cooking liquor (Fardim 2011, p. 248). Sulphite solution may also contain a small amount of sodium carbonate, bicarbonate or hydroxide as a buffer to prevent a significant pH drop. However, too high alkalinity darkens the pulp and reduces the pulp drainage rate. (Ingruper, Kocurek et al. 1985, pp. 132-133). Sulphite charge has the highest influence on the energy consumption, followed by temperature. Lignin sulphonation softens wood matrix and thus affects energy consumption in the refining stage. (Area, Felissia et al. 2001).

The maximum temperature is found to have a major impact on the yield and the physical properties of the pulp (Area, Felissia et al. 2001). The reaction temperature 160-190°C accelerates the sulphonation reactions of lignin (Fardim 2011, p. 248). Figure 22 shows the effect of cooking temperature and time on cooking yield and amount of reject. Using high cooking temperature the amount of reject is also minimised. Temperature range 165-175°C showed not to have a significant influence on delignification selectivity or pulp viscosity. (Obrocea, Teodorescu et al. 2005). The digester type, conveyor-type or continuous-flow, also determines the reactions temperature. In the conveyor-type digester the temperatures are near 200°C and the cooking time is short while in the continuous-flow digester it is vice versa. (Fardim 2011, p. 249).

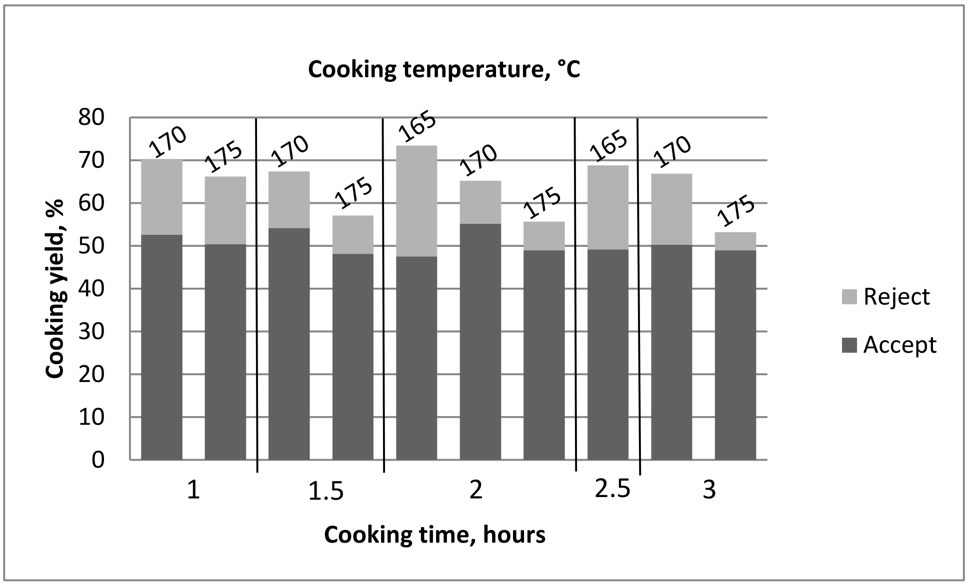


Figure 22. Total cooking yield divided into reject and accept at different cooking times and temperatures. The cooking liquor contained 20% of sulphite and sodium carbonate in a ratio of 3:1, and 0.1% of AQ. (modified from (Obrocea, Teodorescu et al. 2005)).

The cooking time normally used in NSSC process is from 5 to 60 minutes (Fardim 2011, p. 249). Figure 23 confirms that most of the yield loss occurs during the first two hours at the maximum temperature. Delignification is also more efficient during the first hour, after which the degradation of carbohydrates increases. (Singh, Bharati et al. 1982). This finding supports the shorter cooking time.

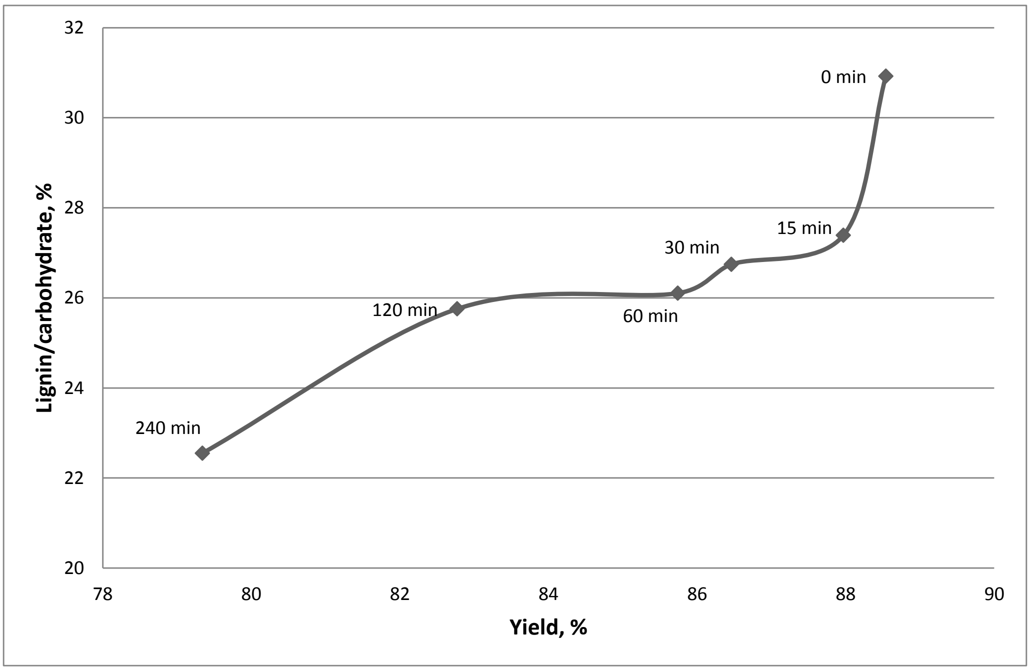


Figure 23. Changes in the lignin-carbohydrate ratio versus the cooking yield. The time of sampling is given as minutes from the beginning of the cook at maximum temperature 150°C. The cooking liquor consists of sodium sulphite (15%) and sodium carbonate (3.5%). (Singh, Bharati et al. 1982).

5.2.2 Pulp properties

NSSC pulp is generally produced for corrugating medium but it can be used also together with kraft pulp in the linerboard and the bag grades (Area, Felissia et al. 2001). This type of end product demands high stiffness, and good crush resistance. The use of NSSC pulp in production of printing papers, greaseproof papers, and bond papers is also possible. (Sixta, Potthast et al. 2005, p. 1110).

In NSSC process it is essential to find a compromise between the degree of delignification and the pulp properties (Singh, Bharati et al. 1982). The yield is normally in the range of 75-85% on wood, but it can be lower in certain applications (Fardim 2011, p. 250). The lower yield means improvements in the mechanical properties and a decrease in energy consumption of refining. Though, at the same time bulk and brightness will suffer. (Area, Felissia et al. 2001). Concerning the end product quality requirements fibre length and strength are not as important as fibre stiffness (Fardim 2011, p. 248).

Temperature and sodium sulphite charge in the NSSC process seem to have a major influence on the pulp mechanical properties. Brightness is affected positively only by the amount of sodium sulphite used. (Area, Felissia et al. 2001). However, the use of alkali results in alkaline darkening of the pulp but this is not critical since normally NSSC is applied unbleached (Rehbein 2010). The best mechanical properties for poplar NSSC pulp were found at temperature 186°C, in 30 minutes, using 11.6% of sodium sulphite and 3.05% of sodium carbonate on o.d. wood (Area, Felissia et al. 2001).

5.3 Multistage cooking

Two-stage sulphite processes were originally developed to overcome the pulping difficulties of certain resin-rich wood species. Several alternative process combinations were introduced during 1950's and 1960's. Some of them were further proceeded to a mill scale. (Sixta, Potthast et al. 2005, p. 465). The difficulties in pulping of some softwood species with the conventional sulphite process were due to the presence of certain extractives. These phenolic compounds together with acid cooking liquor caused lignin to condense by phenolizing the alpha-carbons of lignin before they were sufficiently sulphonated by the sulphite ion. (Sanyer, Keller et al. 1962).

Sanyer et al. tested several two and three stage sulphite pulping processes including bisulphite-neutral, bisulphite-acid, neutral-acid, bisulphite-acid-neutral, and neutral-acid-neutral sulphite processes. The largest variation among the sulphite pulps was seen in the glucomannan content, whereas the variation in the xylan content was lower. Another significant difference was observed in the microscopic structure of the cell wall and the native cellulose fibrils. The fibrillar bundles in kraft pulp are larger in diameter than those of sulphite pulps. In addition, the crystallites are wider and more perfectly developed. This results in an increased swellability of sulphite pulps, which may be attributed to the large amount of glucomannan retained in the pulps. (Sanyer, Keller et al. 1962). In this chapter two-stage processes called Stora and Sivola processes are presented. Both processes have been operated in full mill scale.

5.3.1 Neutral-acid sulphite process

The process was developed by Stora Kopparsberg in Sweden in 1950’s and it was applied in several companies’ pulp mills (Croon 1965). The interest to develop the two-stage neutral-acid sulphite cooking method, also called Stora process, originated in the flexible use of wood raw material (Lagergren 1964). The sulphonation of lignin in the first stage prevented harmful condensation reactions of lignin with phenolic compounds, which enabled also the use of extractive-rich pine heartwood (Sjöström 1981, p. 118). The second stage carried out in acid conditions was aimed to be the main delignification phase (Lagergren 1964).

The other advantage of this process besides widening the raw material base was a significant yield improvement. The softwood pulp produced in the two-stage process gave 5-7% higher yield on wood compared to the conventional acid sulphite pulp, which is shown in Figure 24. (Sjöström 1981, p. 118) The yield increase was mainly due to deacetylation of glucomannan, which protects the molecule against acid hydrolysis and diffusion in the second cooking stage (Croon 1965). It was believed that the deacetylated glucomannan is more closely hydrogen bonded to the cellulose microfibrils or partly crystallized in which state its resistance toward acid hydrolysis is improved (Sjöström 1981, p. 119). Other factors, such as the more selective delignification and the better retention of xylan as a consequence of increased temperature and longer cooking time in the first stage, may also contribute to the yield increase (Croon 1965).

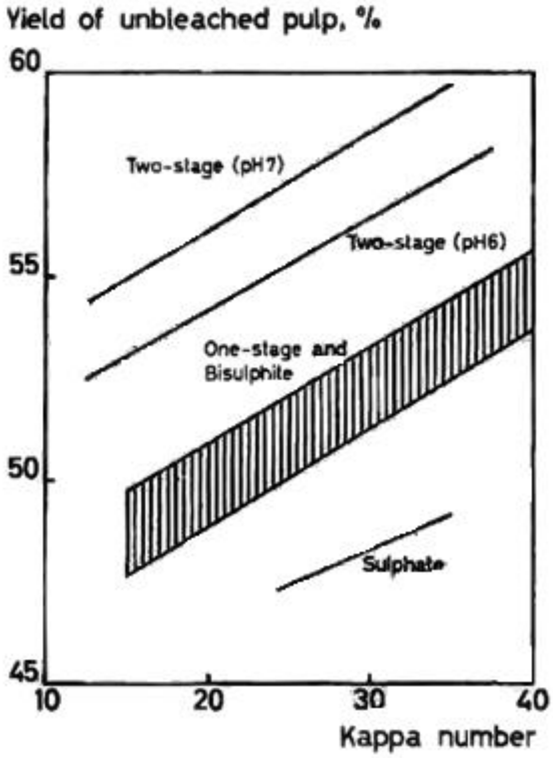


Figure 24. Cooking yield versus kappa number of different pulp types. The yield advantage of the two-stage sulphite processes over the acid sulphite and the sulphate processes is undeniable. (Lagergren 1964).

The Stora process involved a two-stage sodium-base sulphite pulping, a chemical depitching and a chemical recovery process (Lagergren 1964). The cooking during the first stage was carried out at neutral or slightly acidic pH. The reaction time of the initial stage depended on the wood species. At the beginning of the second cooking stage pH was lowered by adding SO_2, and depending on temperature (135-145ºC), the cooking was carried out for around 2-4 hours. (Sixta, Potthast et al. 2005, p. 472). The pitch problem caused by high extractives content was resolved in the Stora process with a chemical de-pitching of the unbleached pulp by caustic treatment. The normal pitch content after bleaching did not exceed 0.1%. (Lagergren 1964).

The first stage carried out at pH 6-7 had the greatest impact on pulp quality and cooking yield. Quality and yield could be affected by adjusting of the three main factors: temperature, time and pH. (Lagergren 1964). The maximum temperature for pinewood in the first stage should have been over 150ºC to avoid large amount of screenings because of impregnation difficulties (Croon 1965). However, too high temperature caused decomposition of carbohydrates (Lagergren 1964). The yield obtained in the first stage seemed to be a clear function of temperature and pH (Sixta, Potthast et al. 2005, p. 472). The inflexion point shifted toward lower pH when the temperature increased as is shown in Figure 25. For temperature above 125ºC the maximum yield during the first stage was reached at pH 6-7. (Croon 1965). Wood species containing phenolic extractives, such as pine, required prolonged cooking time up to 4-6 hours while for other wood species it could be significantly shorter (Lagergren 1964). The conditions in two-stage pulping were different for hardwoods such as birch and aspen because of their higher xylan content. The first stage should be carried out at pH 8-9 and at temperature 150ºC during 1-2 hours. In the second stage the temperature could be significantly lower (130-135ºC) to obtain the best yield gain. (Croon 1965).

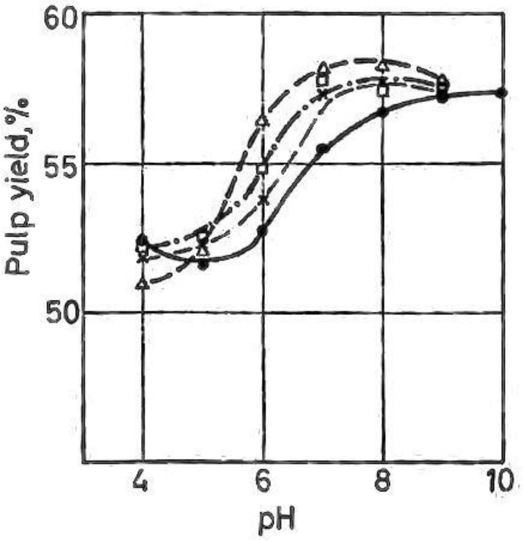


Figure 25. The development of pulp yield against cooking pH during the first stage. The conditions were —●— 125°C, 1.5 h; —×— 140°C, 1h; —□— 150°C, 1h; —Δ— 160°C, 1h. The maximum pulp yield is obtained around pH 7 using higher temperatures and at pH 9 when the temperature is the lowest. (Croon 1965).

