The initial phase of the sodium bisulfite pulping of softwood dissolving pulp

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Abstract

Single stage sodium bisulfite cooking was carried out on either spruce or pine wood chips to investigate the influence of several process parameters in the initial phase of such a cook i.e. between 60 % and 100 % pulp yield. The cooking experiments were carried out in the laboratory with either a lab prepared or a mill prepared cooking acid and the temperature and time in the initial stage were varied. The influence of dissolved organics and inorganics components in the cooking liquor on the final pulp properties and side reactions were investigated. The impact of temperature and time on the pulp components were analyzed with respect to carbohydrates, lignin, extractives and thiosulfate. Kinetic equations were developed and the activation energies for delignification and carbohydrate dissolution were calculated using the Arrhenius equation.

It was found that if using a mill prepared cooking acid, this had a beneficial effect with respect to side reactions, better extractives removal and higher pH stability during the cook, compared to a corresponding cook with a lab prepared cooking acid. Cooking with mill prepared and lab prepared cooking acids showed unchanged behavior with respect to delignification and cellulose degradation, but the lab acid experiments resulted in a higher thiosulfate formation during the cook. The cellulose yield was not affected at all during the initial phase of the sulfite cook verifying earlier results by other researchers. The temperature had an influence on both the delignification rate and the rate of hemicellulososes removal. The corresponding activation energies were found to increase in the following order; cellulose, xylan, glucomannan and lignin. The cooking temperature could thus be used to control the cook to a given carbohydrate composition in the pulp after the initial phase of the cook.

Keywords: Activation energy, bisulfite pulping, cellulose, delignification, extractives, glucomannan, hemicellulososes, lignin, pine, spruce, thiosulfate, total SO₂ and xylan.
Sammanfattning

Denna licentiatavhandling behandlar enstegs natriumbisulfitkokning av gran respektive tallved och syftet var att undersöka ett antal olika processparametrars inverkan på initialfasen av koket d.v.s. intervallet 60-100% massautbyte. Kokförsöken utfördes i laboratorieskala med antingen fabriksframställd eller laboratorieframställd koksyra där koktid och koktemperatur varierades. De två typerna av koksyra medförde att halten av löst organiskt och oorganiskt material i vätskefasen blev olika och därmed blev det möjligt att studera deras inverkan på den slutliga massasammansättningen samt på omfattningen av olika sidoreaktioner. Inverkan av temperatur och tid undersöks med avseende på hur de påverkade massans innehåll av cellulosa, hemicellulosa, lignin, extraktivämnen samt hur bildningen av tiosulfat påverkades. Kinetiken för utlösningen av dessa komponenter studerades specifikt och resultaten sammanfattades med hjälp av Arrhenius ekvation. Resultaten från studien visade att om en fabrikstillverkad koksyra användes istället för en laboratorietillverkad så medförde det minskad tiosulfatbildning och minskat extraktivämnesinnehåll i massan samt stabilare pH under koket. Delignifiering och cellulosanedbrytning påverkades däremot inte av en sådan förändring. Ökad temperatur ökade delignifieringshastigheten samt hastigheten för utlösning av xylan och glukomannan. Högre temperatur i initialfasen påverkade inte utlösningen av cellulosan. Koktemperaturen kan därmed användas för att styra koket så att man kan få massor med olika kolhydratsammansättning efter initialfasen.
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List of papers

The following papers are included in the thesis

**Paper 1:** The initial phase of sodium bisulfite pulping of spruce, Part I
Raghu Deshpande, Lars Sundvall, Hans Grundberg and Ulf Germgård
*Accepted for publication in Cellulose Chemistry and Technology*

**Paper 2:** The influence of the temperature on the initial phase of sodium bisulfite pulping of spruce
Raghu Deshpande, Lars Sundvall, Hans Grundberg and Ulf Germgård
*O Papel, Volume 76, num.4, pp. 56-61, April 2015.*

**Paper 3:** The initial phase of sodium bisulfite pulping of pine, Part I
Raghu Deshpande, Lars Sundvall, Hans Grundberg and Ulf Germgård
*Manuscript*

**Paper 4:** The initial phase of sodium bisulfite pulping of pine, Part II
Raghu Deshpande, Lars Sundvall, Hans Grundberg and Ulf Germgård
*Manuscript*
The author’s contribution to the papers

Paper 1: Performing the experimental work and interpretation of the results. The article was written in collaboration with the co-authors

Paper 2: Data analysis and interpretation of the experimental results. The majority of the writing was done by the principal author and with collaboration from co-authors

Paper 3 & 4: Performed the experimental work, evaluation & interpretation of the results and writing the main part of the manuscript.

Related materials

“The magic of sulfite pulping: The critical first stage of a dissolving pulp cook”, Poster presentation at the Avancell conference at Chalmers University of Technology, Gothenburg, Sweden, October 8-9, 2013.
1. **Background**

1.1 **The composition of the wood**

Wood is a heterogeneous biological material consisting of cellulose, hemicelluloses, lignin and small amounts of extractives, proteins and inorganic components. Cellulose, hemicelluloses, lignin and other components are present in varying compositions in the fiber wall where the actual composition is depending on the species, growth place and age of the trees. Wood consists of two main components which are present in large quantities i.e. carbohydrates and lignin which represent almost 95% of wood components. The carbohydrate components of the wood, also called holocelluloses, consist mainly of cellulose and hemicelluloses. The cellulose is usually present in the range of 40-45 % consisting exclusively of β-glucose units linked by β 1-4 glucosidic bonds to each other (Casey 1980). The hemicelluloses comprise 25-35 % of the dry weight of the wood and are the second most abundant polysaccharides next to cellulose. The other fraction of the wood is lignin which is present in the range of 20-30 % in the wood. It is well known that the lignin is chemically bonded to the carbohydrates (Björkman 1956, Kosikova et al. 1979, Eriksson et al. 1980). Lawoko proposed that there are two types of lignin in the trees, one being associated with glucomannan and other linked to xylan (Lawoko 2005). Lignin is a polymeric compound made up of three building units of phenyl propane units called coumaryl alcohol, sinapyl alcohol and coniferyl alcohol (Freudenberg 1968, Sjöström 1993). The cellulose has a high degree of polymerization of around 10,000-15,000 units and hemicelluloses have a degree of polymerization of around 200-400 units in wood (Axelsson et al. 1962). The chemical compositions of some wood tree species are given in Table 1.
Table 1: Chemical composition of some wood species (mass %), (Ljungberg 2007).

<table>
<thead>
<tr>
<th></th>
<th>Cellulose</th>
<th>Lignin</th>
<th>Glucos- mann</th>
<th>Xylan</th>
<th>Extractives</th>
<th>Other polysac</th>
<th>Others</th>
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<tr>
<td><strong>Softwood</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Norway Spruce</td>
<td>41.7</td>
<td>27.4</td>
<td>16.3</td>
<td>8.6</td>
<td>1.7</td>
<td>3.4</td>
<td>0.9</td>
</tr>
<tr>
<td>(Picea abies)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Hardwood</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Birch</td>
<td>41.0</td>
<td>22.0</td>
<td>2.3</td>
<td>27.5</td>
<td>3.2</td>
<td>2.6</td>
<td>1.4</td>
</tr>
<tr>
<td>(Betula verrucosa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.1.1 Cell wall structure

The wall of a typical wood cell is composed of several layers, which are formed as new cells are created at the cambium layer as shown in Figure 1. The middle lamella, composed mainly of lignin, serves as the glue bonding adjacent cells together. The wall itself is made up of a primary wall and a three-layered secondary wall, each of which has distinct alignments of micro-fibrils. Micro-fibrils are thread like bundles of cellulose molecules, interspersed with and surrounded by hemicelluloses molecules and lignin.

