Niklas Kvarnlöf

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DISSERTATION

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“It is not the critic who counts; not the man who points out how the strong man stumbles, or where the doer of deeds could have done them better. The credit belongs to the man who is actually in the arena, whose face is marred by dust and sweat and blood; who strives valiantly; who errs, who comes short again and again, because there is no effort without error and shortcoming; but who does actually strive to do the deeds; who knows great enthusiasms, the great devotions; who spends himself in a worthy cause; who at the best knows in the end the triumph of high achievement, and who at the worst, if he fails, at least fails while daring greatly, so that his place shall never be with those cold and timid souls who neither know victory nor defeat.”

(T. Roosevelt, Paris, 1910)
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Abstract

The conventional viscose manufacturing process is a mature process that requires improvement with respect to its environmental impact as well as its production cost structure. A research study has therefore been carried out with the aim of improving the reactivity of dissolving pulp used in order to reduce the amount of chemicals used in the viscose production process. This reduces costs and, albeit indirectly, lessens the environmental impact.

The work described in this thesis showed that, whilst maintaining a good quality viscose dope, it is possible to enhance pulp reactivity and use less carbon disulphide in the production of viscose using two entirely different pretreatment methods: one chemical and one enzymatic.

The chemical method used pressurized oxygen after the mercerization step, which increased the reactivity of the alkali cellulose. The viscose dopes produced from the alkali cellulose treated with pressurized oxygen had lower filter clogging values, $K_w$, compared to those produced conventionally. The temperature and oxygen treatment time of the alkali cellulose were, however, crucial for the quality of the viscose produced.

Five different cellulase preparations were compared with respect to their ability to enhance the reactivity of dissolving pulps. The enzyme with the best performance of the tested was a cellulase of a mono component endoglucanase preparation called Carezyme®. This enzyme treatment was optimized with respect to the preparation of the viscose dope. The study showed that enzyme treatment could be carried out under conditions of industrial interest as far as temperature, enzyme dose and reaction time are concerned. A re-circulation study of the enzyme showed that it was possible to re-use the spent press water from the enzyme treatment step several times, and thus lower the production cost. Some of the viscose process stages were modified to fit the enzyme-treated dissolving pulp properly; a comparison between viscose made from enzyme-treated pulp and viscose made from conventional pulp showed that the former samples had a lower $K_w$. 
This indicates indirectly that enzyme pretreatment could reduce the carbon disulphide charge in the viscose manufacturing process. An initial study of how the Carezyme® influenced different cellulosic materials was also performed.
List of papers

I. The effect of modifying the oxidative pre-aging conditions in the manufacture of viscose from wood pulp
Niklas Kvarnlöf, Ulf Germgård and Carl-Axel Söderlund

II. Enzymatic treatment to increase the reactivity of a dissolving pulp for viscose preparation
Niklas Kvarnlöf, Ulf Germgård, Leif J. Jönsson and Carl-Axel Söderlund.

III. Optimization of the enzymatic activation of a dissolving pulp before viscose manufacture
Niklas Kvarnlöf, Ulf Germgård, Leif J. Jönsson and Carl-Axel Söderlund

IV. Pressurized oxygen treatment of alkali cellulose prior to the preparation of viscose dope
Niklas Kvarnlöf, Ulf Germgård, Leif J. Jönsson and Carl-Axel Söderlund
(Paperi ja Puu 89(7-8), p. 431-435, 2007)

V. Modification of the viscose process for enzymatically pre-treated dissolving pulps
Niklas Kvarnlöf, Ulf Germgård, Leif J. Jönsson and Carl-Axel Söderlund
(Accepted for publication in Paperi ja Puu, November 2007)
1 Introduction

1.1 History

In 1846 Christian Friedrich Schönbein tried to produce ozone in his laboratory in Basel by mixing different acids. He even added paper to his mixtures which, in those days, was made of rags. Although he did not produce any ozone, he discovered that the paper showed very different characteristics after this treatment, and continued his tests using another cellulosic material, namely raw cotton. When he removed the cotton from the acid bath (a mixture of sulphuric and nitric acid), washed and dried it, the sample looked the same as before but felt much rougher. Then, when he struck the cotton with a hammer, it exploded without any source of ignition. Schönbein had inadvertently invented nitrocellulose. This was the starting point for the chemistry of cellulose derivatives. Schönbein treated his newly found material with different solvents and discovered that it easily dissolved in a mixture of ether and alcohol, producing a sticky and thick solution. Schönbein had thus succeeded in transforming the normally insoluble cellulose into a soluble form (1).