The properties of the two-stage pulp have many similarities with neutral-sulphite pulps. Fibres with increased hemicellulose content have higher tendency to swell and become flexible, which improves fiber-fiber bonding. This also results in high tensile strength at a low degree of beating. However, tensile strength is improved at the expense of a decrease in tear strength and opacity. (Lagergren 1964). The bleached two-stage pulp has been used in grease proof and tracing papers, in printing and writing paper applications, in copying paper, in soft tissue and as aminoplastic filler pulp (Croon 1965).

5.3.2 Sivola process

The Sivola sulphite cooking and recovery process was developed in the early 1950's for the use of the Rauma pulp mill in Finland (Sanyer, Keller et al. 1962). The aim was to develop a method which could convert resinous pine heartwood into high alpha cellulose dissolving pulp (Hassinen & Räsänen 1974). The original process consisted of a sodium bisulphite stage followed by an alkaline stage without interruption of cooking in the middle (Pascoe, Buchanan et al. 1959). Later on several variations of this process were developed (Sanyer, Keller et al. 1962). The cooking concepts of the bisulphite-neutral sulphite, the acid-bisulphite-neutral sulphite, and the bisulphite-acid sulphite-soda are all variations of the Sivola process (Sixta, Potthast et al. 2005, p. 468).

The three-stage sulphite process used in the Rauma mill in Finland produced mainly dissolving pulp but paper-grade pulps were also possible to cook with one to three-stages depending on the quality requirements. The cooking diagram is presented in Figure 26. The first stage acting as impregnation and principal sulphonation stage is carried out with sodium bisulphite liquor at pH 3-4. The second stage reproduces conventional acid sulphite stage, where the viscosity of the pulp is controlled. In the third stage sodium carbonate is added to neutralize the cook. Compared to kraft process the foaming tendency in washing and the chlorine consumption in bleaching are significantly lower in the Rauma process. (Hassinen & Räsänen 1974).

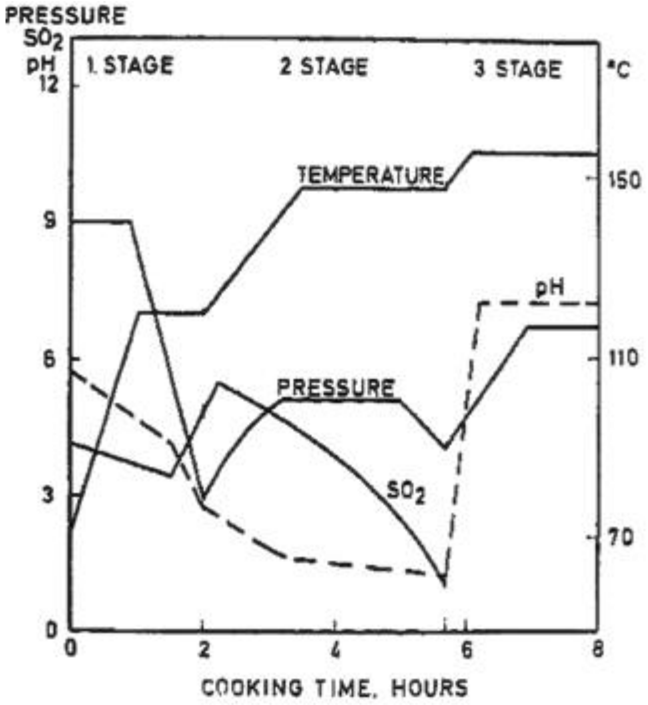


Figure 26. The cooking diagram of the three-stage sulphite process, also called the Rauma process (Hassinen & Räsänen 1974).

In general, these pulps have strength properties comparable with kraft pulps. They are light in colour and easy to bleach to high brightness. The yield of the two-stage bleached pulp is in the same range with kraft pulps. Cooking time is longer but not as high temperature or pressure is needed as in kraft process. (Pascoe, Buchanan et al. 1959).

5.4 Sulphite based biorefinery

Today the sulphite process is used for the production of paper- or dissolving-grade pulps (Fatehi & Ni 2011). However, the goal of the forest products industry has long been to convert the forest biomass also to value-added fuels and chemicals along the traditional wood products, such as timber, fibreboard, pulp and paper (Elumalai & Pan 2011).

During any type of sulphite process lignin and some part of hemicelluloses are dissolved as a sulphite spent liquor (SSL), which is separated from the pulp (Fatehi & Ni 2011). The common method today is still to burn the organic solids in the sulphite spent liquor for the generation of energy and the recovery of the cooking chemicals (Stenius 2000, p. 85). However, SSL is a source of valuable by-products such as ethanol, proteins, vanillin and lignosulphonates (Fardim 2011, p. 226).

The composition of the SSL depends strongly on the wood type used in the pulping process, which is shown in Table 7 (Pereira, Portugal-Nunes et al. 2013). Also the type of the sulphite process determines how high the content of the lignocellulosic material is in the spent liquor. The dissolving pulp-grade spent liquor contains more lignocellulosic material than the paper-grade sulphite spent liquor. This is one reason why the utilization of the SSL from the NSSC process is still very limited. In industrial practise the SSL is usually treated in the wastewater treatment plant when the lignocellulosic material is wasted. (Fatehi & Ni 2011). No publication on the utilization of the SSL from the NS-AQ process was found.

Table 7. The general chemical composition of the softwood sulphite spent liquor (SSSL) and the hardwood sulphite spent liquor (HSSL) (Pereira, Portugal-Nunes et al. 2013).

	SSSLs (g L^{-1})	HSSLs (g L^{-1})
Lignosulphonates	110.0–120.0	77.6–78.8
Mannose	21.0–27.0	7.6–9.4
Glucose	7.0–9.7	2.2–2.4
Galactose	4.7–6.0	4.4–4.6
Xylose	9.0–11.0	24.1–25.1
Arabinose	0.69–2.0	7.5–8.1
Acetic acid	3.0	9.5–9.7
Furfural	0.2	Traces
SO_2	0.5	–[a]
Extractives	Traces	Traces

[a] Data not available.

Resulting from the nature of the biomass, the main volumes of the output products are predetermined. The major challenge for every biorefinery is the continuously fluctuating market demand of these products, which is never in balance with the production volumes. (Roedsrud, Lersch et al. 2012). Also the costly and complex separation technologies are one reason for why the by-product utilization has been of limited practical interest. The value of the final products has to be high enough to be an economically attractive alternative to start the production. (Stenius 2000, p. 86). In the sulphite mill biorefinery, pulp is still seen as the major product for papermaking or as a sugar source for biochemicals. The model in Figure 27 suggests the use of the sludge and the sulphite spent liquor for production of biochemicals, which would allow the flexible use of these streams for the final product requirements. (Lai & Bura 2012).

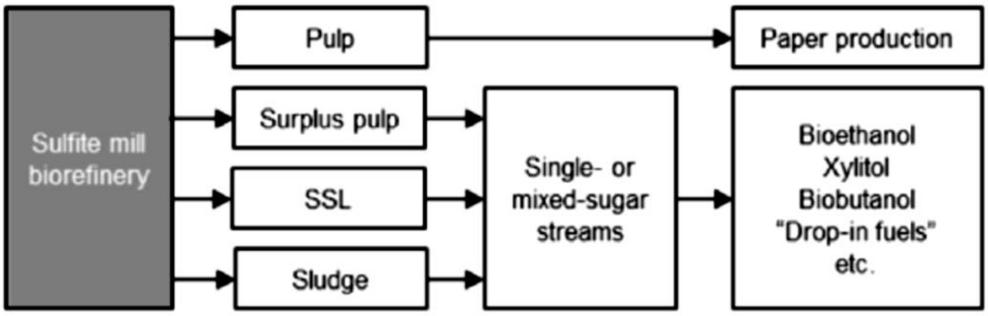


Figure 27. The suggested process scheme for a sulphite mill biorefinery utilizing different sugar streams for production of several biochemicals (Lai & Bura 2012).

Sulphite based dissolving-pulp mills have taken the leader positions in the transition from the traditional pulp mills to the biorefineries. Since the pulp yield is significantly lower compared to the conventional kraft and sulphite pulp mills, these mills need to efficiently utilize also the dissolved material. (Fardim 2011, p. 695). The Borregaards plant in Sarpsborg, Norway is a good example of the today's existing biorefinery. The plant has four main products lines, cellulose, ethanol, lignins and vanillin, which are seen in Figure 28. (Roedsrud, Lersch et al. 2012). Dömsjö Fabriker, in Örnsköldsvik Sweden is another example of biorefinery, which is a two-stage sodium sulphite pulp mill. According to the production of dissolving pulp the mill produces lignosulphonates to be used as additives in different industries, and ethanol to be used as an automobile fuel (Fardim 2011, pp. 697-699). Tembec Temiscaming mill in Canada produces high purity cellulose pulp by sulphite process around 400 000 tons annually. The lignosulphonates are used as binders in animal feed, limestone and fertilizers, as surfactants and dispersants in textile dyes, cement, concrete, wax and asphalt emulsions, and also transformed into carbon black. Hemiselluloses are fermented to ethanol with a production capacity of around 18 million litres per year. (Magdzinski 2006).

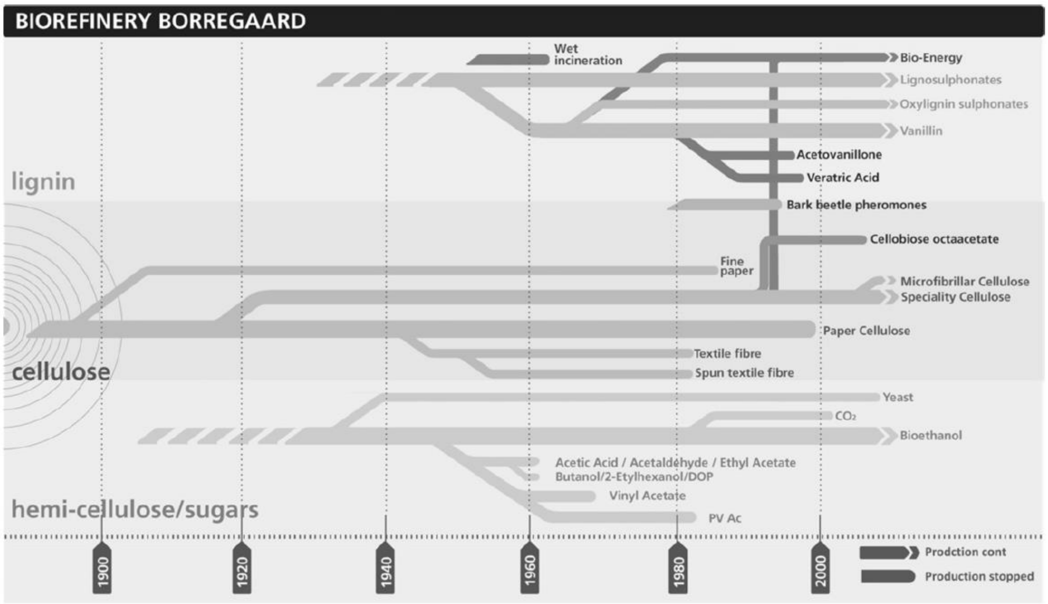


Figure 28. The existing and abandoned production lines in the history of the Borregaards biorefinery in Sarpsborg, Norway (Roedsrud, Lersch et al. 2012).

5.4.1 Lignosulphonates

It is claimed that only 2% of the lignin dissolved in pulping operations worldwide is recovered and marketed. About 90% of this lignin is lignosulphonates obtained in sulphite processes. (Ringena, Saake et al. 2005). Lignosulphonates are commercially used as raw material in several applications such as industrial detergents, concrete additives, cements dispersants, asphalt emulsifiers, compressed material binders, plasticizers, peptizers, stabilizers, glue, adhesives, and feedstock for chemical processing (Restolho, Prates et al. 2009). The by far largest utilization of lignosulphonates is as dispersants in concrete (Areskogh 2011).

The lignosulphonates are neutralized sulphonated lignin fragments dissolved in the cooking liquor (Fardim 2011, p. 226). The hydrophilic sulphite groups and hydrophobic aromatic structures provide lignosulphonates with amphiphilic properties (Areskogh 2011). Their adhesion and dispersion properties makes them useful for several applications (Sjöström 1981, p. 198). However, the overall structure of this macromolecule is still under investigation (Myrvold 2008). There is a strong indication that lignosulphonates behave as flexible polyelectrolytes in aqueous solution (Gardon & Mason 1958). In the presence of a suitable electrolyte this randomly branched molecule, presented in Figure 29, becomes coiled but loosened and elongated by removing the salt (Myrvold 2008).

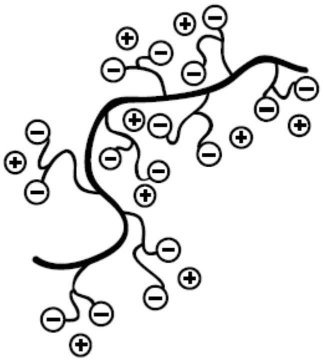


Figure 29. A schematic view of the structure of the branched lignosulphonate molecule (Areskogh 2011).

In comparison with kraft lignin, lignosulphonates have a wider variety of uses as a by-product because of its solubility in water (Fardim 2011, p. 203). However, this is a challenge since lignosulphonates cannot be precipitated by decreasing pH like the dissolved lignin in the kraft spent liquor. Several separation technologies have been studied including ion exchange, dialysis, electrodialysis, ultrafiltration and reverse osmosis. (Fatehi & Ni 2011). Resulting from the problems in development of the separation technologies and also due to the fuel value of the sulphite spent liquor, commercial utilization of the liquor components have been obstructed (Stenius 2000, p. 85).