![Figure 1. Model of typical wall structure of a fiber. The cell wall consists of: P-primary wall; S1, S2, S3-layers of the secondary wall; ML-middle lamella, the amorphous, high-lignin-content material that binds cells together. (Koch. P. 1985, Cote. W. A. 1967).](image)
1.1.2 Cellulose

The carbohydrates fraction constitutes the majority of the wood composition and with cellulose being a major part of carbohydrates fraction. Cellulose is a linear polymer consisting of β-glucose units linked by β 1-4 glucosidic bonds to each other and has a chain length (degree of polymerization) of up to 10,000-15,000 glucose monomer units. Each D-anhydro glucopyranose unit possesses hydroxyl groups at C2, C3, and C6 positions, capable of undergoing the typical reactions known for primary and 2 secondary alcohols. Cellulose has a strong tendency to form intra- and inter-molecular hydrogen bonds by the hydroxyl groups on these linear cellulose chains, which stiffens the straight chain and promotes aggregation into a crystalline structure and give cellulose a multitude of partially crystalline fiber structures and morphologies (Klemn et al. 2005). The structure of the cellulose is as shown in the Figure 2.

![Cellulose structure](image)

Figure 2. The structure of cellulose (Timell, 1957).

The linearity of cellulose molecule leads to a strong tendency for these molecules to interact together, whereby they bundle together to form microfibrils consisting of both highly ordered crystalline and less ordered regions. Wood in a living tree has a dry solid content of approximately 40-50 % i.e. about 50 % of the weight of fresh wood is water.

1.1.3 Hemicelluloses

Hemicelluloses are the other carbohydrates in the wood and these have a degree of polymerization of about 200-400 units (Sjöström 1993, Croon
& Enström 1962). The hemicelluloses have a less orderly structure and they are amorphous in nature (Simonson 1963, Meier 1958). The hemicelluloses content in wood is 25-35 % of the dry matter and this number is higher in hardwood compared with softwood.

**Softwood hemicelluloses**

The two most important hemicelluloses are O-acetyl-galactoglucomannan, which is commonly denoted as “glucomannan”, and arabino-(4-O-methyl-glucurono) xylan which is known as “xylan” (Hamilton and Thompson 1958, Jacobs and Dahlman 2001). Softwood hemicelluloses mainly comprises of galacto-glucomannans which have a backbone of glucose and mannose monomers with galactose substituents. The galactoglucomannan constitutes about 20 % of the dry matter in softwood. An important structural feature is that the C-2 and C-3 positions in the chain units are partially O-acetylated, on the average of one group per 3-4 hexose residues. These acetyl groups are easily cleaved by alkali. The galactoglucomannan of softwood is divided into two types differing in galactose content. The fraction with low galactose content has a galactose: glucose: mannose in the ratio of 0.1: 1: 4, whereas the galactose-rich fraction has a ratio of 1: 1: 3. Glucomannan is divided into two fractions, depending on the monomer ratio. One fraction has a low ratio of galactose monomers whilst the other is rich in galactose units (Sjöström 1993). The structure of O-acetyl galactoglucomannan is shown in Figure 3.

![Figure 3. The structure of O-acetyl galactoglucomannan.](image-url)
In softwood the xylan content is relatively low i.e. about 5-10 % of dry materials. Xylans mainly consist of (1-4) linked β-D-xylopyranose units as shown in Figure 4. They are partially substituted at C-2 by 4-O-methyl-α-D-glucuronic acid groups, on the average, two residues per ten xylose units. The framework also contains 1.3 residues of α-L-arabinofuranose per ten xylose units. Due to the furanosidic structure of the arabinose side chains, they are easily hydrolyzed by acids.

Figure 4. The structure of arabino-(4-O-methyl glucorono) xylan.

1.1.4 Lignin

The lignin is a three dimensional network polymer consisting of phenyl propane units with different substituents on phenolic groups as shown in Figure 5 and it’s concentration is high mainly in the region of the middle lamella (Adler 1977 & Freudenberg 1968). The proportion of these three alcohols in a lignin polymer varies between softwood and hardwood as well as between different species.

Figure 5. Three important building blocks of lignin polymer are, a) p-coumaryl alcohol, b) coniferyl alcohol & c) sinapyl alcohol.

Softwood lignin, which is about 25-30 % of the dry mass of softwood, contains almost exclusively polymerization of coniferyl alcohol units.
Hardwood lignin, which is about 20-25 % of the dry mass of wood, is composed of coniferyl and sinapyl alcohol and is often called “guaiacylsyringyl lignin” (Sjöström 1993). Lignin is bound together to the cellulose and hemicelluloses (Glennie & McCarthy 1962). The position of lignin within the lignocellulosic matrix can be seen in Figure 6.

![Figure 6. The position of lignin within the lignocellulosic matrix (Kuhad & Singh 2007).](image)

The cellulose is surrounded by a monolayer of hemicelluloses and embedded in a matrix of hemicelluloses and lignin. Furthermore lignin specifically creates a barrier to enzymatic attack while the highly crystalline structure of cellulose is insoluble in water. The hemicelluloses and lignin create a protective sheath around the cellulose (Stenius 2000). Most isolated lignins are brown amorphous powders. Depending on the preparation method used and on the fraction represented of the total lignin, there are some changes correspondingly in color and shape.

### 1.1.5 Extractives

Wood also contains non cell wall components called extractives which are low molecular weight organic compounds (Sjöström 1993). These substances are obtained by extraction of the wood meal or pulp with organic solvent like ether, acetone, ethanol etc. or water. Usually wood contains of 1-5 % extractives and it comprises of heterogeneous group of different compounds such as resin acids, terpenes, fats and waxes. The
extractives in the wood provide protection to trees against bacteria, fungus, bacteria and animals. Some of these substances also give each type of wood their characteristic properties such as color and permanency. Extractives can be broadly divided into two groups, namely lipophilic and hydrophilic extractives. The lipophilic extractives are insoluble in water and comprises of oleoresins (resin acids, terpenes), fats (triglycerides, fatty acids, sterols, steryl esters) and waxes (C-22+ long chain compounds). The hydrophilic extractives consist of phenols, polyphenols, salts and sugars. The presence of extractives in the wood reduce pulp yield, increase pulping and bleaching chemical consumption and create problems such as foaming during pulping and papermaking if not removed (Wise 1962).

1.1.6 Inorganic materials

The wood also contains small amounts of inorganics in the ranges from 1-2 % for debarked wood and 2-5 % for bark (Sjöström 1993). The inorganic content in the wood is measured as ash content and is composed of calcium, magnesium, manganese, silica, iron, aluminium, potassium, chloride etc. The bark of the wood is rich in these inorganics components and efficient debarking of the logs is therefore important to get rid of these inorganics which are not desired in pulping systems. The makeup chemicals used in the pulp and paper industries also contributes to the buildup of these inorganic elements in the pulp system.