Following Schönbein’s discovery of nitrocellulose, several other chemists started to take an interest in the chemistry of cellulose. In 1857, a German named Eduard Schweitzer discovered that cotton could be dissolved in a mixture of cupric oxide and ammonium, and that the cellulose could be regenerated in a fibrous form when the mixture was pressed through a spinneret immersed in water. The method was of no significance until it was used in Germany, forty years later, in the production of so-called “cupric silk”. The mixture of cupric oxide and ammonium is still called “Schweitzer’s reagent” (2).

In 1883 the Englishman J. W. Swan was granted a patent in London for a method of producing artificial fibres. He was not at all interested in cellulose as a material for textile manufacture as he was trying to compete with Thomas Alva Edison in making wire filament for light
bulbs. After many failures, he finally tried to dissolve “Schönbein’s
solution” (cellulose in an ether-alcohol mixture) in glacial acetic acid. When he
passed the solution through a “spinning bath” of alcohol, the
solution transformed into fibres which he could then use to make wire
filaments. Thus it was actually an electro-technician who was a pioneer
for the textile industry in his search for a filament material. He did, of
course, understand that his fibre thread could be used for textile
purposes, as he presented it at the “Invention Exhibition” in London in
1885. He called the fibre “Artificial Silk” (3).

One of the founders of the artificial fibre industry was a French count
named Chardonnet. At about the same time as Swan began his light
bulb production, the Count proposed a patent claim for an “artificial
silk-like textile material” to the “L’Académie des Sciences” in Paris (4).
Chardonnet had come up with the idea the first time he visited a
factory that manufactured cellulose, as he had noticed the silky gloss
on the cellulose when it came out of the boiler. Chardonnet was well
aware of the method for producing nitrocellulose but he had to
develop a satisfactory spinning solution and a spinning machine: the
former was a chemistry-orientated problem and the latter a technical
one. Chardonnet, however, solved both problems and, in 1885, he was
granted his patent, which was the first of many in the field of artificial
fibres. The method developed by Chardonnet was similar to Swan’s.
Nitrocellulose was dissolved in ether and alcohol and then extruded
through fine filaments of glass at a pressure of 40-50 atm. The
nitrocellulose coagulated into fibres when the solution had evaporated
(5).

In summary, the dissolving of cellulose was Schönbeins invention,
Swan produced the first artificial fibre and Chardonnet industrialised
the method. These three men, a German, an Englishman and a
Frenchman, can be credited with the development of the manufacture
of regenerated cellulose fibres.
The beautiful Chardonnet silk was admired by many when it first reached the market but, as smooth as it was to the touch, it was dangerous and flammable to its wearer. On one occasion, some ash happened to fall from a cigar onto a woman’s dress made of the fabric. The poor woman lit up like a torch and died tragically of the burns she received. This was, of course, a major setback for the Chardonnet industry. He later successfully denitrated the cellulose, thus reducing the flammability of the fibre considerably. Although confidence in this artificial silk returned with time, manufacturers labelled it as being ‘non-explosive’ for many years to come. Another problem for Chardonnet silk was that it did not become the cheap fibre that many had hoped for. Production costs increased steadily as chemicals became more expensive. The “cupric silk method” that Schweitzer invented gained more ground at the time, but even this method was expensive. Even though the quality of this artificial silk could not compete with that of natural silk, it was used more and more in the textile industry due to its beautiful finish and processability. Only large and financially strong companies could, however, afford to produce the silk. When the manufacturers did their utmost to cut expenses in making Chardonnet and cupric silks, another competitor appeared on the market. This competitor was the viscose fibre, which was much less expensive to produce than its predecessors (6).

Mercer observed, in 1850, that when cotton was immersed in a solution of strong caustic soda, it shrank in both width and length. It also became stronger and its dye affinity was improved (7). Another forty years later, Lowe discovered that the “mercerized” cotton (the sodium hydroxide treatment of cellulose was named after its inventor) could be stretched to produce a permanent increase in lustre (8).