Other lignin-based chemicals are obtained by degrading lignosulphonates to low molecular weight substances. The most important product obtained from softwood lignosulphonates is vanillin. (Sjöström 1981, p. 198). Several methods exist for the production of vanillin from lignin but the first step is always the oxidation of the sulphite spent liquor (Fatehi & Ni 2011). Vanillin is used as an ingredient in the food industry, but the existing market is almost fully saturated with the synthetically produced vanillin (Areskogh 2011).

5.4.2 Sugars

Similar carbohydrates and their degradation products to those formed after hydrolysis of wood, are possible to recover from the sulphite spent liquor (Sjöström 1981, p. 199). The carbohydrates in sulphite spent liquors have been traditionally used in the production of ethanol and single cell protein (Stenius 2000, p. 86). Ethanol production from softwood SSL is already an industrial practise in North America and Europe. On the contrary fermentation of the hardwood SSL to ethanol is still under investigation. (Pereira, Portugal-Nunes et al. 2013). The challenges in ethanol production from the SSL have been the low nutrient concentration, the presence of inhibitors, the large portion of xylose in the case of the hardwood SSL, and the limitation of the usable yeasts (Fatehi & Ni 2011).

The fermentation methods have played a major role in the industrial processing of the carbohydrates (Stenius 2000, p. 86). Glucose fermentation produces fuels like ethanol, organic acids such as lactic acid, and solvents (acetone, butanol), whereas xylose fermentation produces ethanol and xylitol, and catalysed dehydration of glucose produces furfural (Restolho, Prates et al. 2009). Though monosaccharides and their conversion products such as furfural can be separated from sulphite spent liquor, the complex separation technologies and alternative raw material sources have limited the practical interest (Sjöström 1981, p. 199).

Acetic acid and furfural are well-known inhibitors hindering the fermentation process of sugars, but also valuable sources of different applications (Afonso 2012). The neutral sulphite spent liquor from hardwood contains a significantly high proportion of acetic acid compared to the other organic compounds (Stenius 2000, p. 86). Acetic acid is a source of vinyl acetate monomer applied in paints and adhesives, acetic anhydride applied in the production of cellulose acetate, and acetate esters which are commonly used as solvents for paints, inks and coatings. Furfural is used in many applications as in the production of fertilizers, plastics, paints, and resins, and as an intermediate in the production of furan and tetrahydrofuran (solvents). (Afonso 2012).

It is possible to convert the xylose in the SSL to xylitol by hydrogenation or fermentation. The hydrogenation is already a commercialized method yet the fermentation is also intensively studied. Hardwood SSL contains more xylose than softwood SSL making it a desirable raw material for xylitol production. (Fatehi & Ni 2011). Xylitol is mainly used as a sweetener because of its interesting ability to prevent dental caries (Sjöström 1981, p.193).

EXPERIMENTAL PART

6 Materials and methods

To study the delignification effect of sodium sulphite at neutral conditions, several small scale cooking experiments were performed. The process variables tested during these trials were Na_2SO_3 charge, AQ charge, initial pH, cooking time, reaction temperature and impregnation time. The small scale cooks were carried out in 1 litre air-heated autoclaves. Based on the results obtained from small scale cooks one large scale cook in a 15 litre rotating digester was performed. The reasonable reaction conditions, which resulted in pulp with low kappa number but high yield, were selected. The pulp properties tested after each cook were kappa number, total yield, screenings, brightness, viscosity and the sulphonic acid group content. All standard methods used in the experiments are listed in Appendix 1.

Since delignification was known to slow down significantly after a certain kappa number level, the pulp produced in the large scale was further processed in the oxygen delignification stage. The aim was to study how low kappa number could be reached without deteriorating pulp properties and especially the obtained pulp yield considerably. Single and multistage oxygen delignification trials were performed with varying alkali charge, reaction time and temperature. The pulp analyses of the cooking trials were carried out in the case of the oxygen delignification as well, except the sulphonic acid group content measurements.

High kappa pulp is normally used in unbleached paper grades, and little research has been performed of the bleaching of these pulps. Three common bleaching sequences were carried out for the oxygen delignified pulp to have an idea of the bleachability of the neutral sulphite pulp. The target was to obtain a fully bleached pulp with a moderate chemical consumption.

Pulp samples, both bleached and unbleached, were selected for the lignin and the carbohydrate analyses. The analysis was essential to make conclusions on the factors preserving carbohydrates through delignification.

6.1 Wood raw materials

The wood material used in the pulping experiments was fresh Finnish pine chips (*Pinus sylvetris L.*). The chips were screened to remove the oversized chips and the fine fraction according to the standard SCAN-CM 40:01. The purpose was to compensate for the inhomogeneity of the impregnation caused by the thick chips. According to the standard, chips were classified by thickness screening the chips for a specific time through a stack of horizontal screen trays having slots of different sizes. The screened chips were analysed for the dry matter content according to SCAN-CM 39:94. Depart from the standard instructions the weighing of the chips after drying was carried out only once. The thickness distribution and the dry matter content are presented in Table 8. The accepted fractions sizes for the experiments were 13 Ø, 7 Ø, and 3 Ø.

Table 8. Chip thickness and thickness distribution according to SCAN-CM 40:01 and the chips moisture content according to SCAN-CM 39:94.

Thickness and thickness distribution **SCAN-CM 40:01**	
Fraction	%
45 Ø	0
8 \\	1.6
13 Ø	67.9
7 Ø	24.4
3 Ø	4.5
0	1.6
Accepted fraction:	96.8
Dry matter content SCAN-CM 39:94	46.65

6.2 Small scale cooks

The small scale cooks were performed in 1 litre air-heated autoclaves (Muru). The target kappa number was set to 50. The aim was to find the right cooking conditions to meet this target. The cooking liquor was prepared by diluting solid Na_2SO_3 into deionized water at the room temperature and by adjusting the pH of the liquor with 4 N H_2SO_4. Sodium sulphite water solution has pH around 9.5 and H_2SO_4 was needed to decrease the pH. The autoclaves were first filled in with the chips, after which the solid AQ powder and the cooking liquor were added. The autoclaves were pressurized with N_2 gas into 5 bars, before the reaction could be started. The aim of pressurizing was to improve impregnation of the cooking liquor because it was not possible to carry out chip presteaming.

The experiments were executed in four batches, each batch comprising of six autoclaves. The cooking parameters in the first three batches were:

Charge of the o.d. chips	100 g
Na_2SO_3 charge	30-50% on o.d. wood
AQ charge	0-0.2% on o.d. wood
Initial pH	7.5-9
Liquor to wood ratio	4 l/kg
Impregnation at 80°C	30 min
Temperature rise to max. T	1°C/min
Max. T	165/180°C
Time at max. T	180-300 min
Pressure	5 bars

The fourth batch contained a longer impregnation stage at 140°C. The different impregnation stages and the temperature rise to the maximum cooking temperature are presented in Figure 30. The purpose of this longer impregnation was to improve the impregnation of the cooking liquor and to give more time for the glucomannans to stabilize. The cooking parameters in this case were:

Charge of the o.d. chips	100 g
Na_2SO_3 charge	25-30% on o.d. wood
AQ charge	0.1% on o.d. wood
Initial pH	8
Liquor to wood ratio	4 l/kg
Temperature rise to 140°C	1°C/min
Precook at 140°C	120 min
Temperature rise to max. T	2°C/min
Max. T	180°C
Time at max. T	120-240 min
Pressure	5 bars

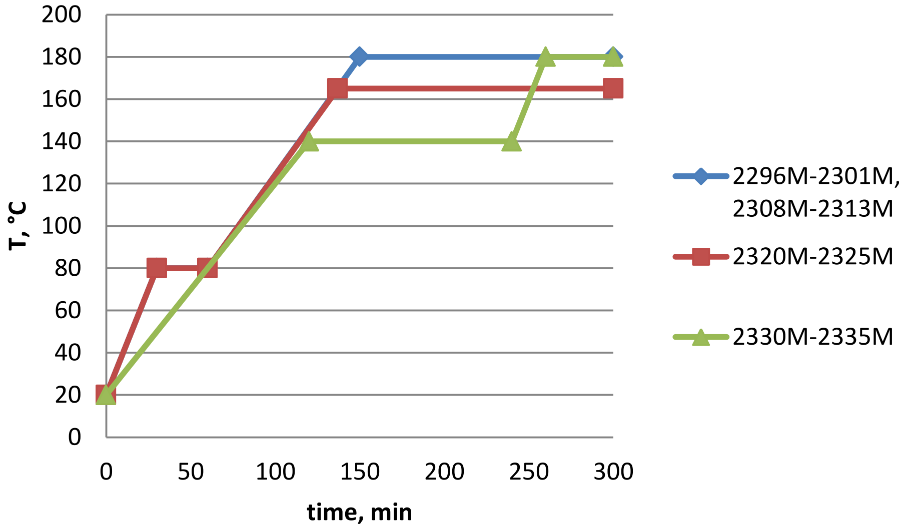


Figure 30. The temperature rise to the maximum cooking temperature of the small scale cooks. The numbers on the right side are the cooking numbers of the each autoclave, and the one batch consists of the six autoclaves.

The precise cooking parameters (which were varied depending on the cooking number) are presented in Appendix 3. After the defined cooking time at the maximum temperature and cooling down the content of the autoclaves were emptied into wire bags, the spent liquor samples were taken and the pulps were washed with deionized water. After soaking the pulp samples overnight the pulps were disintegrated in a British disintegrator, screened in a TAP03 laboratory screen with 0.15 mm slots, drained on a suction filter and spin-drier, and homogenized by hand. The gravimetric total yield and the amount of rejects were determinated and kappa number (ISO 302:2004), brightness (ISO 2470) and viscosity (ISO 5351:2004) were analysed from laboratory sheets. The spent liquors were analysed for final pH.

The amount of sulphonic acid groups existing in the pulp after cooking was measured. The method chosen was conductometric titration (SCAN-CM 65:02), which determines the content of total acidic groups in the pulp. The total acidic groups in the case of the sulphite pulp mean the sum of carboxylic acids and sulphonic acid groups.

6.3 Large scale cook

The large scale cook was performed in a 15 litre rotating digester. The cooking conditions were chosen after analysing the results of the small scale cooks. Contrary to the small scale cooks it was possible to execute a presteaming stage but the cooking pressure has to be kept on a lower level. Figure 31 shows the temperature rise to the maximum temperature compared to the small scale cooks. The following cooking conditions were used:

Charge of the o.d. chips	2250 g
Na_2SO_3 charge	30% on o.d. wood
AQ charge	0.1% on o.d. wood
Initial pH	8
Liquor to wood ratio	4 l/kg
Pre-steaming at 110°C	10 min
Pressure	5 bars
Impregnation at 80°C	30 min
Temperature rise to 180°C	1°C/min
Time at max. T	240 min

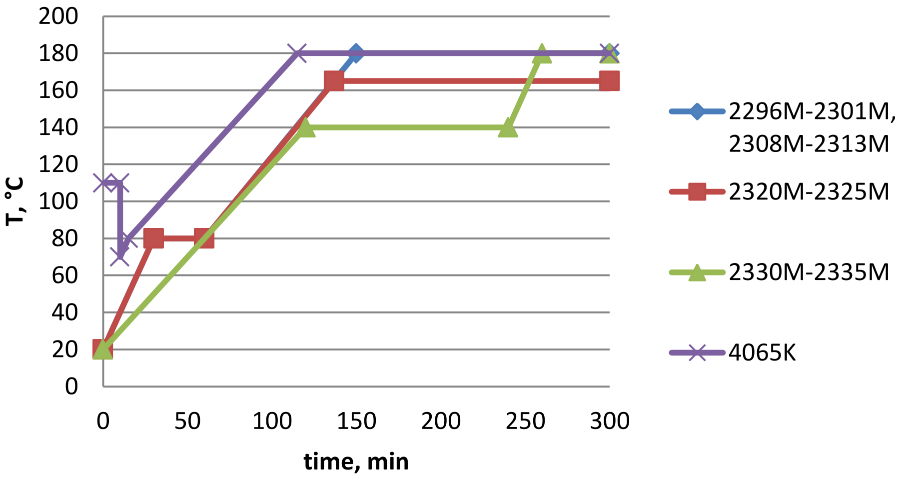


Figure 31. The temperature rise to the maximum cooking temperature of the small scale cooks and the large scale cook (4065K). The numbers on the right side are the cooking numbers of autoclaves, and one batch consists of six autoclaves.

The pulp was washed over night in a tank by diluting the suspension 7 times to the consistency of 5% followed by thickening to the consistency of 15%. After the washing stage the pulp was disintegrated in a 50 l rod disintegrator and screening was carried out in two stages. The slot size of the first screen was 1.0 mm and the second one 0.3 mm. However, the flat screens were ineffective for the stiffest fibres and plugged. The fibre like material in the reject was disintegrated again in the British disintegrator, screened in the TAP03 laboratory screen with 0.15 mm slots, drained on the suction filter and the spin-drier, and homogenized by hand. This portion of the pulp was later mixed with the pulp screened in the flat screens. After screening the pulp was spin-dried and homogenized. The gravimetric total yield and the reject content were determined, and kappa number (ISO 302:2004), brightness (ISO 2470) and viscosity (ISO 5351:2004) were analysed from a laboratory sheet. The spent liquor was analysed for final pH. The process conditions are presented in Appendix 3. The pulp was further processed in the oxygen delignification stage.

The amount of sulphonic acid groups existing in the pulp after cooking was measured. The method chosen was conductometric titration (SCAN-CM 65:02), which determines the content of total acidic groups in pulp. The total acidic groups in the case of the sulphite pulp means the sum of carboxylic acids and sulphonic acid groups.

6.4 Oxygen delignification

The pulp was oxygen delignified in a fluidizing modified Quantum Mark IV reactor. The initial kappa number was 59 and the target kappa level was set to 30. Both single and multiple stages were tested. The process variables were NaOH charge, temperature, and time, which are presented in Table 9 as well in Appendix 4.