1.2 Pulp

1.2.1 Sulfite pulping versus Kraft pulping:

The global production of sulfite pulps is much smaller (<4 %) than the global production of kraft pulps. Sulfite pulps are mainly used today as a special pulp rather than being used as an alternative market pulp grade for kraft pulps (Sixta 2006). The main reasons for the more limited applicability of sulfite pulps are as follows:
It is not possible to use pine and other resinous wood raw material in the acid cooking process due to high risk of lignin condensation reactions which limits the raw material base of sulfite pulping.

The strengths of sulfite pulps are generally not as good as those of kraft pulps.

Environmental pollution, recovery of costly cooking chemicals and pollution abatement has in many cases been more expensive to solve and this has decreased the cost-competitiveness of sulfite process compared to kraft pulping process.

The sulfite process is characterized by its high flexibility, for example its selective removal of hemicelluloses compared to the kraft process. Another example is the fact that in principle the entire pH range can be used in sulfite pulping while kraft pulping can only be done at alkaline pH. Thus, the use of sulfite pulping permits the production of different types and qualities of pulps for a broad range of applications. The biorefinery approach in the sulfite process when producing the dissolving grade pulp is another advantage compared to kraft process, as the bioethanol and lignosulfonates are the easily obtained byproducts, which makes the sulfite process more feasible and economical.

The sulfite cooking process is based on the use of sulphur dioxide (SO₂) and its ions and a cation (base) such as calcium, sodium, magnesium or ammonium. Today, the use of the relatively cheap calcium base is outdated, because the cooking chemicals used in a calcium sulfite cook cannot be recovered. The dominating sulfite pulping process in Europe is magnesium sulfite. Both magnesium and sodium bases allow chemical recovery. Two types of sulfite pulping processes are commercially used today i.e. the acid sulfite and the bisulfite process.

### 1.2.2 Acid sulfite and bisulfite pulping processes

The acid sulfite pulping process is carried out with an excess of free sulfurous acid in a range of pH 1-2, while bisulfite pulping is carried out under less acidic conditions in a pH range of 3-5. The main cation used in acid sulfite pulping is the calcium base and it operates in the highly
acidic range of pH 1-2. The other soluble cations like sodium, magnesium and ammonium were introduced in sulfite pulping which helped to operate the sulfite cooking range above pH 2. Magnesium cation is used in bisulfite pulping up to pH 5. Sodium and ammonia cation offers a wide range of operating pH from acidic to alkaline (Woodings 2001). The use of calcium as the base in the sulfite process has the disadvantage in the low calcium solubility which restricts calcium sulfite pulping to low pH (<2 pH) cooking only. It is also important to have a high free SO$_2$ concentration in the liquor phase. Finally it is not possible to recycle and reuse the cooking chemicals after the cook which leads to high pollution of the water recipients. The ammonium cation on the other hand is applicable over a wide range of operating pH up to pH 11, but produces darker unbleached pulps, more bleaching chemicals are required and problems are associated with chemical recovery and regeneration. Sodium and magnesium cations give better results with respect to pulp quality and they also have good chemical recovery systems (Annergren et al. 2014). Magnesium based sulfite mills have better chemical recovery system than sodium sulfite mill recovery systems. Acid sulfite dominates as the major dissolving grade pulp production worldwide and covers approximately 60-65 % of total dissolving grade pulp production (Sixta 2006).

The effectiveness of delignification during acid sulfite pulping has been attributed to both sulfonation and hydrolysis reactions. The former reaction type makes the lignin more hydrophilic by introducing the sulfonic groups, and the latter breaks ether bonds and creates new phenolic groups, thereby increasing the hydrophilicity of lignin as well as lowering its molecular weight. The reaction mechanisms involved in delignification during acid sulfite pulping have been studied using model compounds (Gellerstedt et al. 1971), who showed that the sulfonation of lignin occurred mainly at the α-position of lignin whereas the β-aryl ethers remained stable. It has also been proposed that the dissolution of lignin is retarded by lignin condensation reactions taking place during the pulping (Gellerstedt 1976, Kaufmann 1951).
Bisulfite cooking process is suitable for producing medium grade papers (newsprint and writing paper). The active cooking reagent in the cooking liquor is the bisulfite (HSO$_3^-$), SO$_2$ and H$^+$ ion. The bisulfite process became commercially successful during 1950`s when the sodium bisulfite (Arbiso) and magnesium bisulfite (Magnefite) processes were developed (Casey 1980). The resinous wood raw materials like pine and douglas fir can be easily cooked with the bisulfite process while such wood is difficult to cook with acid sulfite cooking because of lignin condensation reactions generated by resins. When these resinous raw materials are used for producing dissolving grade pulp then the sulfite cooking process is carried out with combination of bisulfite cooking as the first stage followed by acid sulfite cooking. The common base that is used in the bisulfite cooking is sodium or magnesium.

### 1.2.3 Dissolving pulp

Dissolving pulp refers to pulps of high purity cellulose content which are used to manufacture various cellulose-derived products such as regenerated fibers or films (e.g., viscose, Lyocell), cellulose esters (acetates, propionates, butyrates, nitrates) for film and fiber forming materials and cellulose ethers (carboxymethyl cellulose, ethyl cellulose and methyl celluloses). Despite the world production of dissolving pulp having been constantly reduced during 1970-2000 a very prominent change in this trend is now taking place. Dissolving grade pulp and cotton linters are the major source of raw material for the production of regenerated cellulose and cellulose derivatives. The increase in the demand for the regenerated cellulose and the high cost of cotton and cotton linters processing restrict their application to certain products (Sczostak 2009). Apart from cotton the use of different hardwoods and softwoods for making dissolving grade pulps has become more successful (Charles 1963). The increasing demand is mainly due to new installations of viscose plants manufacturing regenerated cellulose fibers in Asia. Dissolving grade pulps represent a niche market compared to paper grade with a world production of 5.2 million tonnes in 2011 (Valois...
2012) and the world demand for dissolving grade pulp reached 6.25 million tonnes in 2013 (RISI 2014).

1.3 Sustainability and socio-economy aspects

Both paper pulps and dissolving pulps have their origin in the forest i.e. in the tree and that is definitely a sustainable raw material. However the process improvements and innovative knowledge are the driving factors in achieving a long term sustainable society. The more we produce from the renewable resources, the more it will benefit the society and industries. Increased use of forest based product can result in an expanded fresh plantation activity in many countries and especially in tropical developing countries. This can lead to less generation of carbon dioxide to the atmosphere and hence to less climate change catalyzed problems like heavy rain, landslides etc. Sustainability also helps in providing more jobs in the forest based resources and forest based industries like dissolving pulp production and cellulose based industries like textile fiber spinning.
2. Objectives of this study

It was of interest to study the sodium sulfite process to investigate if its benefits could be better utilized in the future with regard to production of dissolving pulps. Of specific interest was to investigate and verify old results concerning lignin, cellulose and hemicelluloses reactions in the initial part of a bisulfite cook.

1. It was postulated that the pulp composition after bisulfite cook was influenced by the type of cooking liquor used i.e. the mill acid or synthetic lab acid. Therefore it was of high interest to investigate how these different cooking acids influence cooking reactions with respect to its effect on wood components.

2. It was suggested that the cooking temperature during the initial phase of the bisulfite cook had an influence on the delignification rate, carbohydrate degradation and extractives removal. It was of importance to investigate the effect of temperature on wood components.