The pulp and Epsom salt ($MgSO_4 \cdot 7H_2O$) was mixed and heated up to the reaction temperature. Additional water and NaOH were as well heated up to the same temperature separately. The heated pulp was added into the reactor and the water and NaOH were poured evenly on the top of the pulp. The reactor lid was then closed and the suspension was mixed 4 seconds in 30 Hz. The maximum oxygen pressure input was 8 bars, after which the suspension was mixed 4 seconds in 60 Hz. During the reaction pulp was automatically mixed 4 seconds every ten minutes in 15 Hz. Pulp was not washed between oxygen stages, when alkali was added, in the case of the trials number 3322 and 3329. The reactor pressure was released and the lid was opened, and the alkali was poured on the top of the pulp. This of course resulted in a temperature decrease in the reactor but it was not thought to have any significant effect on the final results. After closing the lid, the mixing as in the beginning was repeated and the pressure was increased to 8 bars before starting the reaction again.

Table 9. The reaction conditions of the oxygen delignification experiments.

O_2-trial	3309	3310	3011	3322	3329
Temperature, °C	98	98	110	98	85
Reaction time, min	60	60	60	60+60	60+60+60
Consistency, %	12	12	12	12	12
NaOH charge, %	3	4.5	3	4.2+2.3	4.2+2.3+0
Epsom charge, %	0.6	0.6	0.6	0.6	0.6
O_2 pressure, bar	8	8	8	8	8

After the reaction, the reactor pressure was released and the lid was opened. pH was measured from the pulp and a filtrate sample was taken to analyse the residual alkali (SCAN-N 33:94). The washing was done by the routine method of the laboratory. The pulp was first diluted to 5% consistency with deionized water at the temperature of the preceding oxygen stage. After dewatering the pulp was washed two times with cold deionized water (with the amount equivalent to ten times the amount of abs. dry pulp). Homogenization of the pulp was made by hand.

Laboratory sheets for kappa number (ISO 302:2004), brightness (ISO 2470) and viscosity (ISO 5351:2004) measurements were prepared. The gravimetric yield and the dry matter content of the pulp were as well tested. To confirm the reliability of the gravimetric yield after the oxygen delignification, TOC (Total Organic Carbon) was measured from the spent liquors. These sample analysis were provided by Labtium Oy. The calculation of the yield loss after the oxygen delignification was based on the theoretical generalization of carbohydrate and lignin losses during bleaching, which are presented below.

$$carbohydrate\ loss = \frac{TOC - \Delta k \cdot 0.593}{0.444}$$

$$lignin\ loss = \Delta k \cdot 1.52$$

Based on equations presented above the yield loss in oxygen delignification was calculated according to equation 1. The theoretical equation expresses the bleaching loss by TOC and kappa number measurements.

$$BL - L(\%) = (2.25 \cdot TOC - 0.5081 \cdot \Delta k) \cdot 0.1 \qquad (1)$$

In the equation TOC value is in g/kg and the Δk is the change in kappa number during the reaction.

6.5 Bleaching

The oxygen delignified pulp chosen for the bleaching trials was pulp number 3322 which had a kappa number low enough for bleaching (24). The bleaching experiments were executed in a small scale in a hot water bath according to the VTT laboratory procedures described in Appendix 2. The sequences tested were DEDED, DED and DE_pDP. Brightness (ISO 2470) and kappa number (ISO 302:2004) were measured from the laboratory sheet stabilized with SO_2-water to pH 4.5 after each DE- or DEp-stage. Viscosity (ISO 5351:2004) and the gravimetric bleaching yield were measured from the pulp after the whole bleaching sequence. The conditions of the different bleaching sequences are presented in Tables 10, 11, and 12. In each D-stage, the consumption of ClO_2 was measured as well as the consumption of hydrogen peroxide in the P-stage.

Table 10. The bleaching conditions for the DEDED sequence.

Stage	D_0	E_1	D_1	E_2	D_2
Consistency, %	9	10	9	10	10
Temperature, °C	60	70	70	70	70
Reaction time, min	60	60	180	60	180
ClO_2 charge, % act. Cl	3.86		3.1		1
NaOH charge, %		1.35	0.37	0.9	0.25
H_2SO_4 charge, %	0.82				

Table 11. The bleaching conditions for the DED sequence.

Stage	D_0	E_1	D_1
Consistency, %	9	10	9
Temperature, °C	60	70	70
Reaction time, min	60	60	180
ClO_2 charge, % act. Cl	5.8		2.5
NaOH charge, %		2.0	0.3
H_2SO_4 charge, %	0.98		

Table 12. The bleaching conditions for DEpDP sequence.

Stage	D_0	Ep	D_1	P
Consistency, %	9	10	9	10
Temperature, °C	60	75	70	80
Reaction time, min	60	90	180	100
ClO_2 charge, % act. Cl	5.8		1.5	
NaOH charge, %		1.5	0.15	0.9
H_2SO_4 charge, %	0.98			
H_2O_2 charge, %		0.4		0.3
Epsom, %		0.1		0.5

The washing between bleaching stages was the routine washing method of the laboratory. The pulp was first diluted to the 5% consistency with deionized water at the temperature of the preceding bleaching stage. After dewatering the pulp was washed two times with cold deionized water (with the amount equivalent to ten times the amount of the abs. dry pulp). Homogenization of the pulp was made by hand. After the final bleaching stage the pulp pH was stabilized with SO_2-water to pH 4.5.

6.6 Lignin and carbohydrate analysis

The samples chosen for the lignin and the carbohydrate analysis were the cooked samples numbers 4065K, 2301M, 2310M, 2335M, and the oxygen and the bleaching trial numbers

3322 and 3352. The laboratory sheets prepared from the samples were milled with a Wiley mill using mesh size 30.

The pulp extractives may cause an error in the lignin analysis, so it was necessary to remove them beforehand. An acetone extraction was carried out for the milled samples according to SCAN-CM 49:03 standard method.

The lignin and the carbohydrate analysis were executed according to the laboratory analytical procedure provided by National Renewable Energy Laboratory (NREL/TP-510-42618). The method includes instructions for the measurement of acid soluble and acid insoluble lignin as well as the structural carbohydrates. Acetyl content of the samples was not measured.

The sugar recovery standards (SRS) used to calculate the sugar content of the HPLC samples are in Table 13. These standards correct the losses in sugars occurring during the acid hydrolysis. The SRS results were provided by Markus Paananen, from Aalto University.

Table 13. The sugar recovery standards (SRS) used in the sugar calculations to correct the loss in sugars occurring during the acid hydrolysis.

SRS	%
Arabinose	95.0
Galactose	97.0
Glucose	97.0
Xylose	88.8
Mannose	93.6

7 Results

7.1 Small scale cooks

The aim of the small scale cooks was to find out the optimal cooking conditions, which would result in defibrated pulp with a high yield. This objective was successfully attained, since only three samples in one batch were not enough delignified, and thus were impossible to disintegrate. On the other hand a wide scale of different kappa pulps were cooked, which demonstrated the development of the pulp properties along the proceeding cook. In this chapter the effect of the different process variables on delignification and the yield development are viewed and the main factors in the cooking are identified. At the end of the chapter the pulp properties are compared with the reference kraft pulp properties.

7.1.1 The effect of Na_2SO_3 charge

The first cooking batch including the six samples was executed to find out the scale of Na_2SO_3 charge required and the necessity of AQ addition to produce defibrated pulp. Reaction time, temperature and initial pH were kept constant while the different amounts of Na_2SO_3 with 0.1% AQ and without AQ were dosed. Figure 32 shows clearly, that the 0.1% AQ addition significantly enhanced delignification. At constant cooking time (240 min) it was possible to reach a kappa level below 60 using AQ, while in the cooks without AQ remained all over kappa 70.

However, it was unexpected that the high kappa pulps cooked without AQ could be disintegrated. The reasons could be the effectiveness of the disintegration and screening methods, and/or the severe temperature of 180°C and the long cooking time of 240 min at the maximum temperature, in which the fibres are softened enough allowing easier separation. The Na_2SO_3 charge required to reach the target kappa number of 50 was, without the addition of AQ, very high, about 70% on o.d. wood, assuming delignification rate to depend linearly on chemical charge. While the reaction rate is also increased due to the high temperature of 180°C, it is more economically feasible to add AQ.

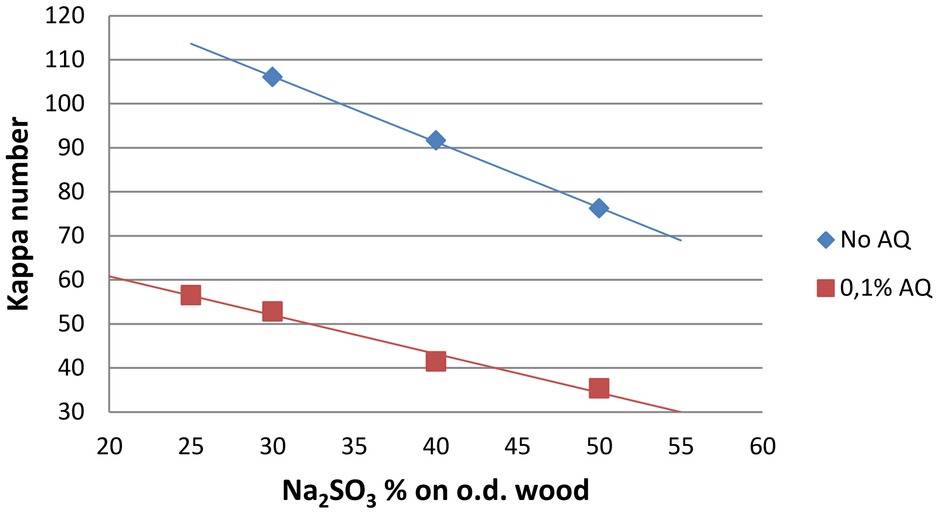


Figure 32. The effect of Na_2SO_3 charge and AQ on the kappa number in cooking. Cooking was carried out at 180°C in 240 min at initial pH 8 using Na_2SO_3 charge 25-50% on o.d. wood.

The effect of chemical charge and AQ addition on the total pulp yield is presented in Figure 33. The total pulp yield does not vary significantly between the pulps produced with and without AQ though there are significant differences in the kappa numbers of these samples. AQ is known to improve cooking selectivity. The yield decrease in the cooks with AQ is thus only caused by the removal of lignin. The result is similar when comparing the estimated carbohydrate and lignin yields (Appendix 3). It is noteworthy that no additional alkalis, such as Na_2CO_3 or NaOH, were used contrary to the experiments found in literature using these as buffer agents. When the chemical charge is high enough, the final pH is maintained over 7.5, which demonstrates the buffer capacity of the Na_2SO_3-liquor. The final pH values in these experiments are presented in Appendix 3.

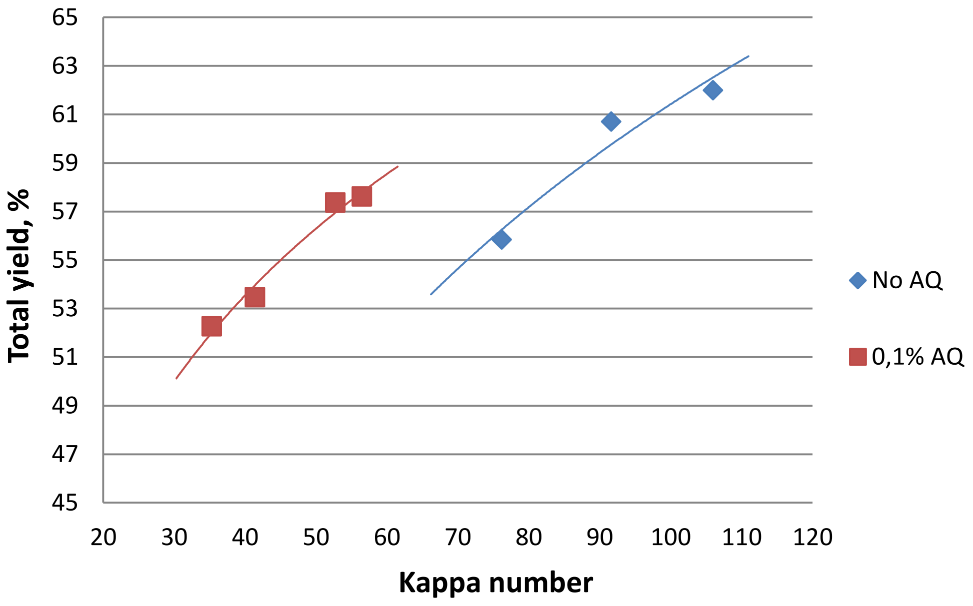


Figure 33. Total yield vs. kappa number in cooking. Cooking was carried out at 180°C in 240 min at initial pH 8 using Na_2SO_3 charge 25-50% on o.d. wood.

Based on these results the Na_2SO_3 charge chosen for the further experiments was 30% on o.d. wood, which corresponds to 19% NaOH on o.d. wood. This is a reasonable amount to reach the target kappa number 50 while preserving the total yield high.

7.1.2 The effect of initial pH

Increasing the initial pH to a slightly alkaline level was hoped to shorten the long cooking time needed. The significant decrease in the pulp viscosity was also considered to be partly related to the neutral pH during cooking. Efforts to verify this effect were made by changing the initial pH from the neutral area to the slightly alkaline.

Figure 34 presents the effect of initial pH on the kappa number and the total pulp yield. Delignification slowed down significantly when the initial pH was dropped from 8 to 7.5, seen as an increase in the kappa number from 53 to 63. The difference between the kappa numbers at pH 8 and 9 was smaller, only 5 units. The total yield did not vary considerably between pH values 7.5 and 9. Initial pH in this scale does not thus have significant effect on the total pulp yield.

Furthermore it is reasonable to maintain the initial pH 8, which is still in the pH area specified in the objectives (pH 6-8). It does not have a significant effect on the total yield, but the decrease in kappa number to the target kappa number level about 50 is obtained. If lower pH-value is considered, it is likely that it is necessary to increase the Na_2SO_3 charge, the reaction time or the maximum temperature to reach the same delignification rate. No improvement was seen in pulp viscosities (Appendix 3). It was decided to maintain the initial pH 8 for the next trials to minimize the degradation of the most vulnerable hemicelluloses by alkali and still keep the delignification in a fast enough level.