3. A further objective was to improve the understanding of the side reactions during the initial phase of the bisulfite cook as these could significantly influence the cooking efficiency. Side reactions involving the formation of thiosulfate and sulfate ions were of high importance and its influence during the cook.

4. Finally the activation energies according to the Arrhenius equation for delignification and for degradation of cellulose and hemicelluloses were needed for better possibility to control and optimize the cook with regard to yield and pulp composition.
3. Materials and methods

Spruce and pine chips were collected from a Swedish pulp mill, screened and classified in a standard chip classifier. The chip classifier had a series of trays (Ø 45 mm, // 8 mm, Ø 13 mm, Ø 7 mm, Ø 3 mm and < Ø 3 mm) and chips retained on the 13 mm tray were used for the experimental trials. Knots and chips with bark were removed manually. The acceptable chips were frozen and stored until needed for the cooking experiments.

Mill prepared bisulfite cooking acid was used for some of the reference experiments; its composition is given in Table 2. Note that the numbers are slightly different compared to the corresponding values in the table in Paper II. The difference is due to a new analysis based on different liquor samples. However, in the majority of the experiments, a lab prepared bisulfite cooking acid was used, the composition of which is also given in Table 2. The starting pH of the cooking liquor used for the bisulfite cooking experiments was always 4.5 measured at room temperature.

Table 2. The composition of the two cooking acids used in the experiments.

<table>
<thead>
<tr>
<th></th>
<th>The mill prepared cooking acid</th>
<th>The lab prepared cooking acid</th>
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</thead>
<tbody>
<tr>
<td>COD, g/l</td>
<td>49</td>
<td>5</td>
</tr>
<tr>
<td>TOC, g/l</td>
<td>18.5</td>
<td>0</td>
</tr>
<tr>
<td>Total SO₂, %</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Combined SO₂, %</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Free SO₂, %</td>
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<td>1.2</td>
</tr>
<tr>
<td>Na₂S₂O₃, g/l</td>
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<tr>
<td>Na₂SO₄, g/l</td>
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<td>0</td>
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<tr>
<td>pH</td>
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<tr>
<td>Lignin, g/l</td>
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<td>Acetone extractives, g/kg</td>
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</tbody>
</table>
The cooking experiments were carried out in a lab digester with 6 autoclaves, each with a capacity of 1 liter. These autoclaves were rotated slowly in a glycol bath where they were heated according to a predetermined temperature profile, Figure 7. The startup temperature was 100 °C and the L/W-ratio was always 4.6. The temperature was raised 1 °C/min up to an intermediate temperature where time was given for the final impregnation of the chips; thereafter the temperature was raised during a period of 1 h, up to the final cooking temperature. It should be noted that the time zero hour (0 h) was defined as the time when full cooking temperature was reached; this means that the time when the autoclaves were mounted into the digester was negative which, in this case is minus 2 h as shown in Figure 7.

![Temperature profile during laboratory cooks](image)

Figure 7. The temperature profile during laboratory cooks at three different cooking temperatures. The L/W-ratio was always 4.6.

This study of bisulfite cooking of spruce and pine was focused on the initial stage of the cook and is referred to as Phase -I in Figure 8, defined here as the part of the cook down to 60 % yield. The rest of the cook is defined as Phase –II, where the pulp yield was below 60 %.
The initial amount of chips in each autoclave was 100 g, calculated as oven dry material. The cooking acid always had a total SO$_2$ content of 2.7 %, a combined SO$_2$ of 1.5 % and a free SO$_2$ of 1.2 %, calculated as SO$_2$. The base (cation) charge was 5 % measured as Na$_2$O on wood. The sulfite cooking liquors were analysed for total SO$_2$, free SO$_2$ and combined SO$_2$ by iodometric titrations. The total SO$_2$ content of the liquor is a measure of the contents of SO$_2$, HSO$_3^-$ and SO$_3^{2-}$ respectively. The combined SO$_2$ value is a measure of the amount of cation in the system and is defined as the amount of SO$_2$ that is needed to produce XHSO$_3$ or X$_2$SO$_3$, where X is the cation, i.e. Ca$^{2+}$, Mg$^{2+}$, Na$^+$ or NH$_4^+$. The free SO$_2$ is the difference between the total SO$_2$ and the combined SO$_2$.

The autoclaves were cooled rapidly at the end of each cook: by submerging them into cold water of about 10 °C to stop further reactions. Pulp and liquor samples were then collected. The pulp samples obtained were washed overnight with distilled water and dried at 45 °C in an oven to air dry equilibrium conditions. A Wiley Mill was then used to grind the dried samples of cooked chips into a wood powder that passed through slots of 0.4 mm (40 mesh). These powder samples were used later for analysis of the components given in Table 3.
Table 3: Testing methods used for the wood and pulp samples.

<table>
<thead>
<tr>
<th>Method</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone extract</td>
<td>ISO 14453</td>
</tr>
<tr>
<td>Klason lignin</td>
<td>Tappi T-UM 250</td>
</tr>
<tr>
<td>Lignin (UV)</td>
<td>Tappi T 222</td>
</tr>
<tr>
<td>Arabinose, Galactose, Glucose, Mannose and Xylose</td>
<td>SCAN-CM 71: 09 *</td>
</tr>
<tr>
<td>Total-S</td>
<td>SCAN-CM 57</td>
</tr>
</tbody>
</table>

*Calculated as anhydrous sugar

The spent cooking liquors were analyzed using the methods shown in Table 4. The composition of the pulp with respect to lignin, extractives, cellulose, glucomannan and xylan, was determined using the Klason and UV methods based on acetone extracted chips.

Table 4: The testing methods on the spent cooking liquors.

<table>
<thead>
<tr>
<th>Method</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>SCAN-N 36</td>
</tr>
<tr>
<td>Lignin</td>
<td>Tappi T-UM 250</td>
</tr>
<tr>
<td>Acetone extract</td>
<td>KA 11. 305</td>
</tr>
<tr>
<td>Sulfite</td>
<td>SCAN-N 36</td>
</tr>
<tr>
<td>Arabinose Total, Galactose Total, Glucose Total, Mannose Total and Xylose Total.</td>
<td>KA 10. 202</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>SCAN-N 36</td>
</tr>
<tr>
<td>Total -S</td>
<td>SCAN-N 35</td>
</tr>
</tbody>
</table>

The carbohydrate monomer values obtained were recalculated to the initial carbohydrate polymers using the correlations of Meier (Meier 1958). Using the softwood data, the carbohydrate content of the pulp was calculated as the percentage of wood based on the monomer results of the carbohydrate analysis according to Equations I, II & III below,

Cellulose= Glucose - (1/3.5) Mannose  
Glucomannan= Mannose (1+1/3.5) + Galactose  
Xylan= Xylose + Arabinose
However, when analyzing the carbohydrates in this way, there is always a significant fraction of the pulp that is not possible to dissolve and it is therefore reported as a “residual” which is at least 10%, but in some cases 20-30%, of the bone dry pulp weight. Some laboratories don´t report this amount at all due to the fact that this amount does not respond to the carbohydrate test and it is therefore considered to be “something else”, although it is well known that wood and pulp consist mainly of lignin and carbohydrates. Moreover, when carbohydrate monomers are analyzed, the results can be reported either with or without the presence of one water molecule per monomer. This water is bound to monomers in its monomer state but not to the monomers in the polymer state. Thus, carbohydrate numbers published for wood and pulp samples have to be checked very carefully to be able to know how the data are obtained and thus to avoid erroneous conclusions being made. The bound water in this study has been subtracted and we have not included the “residual” amount of carbohydrates: our numbers for cellulose, glucomannan and xylan are therefore on the low side compared to numbers reported in, old text books such as Rydholm (Rydholm 1965). The methoxyl groups in the wood and pulp samples were determined by cleaving the methoxy groups with hydroiodic acid (and adipic acid as a catalyst) giving methyl iodide which is then analyzed with GC.

The evaluation of the pulp sample was done using the correlation \( \ln W_i = a \times t + b \), where “\( \ln W_i \)” is the logarithm of the parameter “\( W_i \)”, see Equations (IV-VII). This general equation is the integrated version of a first order reaction, where “\( a \)” is a constant at a given chemical composition, “\( b \)” is a second constant and “\( t \)” is the cooking time. The non-constant cooking chemical concentrations used during the pulping reactions meant that the evaluation of the kinetic data had to be based mainly on the initial chemical concentrations.
\[-\frac{dW}{dt} = k \times W \quad \text{(IV)}\]

\[-\int_{w_o}^{w} \frac{dW}{W} = \int_{0}^{t} k \times dt \quad \text{(V)}\]

\[
\ln W - \ln W_0 = -k \times t \quad \text{(VI)}
\]

\[
\ln W = \ln W_0 - k \times t \quad \text{(VII)}
\]
4. Results and Discussions

The pulp yield, the cellulose yield and the lignin yield were all analyzed and the results are presented in the following figure; Figure 9 shows the pulp yield, the cellulose yield and the lignin yield versus cooking time for one cooking experiment using the lab prepared cooking acid. As can be seen the total pulp yield value at time zero hour (0 h) was less than 100 % because that was the time when full cooking temperature was reached. Thus the difference between 100 % and the actual pulp yield corresponds to the yield loss prior to “time zero” and the yield loss before 0 h was thus obtained. It can be seen from the graph that the correlation of the removal of lignin and the yield loss versus time followed a straight line when the bisulfite cooking was extended to 5 h. The cellulose yield was almost unaffected up to a cooking time of 5 h, where the final pulp yield was about 60 %, due to the highly crystalline and ordered structure of cellulose (Rydholm 1965, Sixta 2006, Sjöström 1993 & Meier 1962). It can be concluded that the yields of both the pulp and the lignin decreased with increasing cooking time: the loss in the pulp yield was greatest because both lignin and carbohydrates were lost during cooking. The delignification reaction with respect to lignin removal followed a first order reaction at different cooking times, as calculated from correlation equation \( \text{“Ln Wi”} \) (see Materials and methods). Note that time zero was defined as the time when full cooking temperature was reached, which means that the time when the autoclaves were mounted into the digester was “minus 2 h”.

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Figure 9: Spruce cooked with lab prepared bisulfite cooking acid. The conditions used were: total SO₂ of 2.7 %, combined SO₂ of 1.5 % and free SO₂ of 1.2 % analyzed in all cases as SO₂. The base charge was 5 %, calculated as Na₂O and on dry chips. Temperature: 154 °C.

The removal of hemicelluloses and lignin during bisulfite cooking with mill prepared and lab prepared cooking acid respectively is shown in Figure 10. The lab prepared cooking acid showed a slightly higher delignification rate than the mill prepared cooking acid after 3 h, thus indicating that the presence of dissolved organic and inorganics had an influence on the reaction rates of the two components. The rate of degradation of hemicelluloses was found to be the same up to a cooking time of 3 h and slightly higher when the mill cooking acid was used during the end of the cook.
Figure 10: The content of hemicelluloses and lignin in spruce pulp during bisulfite cooking using mill prepared and lab prepared cooking acid. Conditions used: 154 °C and SO₂ as given in Figure 9.

The content of total SO₂ versus time is shown in Figure 11. The consumption rate of chemicals during the cook was greater when the mill prepared cooking acid was used, thus indicating that the cooking rate was influenced by the type of cooking acid used. There was a higher chemical consumption rate when the mill prepared cooking acid was used. The COD content of the lab prepared acid was very low (5 g/l) whilst that of the mill prepared acid was high (49 g/l). The higher COD levels in the mill liquor probably acted as a buffering agent, as the pH of the cooking liquor was higher in the latter case and so higher degrees of reactivity were observed at higher COD values. It is thus probable, that the different ions, by-products and COD in the mill cooking acid consumed a certain amount of the charged SO₂. Moreover, this additional reaction seemed to take place early in the cook. In order to compensate for the additional consumption of SO₂, in this case, an additional charge of 0.3 % SO₂ would had probably have been required.
Figure 11: The consumption of cooking acid measured as total SO$_2$ versus cooking time. Conditions used: 154 °C and SO$_2$ as shown in Figure 9.

Figure 12 shows the chemical consumption rate at different bisulfite cooking temperatures. From the figure it can be concluded that when cooking at higher temperature the chemical consumption rate increased and at 165 °C the cooking chemicals were totally consumed after 3 h cooking time. At lower temperatures (142 °C and 154 °C) a significantly longer time had been needed to consume the cooking chemicals to the same extent. The chemical consumption pattern in Figure 12 clearly indicates that the temperature had a significant influence on the chemical consumption rate.
Figure 12: The consumption of lab prepared cooking acid measured as total SO\textsubscript{2}, versus cooking time during bisulfite cooking of spruce. Temperatures used: 142 °C, 154 °C and 165 °C. Conditions used: see Figure 9.

**Activation energy**

The reaction kinetics of carbohydrate degradation and lignin dissolution during pulping have been studied in many ways over the years using model substances, wood meal and wood chips. The objective has been to control and to optimize the cook with respect to yield, lignin content, etc.. The final aims of these studies have been to increase the understanding of sulfite cooking; to find ways of improving the quality and/or yield of the pulp. The earliest investigations on the kinetics of the sulfite process were conducted by Stangeland (1932) and Yorston (1934, 1935, 1965). The high temperature studies were mostly conducted using wood meal or sawdust. The activation energy for the total delignification reaction of spruce wood was, for example found, to be 121 kJ/mole during sodium bisulfite pulping (Dorland et al. 1958). The activation energy for delignification during acid sulfite pulping was found to be lower (88 kJ/mole, Richards et al. 2004) when compared with the Kraft delignification (134 kJ/mole, Vroom 1957).
The Arrhenius equation was applied to calculate the influence of temperature on the initial pulping reaction rate, as shown in Equation (VIII).

\[ k = A \cdot e^{\frac{-E_a}{RT}} \]  

(VIII)

where \( k \) - is the rate constant, \( E_a \) – is the activation energy, \( R \) – is the gas constant, \( A \) - is the Arrhenius constant and \( T \) - is the temperature (K).

Plotting the natural logarithm of the lignin content of the spruce and pine pulps versus cooking time in the initial phase of the cook at different temperatures gave the slopes shown in Figures 13 and 14, respectively. These slopes were used to calculate the delignification rate constants for different temperatures and the activation energy was calculated for delignification. The delignification kinetics followed a first order correlation with respect to lignin removal. Moreover, Figure 8 shows that the lignin content of the initial phase of cook was more than 20 % when the maximum cooking temperature was reached, and then declined to 12 % in the final pulp with an extended cooking time of 5 h.