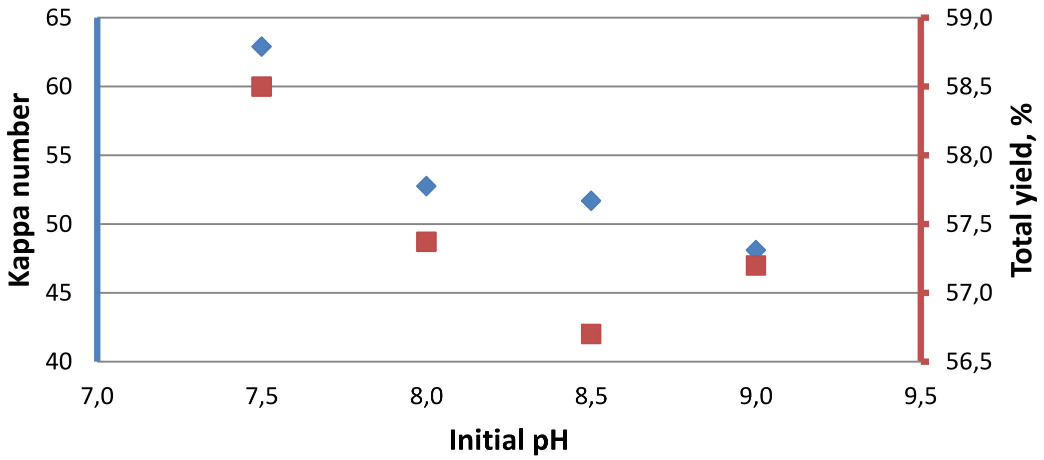


Figure 34. The effect of initial pH on kappa number and total pulp yield (%) cooked 240 min at 180°C with 0.1% AQ using Na_2SO_3 charge of 30% on o.d. wood.

7.1.3 The effect of reaction temperature

The reaction temperature mainly used in the trials was 180°C. Since the addition of AQ was shown to enhance delignification significantly, it was thought that using a higher AQ charge and a lower temperature would give a similar kappa reduction as in the case of the temperature 180°C.

The results showed that increasing the AQ charge did not notably enhance delignification, therefore the AQ charge 0.l% was considered sufficient. However, decreasing the maximum temperature from 180°C to 165°C lead to remarkably slow lignin removal, which can be seen in Figure 35. During the previous trials all pulps were disintegrated in the British disintegrator. This time only the pulps cooked at 165°C with the highest AQ charge (0.15-0.2% on o.d. wood) could be defibrated while the others remained in a chip form. It is concluded that the reaction temperature is one of the main factors affecting cooking, and temperatures significantly lower than 180°C cannot be recommended.

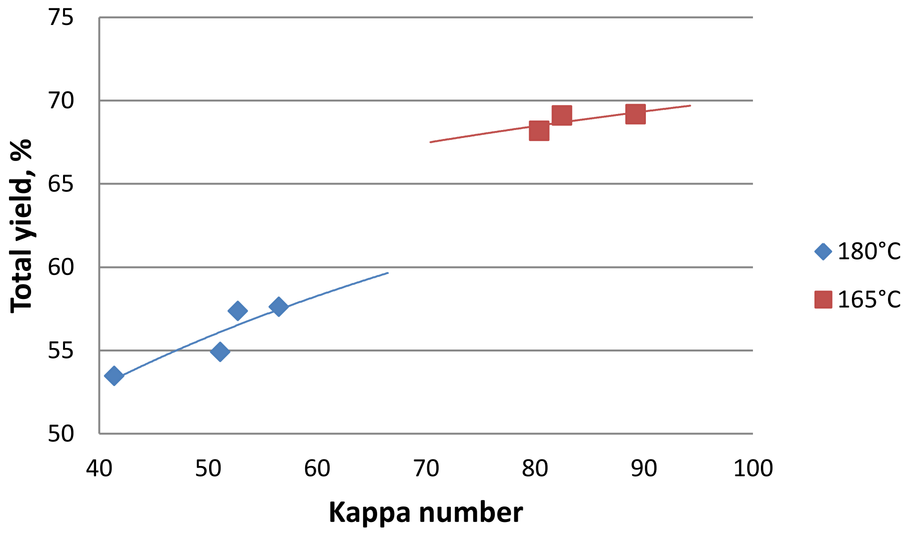


Figure 35. Total yield vs. kappa number at constant cooking time (240 min). The other cooking parameters were: AQ charge 0.1% on o.d. wood, Na_2SO_3 charge *25-50% on o.d. wood, initial pH 8.*

7.1.4 The effect of cooking time

Since a long impregnation time and a slow temperature rise are recommended in the literature, the total cooking time is significantly longer than in kraft cooking. The neutral pH also retards the delignification. To reach the kappa number target 50 at least 180 minutes at maximum temperature of 180°C is required; if Na_2SO_3 charge of 30% and AQ charge of 0.1% on o.d. wood are used. The cooking time is strongly dependent on the other cooking factors such as the chemical charge and the temperature (Figure 36). The samples having the same cooking time at temperature 180°C but a different Na_2SO_3 charge (30/25%) show more variation in the total yield and the kappa number than the effect of cooking time (from 120 min to 240 min). If the Na_2SO_3 charge and the temperature are not high enough, it means prolonged cooking time to reach the target kappa number 50. In practise it was not possible to increase the total cooking time over 300 minutes during these cooking trials. However, increasing the cooking time over 240 minutes at the maximum temperature did not seem to have any significant effect.

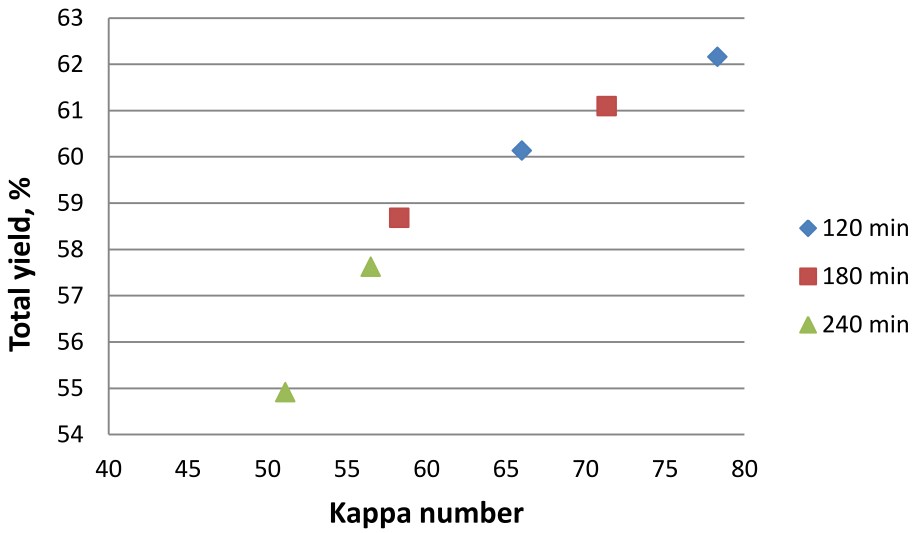


Figure 36. The effect of cooking time on kappa number and total yield. Cooking was carried out at 180°C using Na_2SO_3 charge 25/30% on o.d. wood, AQ charge 0.1% on o.d. wood, and at initial pH 8.

7.1.5 The effect of prolonged impregnation

Slow temperature rise is known to improve delignification by enabling a proper impregnation of the cooking chemicals. It was also thought to provide better conditions for glucomannan to deacetylate and attach to cellulose. It was not possible to execute steaming in the small scale trials, so increasing impregnation time was thought to improve both the delignification and the carbohydrate retention. The longer impregnation time at 140°C did not, however, improve delignification, and the total yield was lower compared to the impregnation at 80°C. This is shown in Figure 37 at kappa level 50, where the total yield difference is up to 2.5% unit. Increasing the temperature directly to 140°C was shown to be too severe. One possibility could be to use both temperature stages 80°C and 140°C in the impregnation, so that the temperature rise to maximum would be carried out in three-phases.

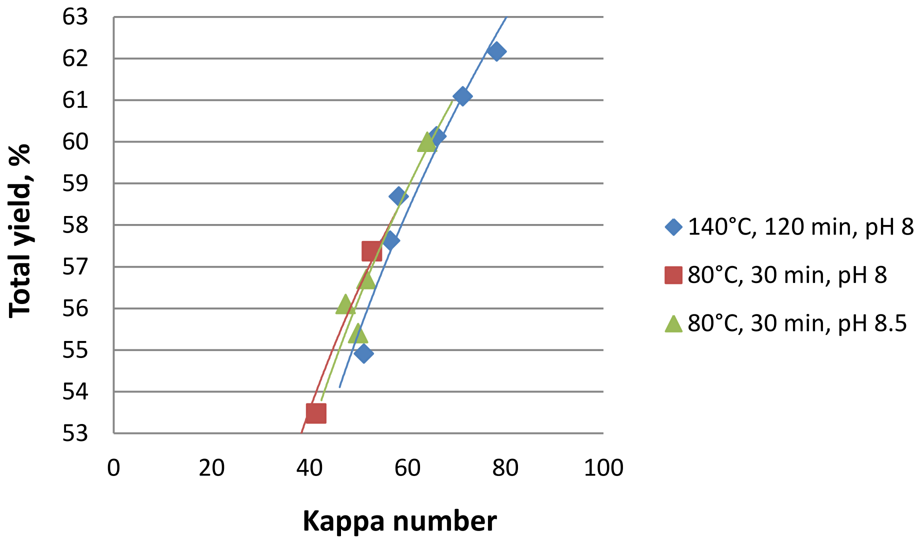


Figure 37. The effect of impregnation on total yield and kappa number. The samples are impregnated 120 min at 140°C or 30 min at 80°C before rising the temperature to the maximum cooking temperature.

7.1.6 Pulp properties

In this chapter the pulp properties compared to the reference kraft pulp are presented. Figure 38 shows the total pulp yield vs. kappa number. The conventional pine kraft pulp from the same wood raw material is used as a reference. The higher total yield obtained from the neutral sulphite cooking compared to the conventional kraft cooking is unquestionable. For example at kappa number 53 the yield of the NS pulp is almost 8 %-units higher than the yield of the kraft pulp. However, if the cooking is extended to reach a lower kappa number than 30 the yield advantage compared to the kraft pulp may be lost.

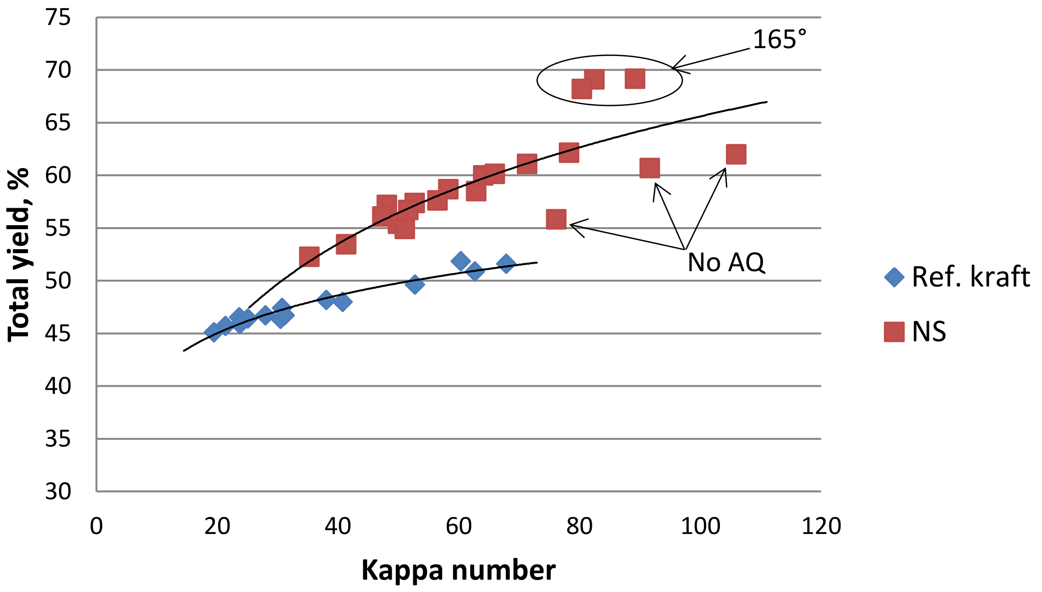


Figure 38. Comparison of the total yield, % on wood in neutral sulphite cooking (NS) vs. the reference kraft cooking. All the results from the neutral sulphite (NS) cooking trials are presented in the figure.

Differentiation of the accept and the reject of the high kappa pulps is difficult to make especially in the case of the neutral sulphite pulp, since the fibres are light in colour. Though the fibres look woody and stiff, not much reject is formed in the screening process. It is concluded that the delignification takes place in the middle lamella making the separation of the fibres is easier. However, it means that the main part of the lignin still exists in the fibre wall. Figure 39 shows the amount of screenings, which is comparable with kraft pulps. Of course the higher kappa number increases the amount of the reject.

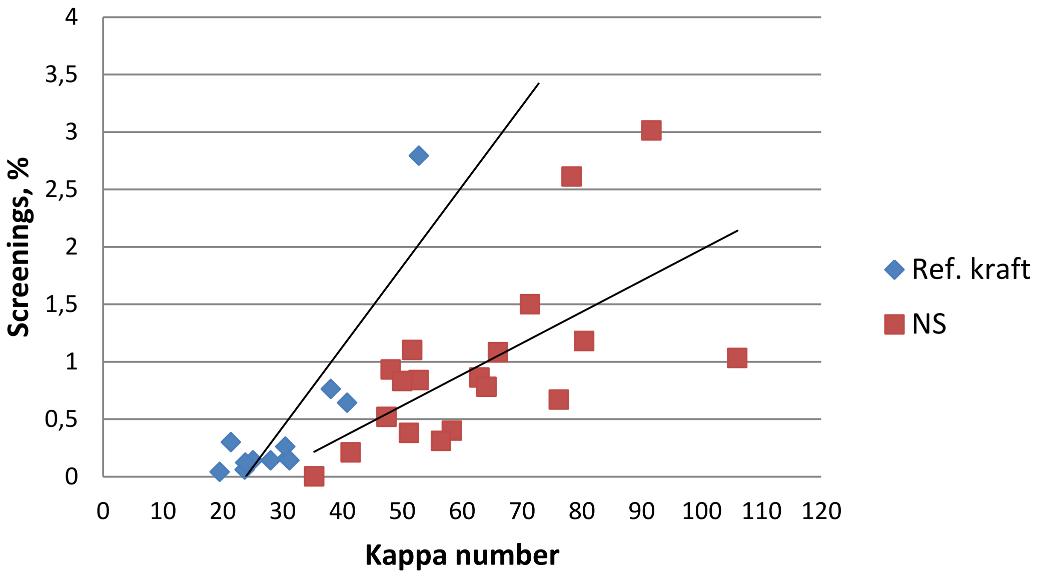


Figure 39. The screenings of the neutral sulphite and the reference kraft pulp cooked to different kappa numbers.