Figure 13. Natural logarithm of the lignin content of the spruce pulp versus cooking time.
Figure 14. Natural logarithm of the lignin content of the pine pulp versus cooking time.

The activation energy for delignification and carbohydrate degradation for bisulfite cooking with spruce and pine were determined and the results are shown in Table 5. Here it can be seen that spruce had a slightly higher activation energy compared with pine.

Table 5. The activation energies for delignification and carbohydrate degradation during the initial phase of bisulfite cooking of spruce and pine wood. The liquor to wood ratio during the experiments was 4.6.

<table>
<thead>
<tr>
<th></th>
<th>Spruce</th>
<th>Pine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>130 ± 5</td>
<td>121 ± 5</td>
</tr>
<tr>
<td>Glucomannan</td>
<td>104 ± 4</td>
<td>91 ± 5</td>
</tr>
<tr>
<td>Xylan</td>
<td>67 ± 5</td>
<td>58 ± 5</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>87±4</td>
<td>81±3</td>
</tr>
</tbody>
</table>
When the activation energy for hemicelluloses degradation was calculated for glucomannan and xylan, it was found that xylan had lower activation energy than glucomannan. When spruce wood was studied the activation energy for glucomannan degradation was 104±4 kJ/mole and for xylan it was 67±5 kJ/mole. The pine wood also showed the same behaviour, with the activation energy of glucomannan (91±5 kJ/mole) being higher than that of xylan (58±5 kJ/mole). The activation energy for hemicelluloses degradation was higher for spruce than for pine (the hemicelluloses content here was the sum of glucomannan, xylan and galactose content). The activation energy for delignification was higher than for degradation of hemicelluloses indicating that a higher temperature favors lignin removal in both spruce and pine wood in the initial phase of a sulfite cook. Thus in the initial phase of a cook a higher carbohydrate yield can be expected at higher temperature with respect to a given lignin content. If, however the contents of cellulose and hemicelluloses in the pulp after the initial phase of a bisulfite cook are compared instead, a higher temperature results in a higher content of cellulose. The activation energy for delignification in our case was about 120-130 kJ/mole which is higher than in acid sulfite cooking (88 kJ/mole, Richards et al. 2004).

**Kinetic results**

The rate of delignification at different temperatures during bisulfite cooking is shown in Figure 15. The rate of delignification was influenced by the rise in the cooking temperature and higher temperature showed faster delignification rate. The delignification kinetics had a first order behaviour at all cooking temperature. A lignin content of 6 % in the pulp was observed after 3 h cooking time at 165 °C as compared to 21 % lignin content at 142 °C. It can thus be concluded that the rate of lignin removal and thus the lignin retention in the final pulp can be controlled by adjusting the cooking time and temperature.
Figure 15: Lignin content versus time for bisulfite cooking of spruce at 142 °C, 154 °C and 165 °C. Conditions used: 2.7 % total SO\textsubscript{2} and 1.5 % combined SO\textsubscript{2}. The cooking acid was prepared in the lab.

Compared with the delignification reactions, which were highly influenced by the temperature, the cellulose was not reactive in the initial phase of the cook, see Figure 16. This behavior is the result of the high crystallinity of the cellulose which makes it difficult for the cooking acid chemicals to penetrate the cellulose matrix (Annergren et al 1959/60/61, Rydholm 1965). The figure shows that even when the lignin content was reduced by as much as 50 %, the absolute cellulose content was more or less unchanged. This very low cellulose reactivity is specific for sulfite pulping: it is quite different to kraft pulping, where the cellulose is slowly degraded from the start of the cook (Wu. S. et al. 2003). Note that the y-axis in the Figure 16 does not cross the x-axis at origo but rather about one hour earlier. The reason for this is that the lignin reactions starts in the impregnation phase already, even though the full reaction temperature is not reached until the time is “zero” hours. The removal of hemicelluloses is also influenced by cooking temperature: higher temperatures favored faster rates of removal. The
cooking temperature can thus be used to control the final pulp yield with respect to delignification and removal of hemicelluloses.

The rate of delignification and cellulose degradation during bisulfite cooking of pine at 142 °C, 154 °C and 165 °C is shown in Figure 17. From the graph it is clear that the cellulose content was unaffected during the initial phase of bisulfite cooking which was due to the high crystalline nature of cellulose. This stable and linear cellulose values verifies the results in an old report that states that the cellulose yield is unaffected until the pulp yield is lower than 50 % (Meier 1962). The lignin removal rate during bisulfite cooking at different temperatures showed that it was impacted by temperature: higher temperatures resulted in faster rates of delignification with less influence on the cellulose yield. This indicates that the high temperature during bisulfite cooking result in low contents of lignin. An earlier study has shown that the energy of activation for sulfite delignification is 84-90 kJ/mole and that the rate of reaction for lignin removal doubles for each 10 °C rise in the maximum cooking temperature (Yorstan et al 1965, Casey 1980).
In a sulfite cook several chemical reactions occur simultaneously: degradation of the lignin, the carbohydrates, the hemicelluloses and finally the degradation of the cooking liquor and formation of by-products such as thiosulfate and sulfate. The formation of thiosulfate hinders the sulfite cooking process by prior phenolation (i.e. introducing reactive functional groups to the lignin molecules) of lignin (Hoge 1954). The reaction of thiosulfate with the sulfonatable groups of lignin causes retardation in the dissolution of the lignin. This lignin condensation reaction is the first step towards a general lignin condensation reaction that can eventually lead to the formation of a black cook (Kaufmann 1951). The amount of thiosulfate formed during the bisulfite cooking of spruce and pine at 142 °C, 154 °C and 165 °C using mill prepared and lab prepared cooking acid are shown in Figures 18 & 19, respectively. It was observed that the formation of thiosulfate was greater when the lab prepared cooking acid was used in both cases. It was also found that the pine wood showed higher values of thiosulfate with cooking time.
compared to spruce wood. The mill liquor cooks showed that the same amount of thiosulfate was formed for both spruce and pine wood chips. An increase in temperature had a positive influence on the thiosulfate formation rates when both the spruce and pine wood chips were used. The thiosulfate concentration at 165 °C decreased at the end of 3 h cooking time, indicating that the thiosulfate was consumed in side reactions with lignin. The formation of thiosulfate at 142 °C & 154 °C, on the other hand showed a steady increase trend. The difference in the thiosulfate value can be attributed to the pH of the cooking liquor, which was lower for the lab acid (final pH of 2.6) than for, mill acid (final pH of 3.5). Bisulfite cooking is more sensitive to the autocatalytic decomposition of bisulfite ions as well as its higher operating temperature (Schöon 1961/1962). As can be seen from Figure 18, the higher temperature influenced the rate of formation of thiosulfate; the lowest thiosulfate value was found at the lowest temperature, i.e. 142 °C, when lab prepared cooking acid was used.

![Figure 18. Content of thiosulfate in the bisulfite cooking liquor. Spruce wood chips cooked with lab and mill prepared cooking acids at temperatures of 142 °C, 154 °C and 165°C. The mill acid was used at 154 °C only.](image-url)
Figure 19. Thiosulfate content in the bisulfite cooking liquor. Pine wood chips cooked with lab and mill prepared cooking acids at temperatures of 142 °C, 154 °C and 165 °C. The mill acid was used at 154 °C only.

The mill and lab acids were tested for pH stability as shown in Figure 20. The initial composition of both cooking acids was the same with regard to total SO₂ and combined SO₂. It was observed that the mill acid showed a lower pH drop than the lab acid, which was probably due to buffering action of its dissolved organic and inorganic components. The initial pH drop was significant in the lab acid when compared to mill acid cook, which had more stable pH profile. Although the initial COD content in both cooking acids varied, the presence of high levels of COD in the mill acid case (49 g/l) seemed to act as a buffering agent in maintaining a more stable pH. The lab acid had a lower COD content (5 g/l) that was mainly due to the inorganics chemicals. The presence of different ions (organic and inorganic components), and hence different levels of COD, probably resulted in different pH profiles with cooking time.
Resins are undesirable in pulp from both quality and pitch deposit aspects (Ingrubber et al. 1993). Depending upon the cooking conditions, the fatty acid esters are saponified during the sulfite pulping process. The resin components of the wood are also sulfonated and their increased hydrophilicity makes them soluble into the liquor. The partial removal of the resins therefore always occurs during sulfite cooking, but it is also dependents upon the dispersed resin particles that are stable in emulsion. Acid sulfite pulping causes terpenes, terpenoids and flavonoids to be partially dehydrogenated. Due to unsaturation resin acids are probably partially polymerized to high molecular weight products (Sjöström, 1993). Fatty acid esters are hydrolyzed to a great extent during an acid sulfite cook and, whilst the saturated resin acids remain unchanged, the unsaturated acids decrease (Erdtman 1949). The contents of extractives in the pulp when mill and lab prepared acids are used during bisulfite cooking are shown in Figures 21 and 22, respectively. It was observed that the levels of extractive were higher in the final pulp when spruce and pine wood chips were cooked with lab prepared acid and lower in pulps produced using mill prepared acid. The difference in the extractives levels was probably due to the greater pH stability of the mill acid than the lab acid. It is probably the presence of
COD in the mill liquor exerted buffering effect giving a higher pH value and thus aiding the removal of extractives.

Figure 21: Contents of acetone extractives in the pulp during bisulfite cooking of spruce using one lab prepared and one mill prepared cooking acid. See Figure 9 for conditions used.

The content of extractives in the pine wood pulp was higher in the lab acid cook than in the mill acid cook as shown in Figure 22. The acidity in lab prepared cooking acid increased with cooking time and it was this drop in pH that hindered the dissolution of the extractives into the liquor. Earlier studies by Mutton (1962) showed that the acidic pH had only a little hydrolysis effect on the extractives, resulting in far less fats and resins being dissolved. Both the shift in the pH during the course of the cook and the presence of dissolved organic components probably had an impact on the dissolution of the extractives into the cooking liquor.
Figure 22. Contents of acetone extractives in the pulp after bisulfite cooking of pine with either a mill prepared acid or a lab prepared acid. See Figure 9 for conditions used.

Figure 23 shows the lignin content of the pulp versus the corresponding consumption of total SO$_2$ and how that correlation is influenced by temperature. As can be seen a higher degree of delignification is obtained at higher temperatures, when compared at a given consumption of total SO$_2$. Thus it seems that the delignification reaction is not only influenced by the cooking chemicals but also by the actual temperature. The lowest lignin content for a given charge of SO$_2$ is thus obtained at the highest temperature.
In sulfite pulping the dissolution of lignin is initiated by the sulfonation of lignin, which forms solid lignosulfonic acid (Rydholm et al. 1959). This is rendered soluble by a hydrolysis reaction in the later part of the cook and is removed from the wood (Wenzl 1970). During sulfonation a large number of sulfonate groups are attached to lignin side chains, and complete sulfonation of all lignin units takes place within a few hours of the sulfite pulping process. Lignin contains a certain amount of methoxyl groups, as seen in Figure 5. The degree of sulfonation of lignin thus can be measured as the ratio of total sulfur and total methoxyl groups in the pulp i.e. the ratio of S/OCH$_3$ as shown in Figures 24 and 25 for spruce and pine respectively. In these experiments the degree of sulfonation for both spruce and pine was almost the same, reaching a maximum value of 0.31 S/OCH$_3$ at three hours of cooking time. The total content of methoxyl in the pulp reduced with increasing cooking time: as the delignification proceeds, the methoxyl groups are lost from the lignin and enter into the liquor phase.
Figure 24: Degree of sulfonation measured as S/OCH$_3$ and the degree of delignification during bisulfite cooking of spruce. See Figure 9 for conditions used.

Figure 25. Lignin removal with cooking time, degree of sulfonation and sulfur content during bisulfite cooking of pine. See Figure 9 for conditions used.
The amount of glucomannan in the pulp versus the corresponding chemical consumption with respect to total SO$_2$ and its correlation with temperature is shown in the Figure 26. For a given chemical consumption the quantity of glucomannan removed was found to be influenced by the cooking temperature. It can be seen from the figure that the greatest reduction in glucomannan was obtained at higher temperatures for a given consumption of total SO$_2$. It can thus be concluded that degradation of glucomannan was influenced by both the total SO$_2$ consumption and the cooking temperature.

![Figure 26. Glucomannan content versus consumption of cooking chemicals for bisulfite cooking of spruce with lab prepared cooking acid. See Figure 9 for conditions used.](image)

Figure 27 shows the xylan content of the pulp versus the consumption of cooking chemicals and how that correlation is influenced by temperature. The higher xylan removal was obtained at higher temperature at a given chemical consumption of total SO$_2$. It can be seen that the xylan removal was influenced by both the cooking temperature and the chemical consumption: higher cooking temperatures favoured the removal of xylan at a given chemical consumption.
The behaviour of the wood components when spruce and pine chips were cooked with bisulfite cooking at 142 °C, 154 °C and 165 °C is shown in Figures 28, 29 & 30, respectively. Figure 28 shows the composition of spruce and pine pulps as a function of the cooking time at 142 °C. It can be observed that there was no loss in the cellulose yield at all, despite the fact that the cook was continued up to 6 h. It is evident from the graph that the removal of lignin had no influence on the cellulose content, as the lignin content reduced with cooking time. The delignification rate influenced the hemicelluloses content, as this was decreased with cooking time. The content of extractives, on other hand was not affected during the cook. The component termed as “balance” in the figure corresponds to the difference between the yield and the amount of lignin analyzed, along with cellulose and hemicelluloses of the pulp components that were not measured, and comprises pectin’s, proteins, ash and other polysaccharides. When wood and pulp are analyzed for their various components (using proximate analysis), there are always some losses in the measurement of the actual content of the material: these were not usually reported in old literatures. The balance in the present study therefore corresponds to the losses caused by analytical
techniques used and the wood components that were not measured. The graph shows that the balance content of the pulp reduced with cooking time. The spruce and pine wood both showed same behaviour with extended cooking time at 142 °C for 6 h with respect to cellulose stability, delignification, removal of hemicelluloses and contents of extractives.

Figure 28. Material balance for the wood components during sodium bisulfite cooking of spruce and pine at 142 °C using lab prepared acid. See Figure 9 for conditions used.