Viscosity and brightness vs. kappa number after cooking are presented in Figures 40 and 41. These results show that the neutral sulphite pulps have high brightness but low viscosity compared to the kraft pulps. The main reason for the low viscosity is unknown but it is generally known, that high hemicellulose content affects the viscosity determined in the cupriethylenediamine (CED) solution. Any direct conclusions of the pulp strength properties cannot be made based on the viscosity results, since the high kappa number also affects the viscosity analysis. Problems such as plugging of the capillaries of the analyzer and variation in the duplicate samples in viscosity analysis are also concluded to originate from the high lignin content of samples. The brightness is significantly higher and more uniform compared to the reference kraft pulps. It seems that the brightness is mainly depending on the cooking chemicals, since alkali is known to cause lignin condensation reactions (Rehbein, Pereira et al. 2010), which darken the pulp.

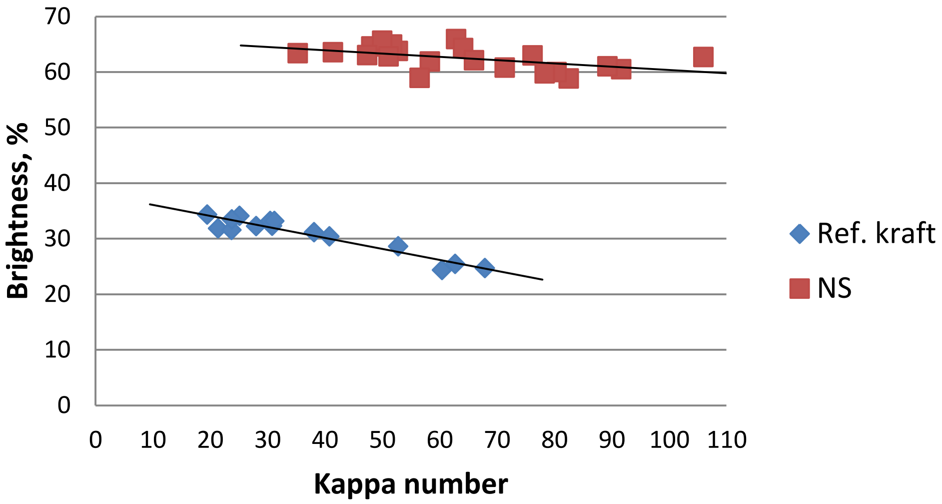


Figure 40. Brightness vs. kappa number of the neutral sulphite pulps and the reference kraft pulps.

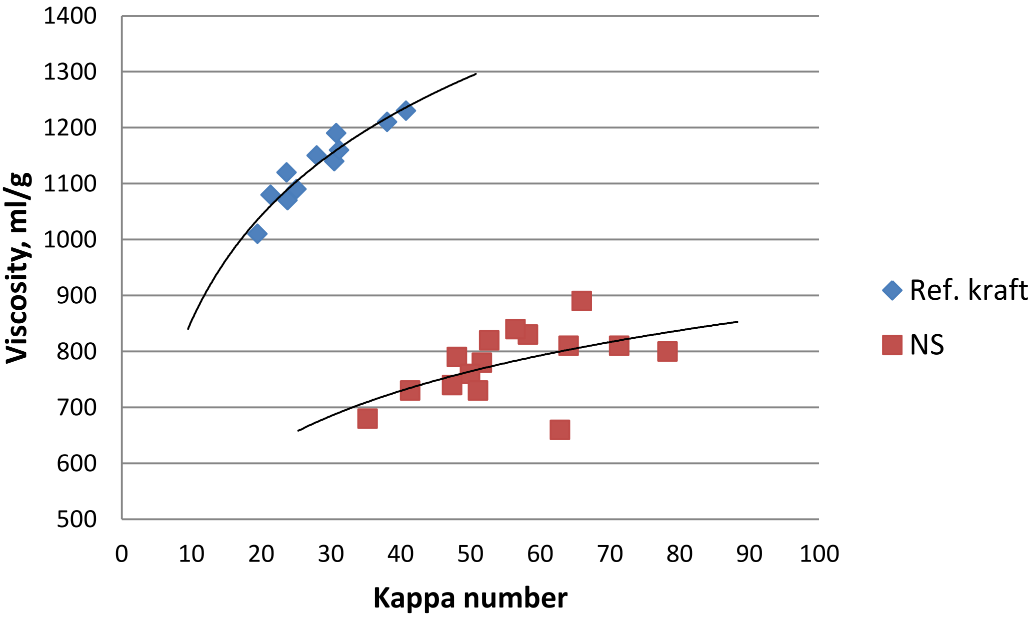


Figure 41. Viscosity vs. kappa number of the neutral sulphite pulps and the reference kraft pulps.

Figure 42 shows the sulphonic acid group content as a function of kappa number. The content of sulphonic acid groups is decreased while the kappa number is decreased, which is logical since the amount of the lignin is decreased. The sulphonic acid groups are thought to be attached only to lignin and not to carbohydrates, though some suggestions of sulphonated carbohydrates have been presented as well. The latter is in agreement with Figure 43, since the content of the sulphonic acid groups is around 100 mmol/kg when the lignin content is zero. These sulphonic acid groups should be found attached to the carbohydrates. The highest amount of sulphonic acid groups measured was approximately 300 mmol/kg. This is at the same level with the sulphonated CMP pulp containing 250-300 mmol/kg. (SCAN-CM 65:02; Heitner & Hattula 1988).

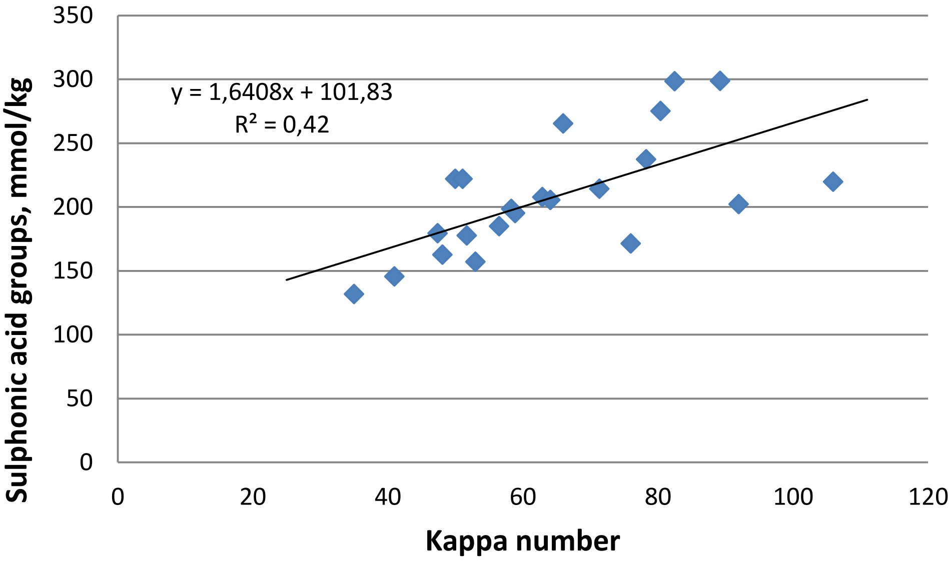


Figure 42. The sulphonic acid group content (mmol/kg pulp) vs. kappa number in the neutral sulphite pulps.

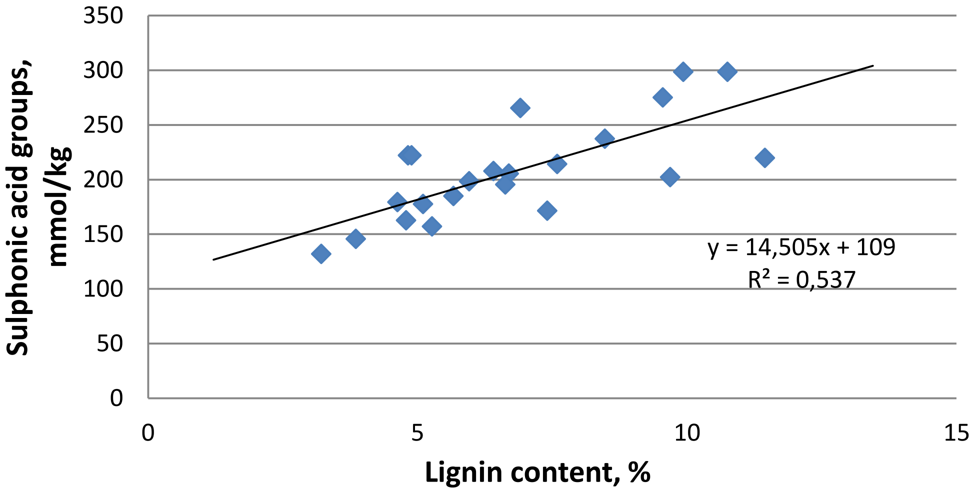


Figure 43. The sulphonic acid group content vs. calculated lignin content in the neutral sulphite pulps.

7.2 The large scale cook

The cooking conditions, which resulted in the target kappa number 50 were chosen to be implemented in a larger scale. The aim was to produce pulp with comparable properties with the smaller scale cooks for the oxygen delignification and bleaching experiments. The cooking conditions from the small scale cook number 2299M were chosen. In the larger scale it was possible to carry out chip steaming, which would improve impregnation. Though, because of the equipment limitations the N_2 pressure was lower than in the small scale cooks.

The results from both cooks are compared in Table 14. The delignification of the larger scale cook (4065K2) was slower or uneven, which is seen as a higher kappa number. The reason might be the lower pressure used. The amount of the screenings was lower in the 4065K2-cook probably because of the different screening apparatus. Brightness and viscosity were also lower, but viscosities were hard to compare because of the high kappa numbers.

Table 14. The cooking results of the small scale cook (2299M) used as a model for the large scale cook (4065K2).

Cook	Kappa number	Tot. yield %	Screenings, %	ISO-brightness, %	Viscosity, ml/g
2299M	53	57,4	0,8	63,8	820
4065K2	59	64,6	0,1	59,9	780

7.3 Oxygen delignification

The objective of the oxygen stage was to lower the kappa number to a level acceptable for bleaching. The single stage process reached the kappa target 30, which meant 45-50% kappa reduction after cooking. The increase in the temperature or the alkali charge did not have a significant effect on the delignification or the pulp yields. The combination of high temperature and high alkali charge was not tested because of a probable deterioration of the pulp yield.

In the two-stage oxygen delignification without an intermediate washing between the stages 60% kappa reduction was attained. However, the pulp yield calculated from the TOC values was poor being only 83% for the pulp processed at 98°C. The lower temperature (85°C) resulted in a 5% -unit´s higher yield at the same kappa number.

The major disadvantage of the oxygen delignification stage was the remarkable decrease in pulp brightness. This brightness loss is due to the darkening of lignin caused by strong alkali. No improvement in brightness was obtained by lowering the temperature to 85°C, contrary to expectation.

Figure 44 shows the total yield calculated on wood and the pulp brightness. The total yield in this figure was calculated from the gravimetric yield, which was believed to be accurate, because of the high volume of the starting pulp. The yield measured by TOC was significantly lower. Precise comparison of these two results is shown in Appendix 4.

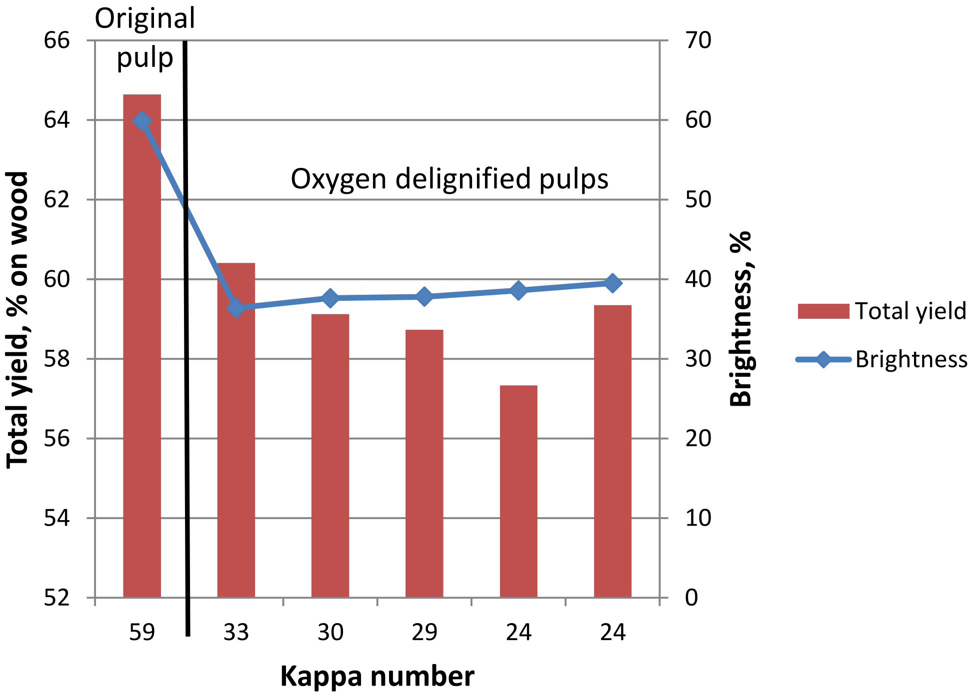


Figure 44. Total yield and brightness as a function of kappa number. The first bar on the left is the original cooked pulp and the rest of the bars represent the oxygen delignified pulps.

The pulp viscosities in Figure 45 were well attained during the oxygen delignification and no significant differences were observed between the samples produced in the one-stage process. In one stage oxygen delignification 10°C increase in the temperature or the higher alkali charge did not show individually effect on the viscosity. In the multiple stages, where alkali was added between stages, the loss in viscosity was notable.

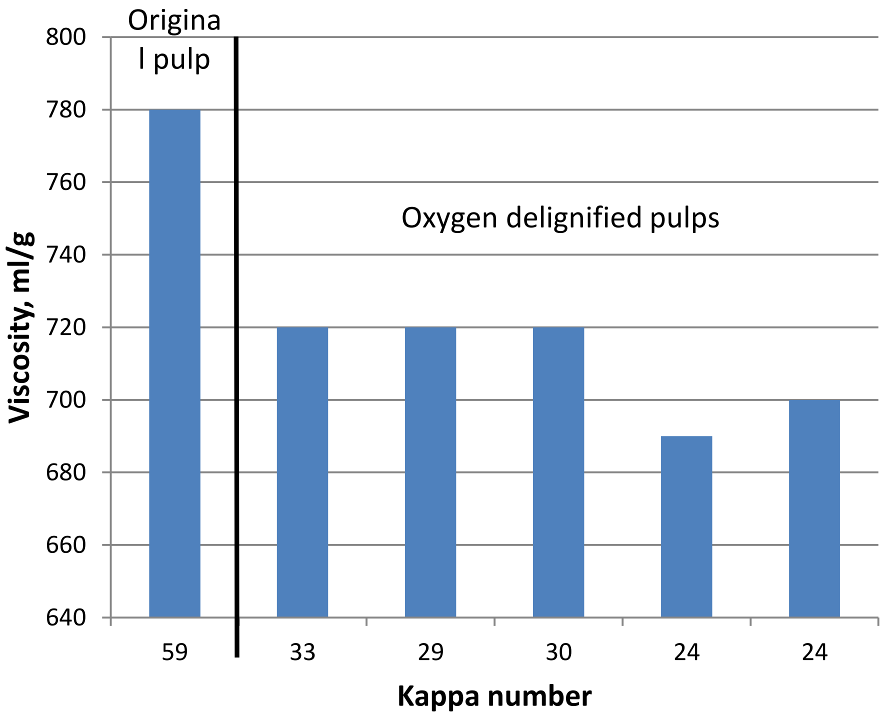


Figure 45. Viscosity as a function of kappa number. The first bar on the left is the original cooked pulp and the rest of the bars represent the oxygen delignified pulps.

7.4 Bleaching

The oxygen delignified pulp kappa 24 was used in the bleaching experiments. The target brightness for the bleaching experiments was set to 89% ISO. The total results and the results of the different bleaching stages are presented in Appendix 5. The final results of the bleaching are shown in Table 15. No significant differences between the bleached pulps are seen. The viscosity is not deteriorated by the bleaching sequences. The chemical consumption is high due to the high initial kappa number after the oxygen delignification. The total ClO_2 charge of the DEDED-sequence is in reality lower than measured due to over bleaching.

Table 15. The total results of the fully bleached pulp.

Bleaching sequences	**DEDED**	**DED**	**DEpDP**
Kappa number	1	1	1
Brightness, %	90	87	89
Viscosity, g/ml	650	690	680
Total ClO_2 cons. as act. Cl kg/t pulp	75	82	72
Total H_2O_2 cons. kg/t pulp	-	-	7
Total yield, % on wood	51	53	48
Total yield, % on wood	55	56	51

Figure 46 presents the kappa number as a function of the ClO2 consumption. The shortest bleaching sequence, DED, needed the highest total ClO2 charge to reach the target brightness.

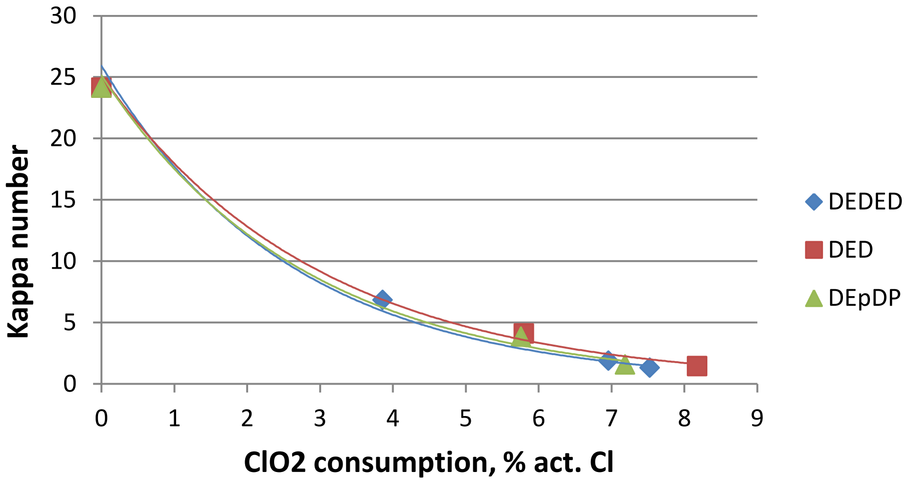


Figure 46. Kappa number as a function of the ClO_2-consumption (% act. Cl). The consumption of ClO_2 in each point is the total consumption of the chemical so far.

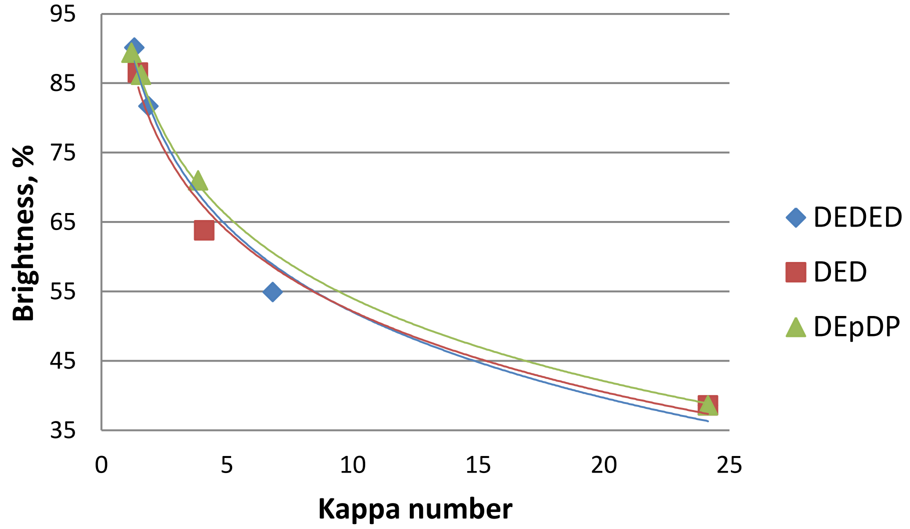


Figure 47. Brightness as a function of kappa number in pulp bleaching.

7.5 Chemical composition

The chemical composition analyses proved the significantly higher carbohydrate retention obtained by the sulphite cooking at neutral conditions. Figure 48 shows that the higher yield of the neutral sulphite pulps compared to the kraft pulp is mainly due to the high glucomannan yield. It is noteworthy that the total carbohydrate yield of the kraft pulp at kappa number 60 and the fully bleached sulphite pulp (3352) are almost at the same level. In this light we can say that the carbohydrate yield gained in the cooking is well preserved over the oxygen delignification and bleaching. The results are found in Appendix 6.

The reference kraft pulp (kappa 60) was produced in a previous study from the same chips as the present NS pulps. So it cannot be assumed that the first two pulps, ref. kraft 60 and

NS 60, would be identical concerning the lignin content though they both are cooked to the kappa number 60.

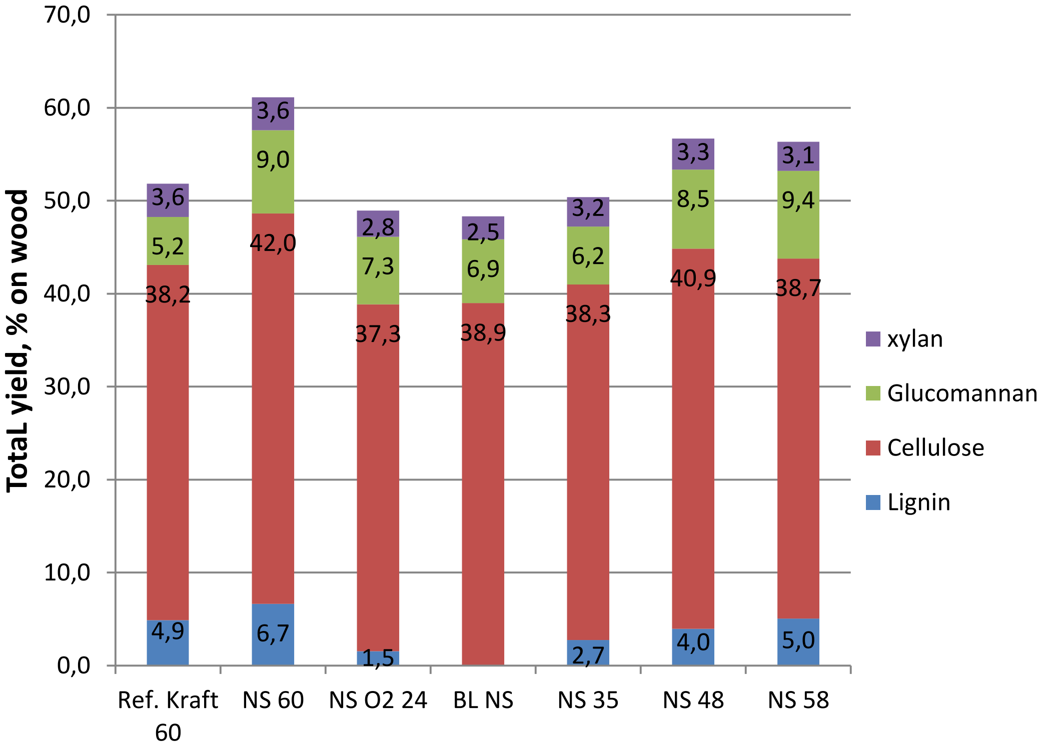


Figure 48. The chemical composition based on the total yield calculated on wood. NS means neutral sulphite cooked pulp and the number represents kappa number.

8 Conclusions and discussion

The cooks carried out with sodium sulphite at neutral conditions resulted in high kappa pulps, which also had a high yield. The target kappa number 50 was reached at temperature 180°C with the cooking liquor composition of 30% Na_2SO_3 on o.d. wood and 0.1-0.15% AQ on o.d. wood. The time at maximum temperature varied between 240-270 minutes and the initial pH between 8 and 8.5. The lowest kappa number gained was 35 and it was reached by using the same conditions as mentioned above expect the cooking liquor contained 50% Na_2SO_3 on o.d. wood and 0.14% AQ on o.d. wood.

Regardless of the wide range of the kappa numbers (35-106) all the pulps were defibrated during the mechanical disintegration and the screening, except three pulp samples cooked at the maximum temperature of 165°C. The other cooking parameters were: the cooking time 240 min, the Na_2SO_3 charge 30-40% on o.d. wood and the AQ charge 0.1-0.2% on o.d. wood. It is concluded that the maximum temperature is one of the critical factors affecting the delignification efficiency. Since only the temperatures 165°C and 180°C were tested, it can be said that the cooking temperature should be 180°C. According to the literature the neutral sulphite cooks are generally made at temperature 170ºC or higher (Chen, Ghazy et al. 1994).

Cooking without AQ resulted in pulp with a significantly higher kappa number and lower viscosity compared to the cooks where AQ was used. It is concluded that AQ is a necessary auxiliary chemical in sulphite cooking at neutral conditions. Both high delignification efficiency and cooking selectivity is obtained by using 0.1% AQ on o.d. wood. The chemical savings are then also notable. Kappa number around 50 is reached by 30% Na_2SO_3 charge with

0.1% AQ and without AQ to reach the same kappa number the Na_2SO_3-charge would be approximately 70% on o.d. wood. According to the literature there are various views of the function of AQ in the sulphite pulping. These experiments confirmed that AQ is acting in the sulphite pulping at neutral conditions but the deeper knowledge of the chemistry behind this remains unknown.

The significant viscosity loss during the cooking remained unknown. It is known that viscosity is better preserved in alkaline pH, but increasing the initial pH to 9 did not make any difference. However, some problems occurring in the viscosity analysis (ISO 5351:2004) may have affected the final results. The samples containing high amount of lignin maybe did not dissolve properly in the CED-solution causing blocks in the analyser. The high hemicellulose content is also known to affect the viscosity analysis. The oxygen delignification or the bleaching experiments had no significant effect on the viscosities. The pulps produced with sulphite cooking are much brighter than the kraft pulps. All the pulp samples had the brightness value between 59-66%.

The sulphonic acid group content measured after cooking were at the same level as the sulphonated CMP pulp containing 250-300 mmol/kg. The results also showed that the content of sulphonic acid groups is around 100 mmol/kg when the extrapolated lignin content is zero, which may indicate that the rest of the sulphonic acid groups are attached to the carbohydrates. The result is interesting since no recent data exist suggesting the existence of the sulphonated carbohydrate structures. Yet further research is needed to confirm that sulphonated carbohydrates exist. In a biorefinery point of view, the sulphonated lignin and carbohydrate fragments are possible sources of new applications. Their structure and chemical properties should be studied more deeply.

The one-stage oxygen delignification resulted in 45-50% kappa reduction and the two-stage delignification up to 60% reduction. The major disadvantage was the significant brightness loss caused by the alkaline darkening of the pulp. The 60% ISO brightness after cooking was decreased below 40% ISO brightness during the oxygen treatment. It was possible to reach a full bright pulp with the bleaching sequences DEDED and DE_pDP. The brightness of the shortest bleaching sequence DED was 87% ISO. The major disadvantage of the bleaching is the high chemical consumption, which is due to the high kappa number after the oxygen delignification. Based on these results the oxygen delignification is not recommended if a bleachable-grade pulp is produced. The lignin preserving bleaching is one option, which should be evaluated.