Figure 29. Material balance for the wood components during sodium bisulfite cooking of spruce and pine at 154 °C using lab prepared acid. See Figure 9 for conditions used.
Figure 30. Material balance for the wood components during sodium bisulfite cooking of spruce and pine at 165 °C using lab acid. See Figure 9 for conditions used.

The material balances for the wood components of spruce and pine pulp during bisulfite cooking at 154 °C and 165 °C are shown in Figures 29 and 30, respectively. It can be seen from the figures that the increase in cooking temperature had an impact on overall wood components, as the rate of delignification was much greater at the higher temperature of 165 °C. The lower lignin content was obtained at 3 h cooking time at the higher temperature. Earlier studies by Salmen & Olsson (1998) and Lawoko (2005) have indicated that the lignin and carbohydrates are bound covalently in the wood, and the higher temperature in our study indicates that delignification favored the breakdown of linkage between lignin and hemicelluloses. Although no LCC studies have been carried out on the sulfite pulping process, and especially the initial stages of cooking, it can be assumed from our results that a higher temperature favors the breakage of linkages between lignin and hemicelluloses (glucomannan, arabinose, galactose and xylan) that in turn, results in the lower content of hemicelluloses in the final pulp. It must be noted that the cellulose
yield showed no changes up to a final pulp yield of about 60% indicating that the higher temperature favored only the removal of hemicelluloses and lignin: this is one of the desired reactions in the production of dissolving grade pulp. It can be assumed from our studies that bisulfite cooking at low temperature (142 °C) favored sulfonation but this resulted in slower delignification rate, whereas higher temperature favoured both sulfonation and a higher rate of delignification. As illustrated by Gellerstedt and Gierer (1971) that the lignin sulfonation occurs at the alpha position in lignin during acid sulfite cooking; the results of our study indicate that sulfonation also accompanied by the simultaneous removal of lignin at higher temperatures. The results obtained in our study also corresponds to Lawoko (2005), who found that xylan was more stable during acidic conditions and that glucomannan was easily removed in acidic conditions, both of which can be seen from our graphs: more glucomannan was removed at higher temperatures and xylan was removed very slowly at this condition.

The content of extractives was almost constant even at the highest temperature, and there was no significant drop in their levels at the end of the cook. Both spruce and pine showed the same behaviour with respect to the rate of delignification, removal of hemicelluloses and content of cellulose during bisulfite cooking at 165 °C. It was also observed that the balance component in the graph decreased with cooking time, thereby indicating that more of the polysaccharides were removed as time progressed. The lower values of the balance component in the final pulp may be attributed to more hemicelluloses being removed. The higher temperature of 165 °C generally favoured a faster rate of delignification, the removal of more hemicelluloses, a stable yield of cellulose and the presence of smaller amounts of the balance component in the final pulp.

Figure 31 shows a basic reaction mechanism between wood chips and the bisulfite cooking liquor. The cooking process starts initially with the impregnation of bisulfite cooking liquor into the chip mass, where the SO₂ and HSO₃⁻ impregnate and diffuse into the wood chips. The reaction between the lignin and cooking liquor in the initial part of the sulfite
cook results in the sulfonation of lignin molecules, which in the later part of the cook are rendered soluble by breakage of bonds between the carbohydrates and the lignin molecules. The fragmented lignin molecules diffuse out of the wood chips into the cooking liquor during the cook. During this course of lignin sulfonation and linkage breaking, the carbohydrate fractions of the wood with respect the hemicelluloses, are also degraded and removed from the chip mass. In our studies it was found that the impregnation and sulfonation was less influenced by the temperature versus the fragmentation reactions.

Figure 31. Reaction steps between wood chips and cooking chemicals during bisulfite cooking.
5. **Pulp mill considerations**

1. Dissolving pulp production by sulfite pulping is always a challenge with respect to the type of raw materials used and the cost of the raw materials. The difference found in the extent of side reactions that take place when using pine compared to spruce will give beneficial inputs to the industry in choosing the best raw materials available. The results from this thesis will also help the industries which uses a blend of raw material furnish, for instance the spruce and pine wood.

2. The activation energies obtained in our studies for the removal of different wood components can be a useful tool in producing sulfite pulps of different compositions and yields.

3. Experimental trials in laboratories are usually conducted with freshly prepared sulfite liquor (sometimes called as synthetic cooking liquor) and the results obtained from these trials are later applied in the pulp mills. There was a difference in the side reactions when two types of cooking acids (i.e. mill acid and lab acid) were used. This is important to consider in future research.

4. The knowledge about the influence of the temperature on side reactions will help pulp mills to use suitable temperature profiles so that side reactions are minimized.

5. It was found from our studies that the lignin content was reduced with cooking time & temperature but the cellulose content was not affected in the initial stages of the cook. This is a useful tool for pulp mills to use this information to produce pulps of required compositions.
6. Conclusions

1. There was no significant impact on the delignification rate or on the carbohydrate degradation rate when either a mill or a lab prepared bisulfite cooking acid was used in the digester. However the extractives removal rate was found to be higher when a mill prepared acid was used, compared to lab prepared acid experiments. The lab acid experiments showed higher thiosulfate formation with prolonged cooking time and pine showed higher thiosulfate values compared with spruce wood. The extractives content in the final pulp was higher when the lab prepared cooking acid was used. There were differences in the reactivity with respect to extractives content, thiosulfate formation and pH profile when either a lab prepared or a mill prepared bisulfite cooking acid was used. The mill prepared cooking liquor showed more pH stability which can be attributed to the presence of dissolved organic and inorganic components.

2. The temperature during the initial phase of a bisulfite cook had an influence on the delignification rate and the hemicelluloses removal. Higher temperatures resulted in faster rates of delignification and hemicelluloses removal. However the cellulose yield was not affected at different cooking temperatures.

3. The side reaction with respect to thiosulfate formation was found to be more pronounced at higher temperatures. Higher thiosulfate formation was found when pine wood was used as compared to spruce.

4. The activation energies for delignification and hemicelluloses degradation during bisulfite cooking were found to be slightly higher for spruce versus pine. Note also that the activation energy for glucomannan degradation was found to be higher than for xylan. This indicates that the hemicelluloses compositions in the final pulp can be controlled.
7. Recommendation for future works

1. LCC (Lignin carbohydrate complexes) should be studied in the initial stages of the bisulfite cook of spruce and pine wood chips and comparison of the results should be obtained. The effect of cooking temperature on the lignin carbohydrate linkages at different cooking times should also be studied.

2. The presence of pinosylvin in a pine wood during sulfite cook at acidic conditions is known to cause many side reactions with respect to hindered lignin sulfonation and condensation reactions. Future studies should therefore also focus on the impact of pinosylvin on pine and on pine/spruce mixed wood furnishes during bisulfite and acid sulfite cooking.

3. Acid sulfite cooking of pine and spruce should be studied as a comparison to this bisulfite studies. Secondly two stage cook with a bisulfite first stage and an acid sulfite second stage should follow.

4. A mill cooking acid contains dissolved organic and inorganic components as was shown in the thesis. This influenced to some extent the cooking process. The COD and the lignin contents of the mill liquor and their impact during cooking and on the final pulp properties should therefore be studied in more detail.
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9. References


Kaufmann, Z. (1951) Über die chemischen Vorgänge beim Aufschluss von Holz nach dem Sulfite prozess. ETH-Bibliothek, Zurich, Switzerland. p. 100.