The cooking yield was significantly higher compared to the reference kraft pulps. The yield gain over correspondin kraft pulp obtained was the same range as the total yield of pine NS-AQ pulp, 8-10% higher than the corresponding kraft cooks (Ojanen, Tulppala et al. 1982). The higher the kappa number the higher this yield advantage seems to be. However, it seems that this yield advantage is lost if the cooking is continued below kappa number 30. Though, this requires cooking conditions, which are not reasonable in practise. The chemical composition analysis confirmed the retention of the carbohydrates. Comparing the results of the cooking samples and the results in Table 4 (Kettunen, Virkola et al. 1979) it is clearly seen that the high yield results from the high glucomannan content. Xylan did not seem to be preserved better however, softwoods contain less xylan than glucomannan. No notable carbohydrate loss was noticed during the oxygen delignification or bleaching, and the total yield on wood was 48-53%.

9 Summary

Sulphite is a strong nucleophile, which can react with lignin under the neutral sulphite pulping conditions thus leading to lignin dissolution. In neutral conditions the acid-base-catalysed degradation of carbohydrates is also significantly slowed down. This results in pulp yield increase, which can be preserved at least partly during the whole pulping process to the fully bleached pulp. This yield advantage compared to the other pulping processes results from the hemicellulose retention, especially glucomannan.

The cooking experiments carried out in the thesis produced high kappa pulps, which had high cooking yield. At the target cooking kappa number 50 the yield was 55% on o.d. wood and the calculated carbohydrate yield 51% on o.d. wood. The kappa number 50 was obtained under the cooking conditions of 180°C, 240 min, 30% Na_2SO_3-charge, 0.1% AQ-charge, the initial pH 8. The brightness of these pulps was over 60% ISO but the viscosities were poor.

The one-stage oxygen delignification resulted in 45-50% kappa reduction and the two-stage delignification even 60% reduction. The total yield and the viscosity did not decrease considerably but the pulp brightness was significantly reduced by the effect of alkali. The bleaching sequences tested DEDED, DE_pDP, and DED resulted in pulps with brightness of 89% ISO and 87% ISO. The disadvantage of the bleaching was the high chemical consumption, though the pulp properties were maintained.

The sulphonic acid groups content of the cooked pulps were between 130 and 300 mmol/kg. The results indicate that part of the carbohydrates is also sulphonated. However, this thought was not confirmed. The chemical composition analysis showed that the high yield obtained during the cooking and bleaching experiments resulted from the preserved glucomannan. Cellulose seemed to stay also highly unaffected.

The further experiments are suggested to find out the chemical structure and the properties of the sulphonated lignin. The possible existence of the sulphonated carbohydrates should be also clarified, and their structure and properties. After this the possible applications of the polymers can be evaluated.

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LIST OF APPENDICES

Appendix 1. Standards and methods used in the laboratory experiments.

Appendix 2. Laboratory procedures for bleaching experiments.

Appendix 3. Cooking conditions and results.

Appendix 4. The conditions and the results of the oxygen delignification trials.

Appendix 5. Bleaching conditions and results.

Appendix 6. The chemical compositions results.

Standards used to measure chips size distribution and dry matter content.

Measurement	**Standard**
Size distribution	SCAN-CM 40:01
Dry matter content	SCAN-CM 39:94

Measurements and standards used in cooking experiments.

Measurement	**Standard**
Pulp dry matter content	SCAN-C 3:78
Total yield	Gravimetric
Reject	Gravimetric
Preparation of laboratory sheets	SCAN-CM 11:95
Kappa number	ISO 302:2004
ISO brightness	ISO 2470
Viscosity	ISO 5351:2004
Total acidic group content	SCAN-CM 65:02
Content of acetone-soluble matter	SCAN-CM 49:03
Determination of structural carbohydrates and lignin in biomass	NREL/TP-510-42618
Total acidic group content	SCAN-CM 65:02

Measurements and standards used in oxygen delignification and bleaching experiments.

Measurement	**Standard**
Pulp dry matter content	SCAN-C 3:78
Total yield	Gravimetric
Reject	Gravimetric
Residual alkali	SCAN-N 33:94
Preparation of laboratory sheets	SCAN-CM 11:95
Kappa number	ISO 302:2004
ISO brightness	ISO 2470
Viscosity	ISO 5351:2004
Content of acetone-soluble matter	SCAN-CM 49:03
Determination of structural carbohydrates and lignin in biomass	NREL/TP-510-42618

Chlorine dioxide stage (D)

The reaction conditions:

Consistency	9%
Temperature	60/70°C
Reaction time	60/180 min

Procedure: The small scale chlorine dioxide bleaching is carried out in a 1l vessel placed in a warm water bath. The active chlorine content of the ClO_2 is measured. Pulp, water and chemicals, NaOH or Na_2SO_4 depending on the pH of the stage, are heated up to a temperature, which will reach the reaction temperature after addition of ClO_2 at the room temperature. Heated pulp, water and acid or alkali, are mixed in the vessel and the pH of the suspension is measured. The ClO_2 is added right before the vessel is placed in a water bath. During the reactions mixing is made by hand in every 15 minutes. After the reaction the residual chlorine and pH are measured, which after the pulp is washed according to the standard laboratory washing method.

Alkaline stage (E)

The reaction conditions:

Consistency	10%
Temperature	70/75°C
Reaction time	60 min

Procedure: The small scale alkaline stage is carried out in a 1l vessel placed in a warm water bath. Pulp and water are separately heated up to the reaction temperature. Alkali is mixed with water before adding the solution into the pulp. After mixing the pH of the suspension is measured before closing the vessel and placing it into the warm water bath. During the reactions mixing is made by hand in every 15 minutes. After the reaction pH is measured and pulp is washed according to the standard laboratory washing method.

Peroxide stage (P)

Reaction conditions:

Consistency	10%
Temperature	80°C
Reaction time	100 min

Procedure: The small scale peroxide stage is carried out in a 1l vessel placed in a warm water bath. At first the concentration of the hydrogen peroxide is measured. Pulp, water and alkali are separately heated up to the reaction temperature. Water, alkali and peroxide are mixed before adding them into the pulp. The suspension is mixed and the pH is measured. The vessel is closed and placed into the water bath. During the reaction mixing is made by hand in every 15 minutes. After the reaction the residual peroxide and pH are measured, which after the pulp is washed according to the standard laboratory washing method.

SO_2-treatment (A)

Reaction conditions:

Consistency	2%
pH	4-5
Temperature	25°C
Reaction time	15 min

Procedure: The pulp is diluted to 2% consistency with 20°C water. SO2-liquor is added drop by drop while mixing and continuously following the pH. When the reaction pH is reached, the pulp suspension is allowed to stand still during 15 minutes. After the reaction pulp is washed according to the standard laboratory washing method.

APPENDIX 3 1(1)

The cooking conditions and the results of the small scale cooks.

Cook	T, °C	t, min	Na_2SO_3 % on o.d. wood	AQ % on o.d. wood	Initial pH	Final pH	Tot. Yield %	Screenings, %	Kappa number	ISO-brightness, %	Viscosity, ml/g	Carbohydrate yield, % *
2296M	180	240	30	0	8,0	7,3	62,0	1,0	106	62,7	690	51,9
2297M	180	240	40	0	8,0	7,6	60,7	3,0	92	60,5	600	52,1
2298M	180	240	50	0	8,0	7,9	55,8	0,7	76	62,9	570	49,3
2299M	180	240	30	0,13	8,0	7,5	57,4	0,8	53	63,8	820	52,7
2300M	180	240	40	0,13	8,0	7,9	53,5	0,2	41	63,6	730	50,1
2301M	180	240	50	0,14	8,1	8,3	52,3	0,0	35	63,4	680	49,4
2308M	180	240	30	0,09	7,5	7,6	58,5	0,9	63	65,9	660	52,8
2309M	180	240	30	0,1	8,5	7,9	56,7	1,1	52	64,9	780	52,2
2310M	180	240	30	0,11	9	7,9	57,2	0,9	48	64,6	790	53,0
2311M	180	180	30	0,13	8,5	7,8	60,0	0,8	64	64,3	810	54,1
2312M	180	270	30	0,09	8,5	7,8	55,4	0,8	50	65,6	760	51,1
2313M	180	300	30	0,12	8,5	7,4	56,1	0,5	47	63,0	740	52,0
2320M	165	240	30	0,1	8	7,6	74,1	74,1	-	-	-	-
2321M	165	240	30	0,15	8	7,7	72,2	72,2	-	-	-	-
2322M	165	240	30	0,2	8	7,8	69,1	38,6	83	58,8	990	60,3
2323M	165	240	40	0,1	8	7,8	73,4	73,4	-	-	-	-
2324M	165	240	40	0,15	8	7,9	69,2	27,9	89	61,0	980	59,7
2325M	165	240	40	0,2	8	8,0	68,2	1,2	80	60,0	970	59,8
2330M	180	120	30	0,1	8	7,8	60,1	1,1	66	62,1	890	54,0
2331M	180	180	30	0,1	8	7,8	58,7	0,4	58	61,9	830	53,4
2332M	180	240	30	0,1	8	7,4	54,9	0,4	51	62,8	730	50,6
2333M	180	120	25	0,1	8	7,5	62,2	2,6	78	59,7	800	54,7
2334M	180	180	25	0,1	8	7,5	61,1	1,5	71	60,8	810	54,4
2335M	180	240	25	0,1	8	7,2	57,6	0,3	57	59,0	840	52,6

The cooking conditions and the results of the large scale cook.

Cook	max. T, °C	t , min	Na_2SO_3 % on o.d. wood	AQ % on o.d. wood	Initial pH	Final pH	Kappa number	Tot. Yield %	Screenings, %	ISO-brightness %	Viscosity, ml/g	Carbohydrate yield, %*
4065K	180	240	30	0,1	8	8,6	59	64,6	0,1	59,9	780	58,8

*calculated carbohydrate yield

APPENDIX 4 1(1)

The conditions and the results of the oxygen delignification trials.

O_2-stage	T, °C	t, min	NaOH % on o.d. pulp	Epsom % on o.d. pulp	Consistency, %	Final pH	Kappa number	Kappa reductio, %	ISO-brightness, %	Viscosity, ml/g	TOC, mg/l	Yield based on TOC, %	Gravimetric yield, %	Total yield, % on wood
3309	98	60	3	0,6	12	9,5	33	44	36,4	720	-	-	93,5	60,4
3310	98	60	4,5	0,6	12	9,8	29	51	37,8	720	7600	89,0	90,9	58,7
3011	110	60	3	0,6	12	9,0	30	49	37,6	720	6900	90,1	91,5	59,1
3322 O_1	98	60	4,2	0,6	12	-	-	-	-	-	-	-	-	-
3322 O_2	98	60	2,3	-	12	9,8	24	59	38,6	690	8500	87,7	88,7	57,3
3329 O_1	85	60	4,2	0,6	12		36	39	38,1	740	5800	91,6		-
3329 O_2	85	60	2,3	-	12	10,9	29	52	38,8	700	6500	90,8		-
3329 O_3	85	60	-	-	12	10,8	24	59	39,5	700	7700	89,1	91,8	59,3

APPENDIX 5 1(1)

Bleaching conditions and results

Bleaching number		**3322**	**3347**	**3352**
D_0				
Cons. 9%	ClO_2 charge, % act. Cl	3,86	5,8	5,8
60°C	ClO_2 consumption, % act. Cl	3,86	5,8	5,76
60 min	*H_2SO_4 charge, %	0,82	0,98	0,98
	Final pH	1,7	2,0	1,9
E_1				
Cons. 10%	NaOH charge, %	1,35	2,03	
70°C	Final pH	10,5	10,8	
60 min	Kappa number	6,83	4,1	
	Kappa reduction, %	71,7	83,0	
	Brightness, %	54,9	63,8	
Ep				
Cons. 10%	NaOH charge, %			1,5
75°C	H_2O_2 charge, %			0,4
90 min	H_2O_2 consumption, %			0,36
	Epsom charge, %			0,1
	Final pH			10,0
	Kappa number			3,85
	Kappa reduction, %			84,1
	Brightness, %			71,0
D_1				
Cons. 9%	ClO2 charge, % act. Cl	3,1	2,5	1,5
70°C	ClO_2 consumption, % act. Cl	3,1	2,38	1,43
180 min	*NaOH charge, %	0,4	0,3	0,15
	Final pH	3,5	4	4,4
	Kappa number			1,59
	Kappa reduction, %			58,7
	Brightness, %			86,2
E_2				
Cons. 10%	NaOH charge, %	0,9		
70°C	Final pH	10,6		
60 min	Kappa number	1,9		
	Kappa reduction, %	72,5		
	Brightness, %	81,7		
D_2				
Cons. 9%	ClO2 charge, % act. Cl	1,0		
70°C	ClO_2 consumption, % act. Cl	0,57		
180 min	*NaOH charge, %	0,25		
	Final pH	6,7		
P				
Cons. 10%	NaOH charge, %			0,9
80°C	H_2O_2 charge, %			0,3
100 min	H_2O_2 consumption, %			0,3
	Epsom charge, %			0,5
	Final pH			10,6
Final SO_2-treatment				
	Kappa number	1,3	1,5	1,2
	ClO_2 consumption, % act. Cl	7,5	8,3	7,2
	H_2O_2 consumption, %	-	-	0,7
	Kappa reduction, %	29,8	64,4	23,9
	Brightness, %	90,1	86,5	89,4
	Viscosity, g/ml	650	690	680
	Bleaching yield, %	95,1	98,2	89,6
Total ClO_2 cons. as act. Cl kg/t pulp		75,3	81,8	71,9
Total H_2O_2 cons. kg/t pulp				6,6
Total yield, % on wood		51,1	52,8	48,2

* for pH adjustment

The chemical compositions results.

Pulp number	Total yield, %	Total lignin %	Cellulose %	Xylan %	Glucomannan %
Ref. Kraft 60	51,85	4,9	38,2	3,6	5,2
4065K2	64,6	6,7	42,0	3,6	9,0
3322	51	1,5	37,3	2,8	7,3
3352	48,2	0,0	38,9	2,5	6,9
2301M	52,3	2,7	38,3	3,2	6,2
2310M	57,2	4,0	40,9	3,3	8,5
2335M	57,6	5,0	38,7	3,1	9,4