In 1891, Three Englishmen, Charles Cross, Edward Bevan and Clayton Beadle, made an interesting discovery in 1891. When they treated cellulose with sodium hydroxide and carbon disulphide, it transformed into a water-soluble complex. These scientists developed this discovery, and the and simply called their highly viscous solution...
“viscose” (5). The viscose could be regenerated into cellulose by treating it with reagents in a spinning bath developed by the Englishman Stearn and the German Müller. The “Topham box”, invented by C.F. Topham, could coil twisted filaments by submitting cellulose solutions leaving the spinning bath to centrifugal force (9). A major advantage of the viscose method was that expensive cotton linters were not needed as raw material: cheaper sulphite softwood pulp could be used instead. The chemicals necessary to produce viscose fibre were also less expensive. Chardonnet silk soon disappeared and cupric silk usage faded as a result of the appearance of cheaper viscose fibre.

The viscose industry had made significant advances in Europe when World War I broke out. Even though it was clear from the outset that artificial silk was only viable for more or less luxurious products, the lack of textile raw material forced manufacturers to adopt viscose fibres instead. The silk threads could be cut into staple fibres and spun like natural fibres cotton and wool rather than just being used as they were (6).

The characteristics of the fibres were overestimated, however, due to the shortage of textile raw material and the very low quality of viscose fibres at that time. Natural textile fibres based on cotton and wool returned after the war, and viscose textiles became more and more rare.

Some scientists, in the meantime, tried to enhance the properties of viscose fibre. Others searched for different ways of producing cellulosic fibre, an example being acetate fibre that competed with viscose fibre in the 1950s through to the 1970s. The production of viscose fibre is still going strong, although it is being adapting towards manufacturing methods free from carbon disulphide.
1.2 The cellulose raw material used to manufacture viscose

As mentioned earlier, it was possible to use inexpensive cellulose raw material, such as bleached sulphite pulps, in the viscose process. No specific dissolving pulps were manufactured in the early 1920s. The newly-founded viscose fibre companies used pulps in their factories, often keeping the pulp suppliers uninformed of what their merchandise was being used for. A problem in those days was poor knowledge of the chemistry and structure of cellulose, and the fact that both cellulose and viscose factories were poorly controlled. This caused severe fluctuations in the quality of viscose fibre. Pulp from one and the same supplier could differ tremendously: the viscose fibre produced could go from good to very poor with the next batch of pulp. Low quality pulp that could not be used for making paper was often shipped to viscose customers (!). All kinds of secrets and rumours flourished around the pulp and viscose industries: e.g. a professor in chemistry declared that it was not a good idea to transport pulp by sea ‘because the movement of the ship would disturb the cellulose molecules and displace them from their normal positions’...

It soon became obvious that viscose customers were more demanding than papermakers, and that the poor quality “waste pulp” was not at all adequate for viscose manufacturers. A special viscose pulp was therefore developed. Unfortunately, only one kind was available at first; after some years, a pulp with lower calcium content was introduced and, later, a whiter pulp for viscose purposes appeared. An even more developed pulp, with an α-cellulose content between 90 and 93%, was produced in Sweden at the beginning of the 1930s. This progress was made possible thanks to the new bleaching method which used elemental chlorine instead of calcium chloride.

Between 1935-38, a German company developed a pulping method for the manufacture of high tenacity rayon cord by pre-hydrolysing wood chips and subjecting them to sulphate cooking (10).
A steady evolution of dissolving pulp has taken place over the years. Today, the main requirements for a highly reactive pulp are: good processability (especially good filterability), high yield and a good overall economy (11). The general minimum specifications of a viscose dissolving pulp are listed in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Cellulose</td>
<td>&gt;89 %</td>
</tr>
<tr>
<td>Extractives</td>
<td>&lt;0.3 %</td>
</tr>
<tr>
<td>Ash content</td>
<td>&lt;0.1 %</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;250 ppm</td>
</tr>
<tr>
<td>SiO₂</td>
<td>&lt;50 ppm</td>
</tr>
<tr>
<td>Iron</td>
<td>&lt;12 ppm</td>
</tr>
<tr>
<td>ISO Brightness</td>
<td>&gt;90 %</td>
</tr>
</tbody>
</table>

1.3 The viscose process currently used.

The production of a spinnable viscose solution starts with the conversion of cellulose into alkali cellulose whereby the raw material is steeped in sodium hydroxide of mercerization strength, i.e. a
concentration of about 18% (w/w). The alkali cellulose complex exists in equilibrium with the sodium hydroxide lye and the formation of the soda cellulose form is accompanied by swelling but no dissolution of the fibres (12).

An oxidative depolymerisation of the alkali cellulose (ageing) follows. This is a homogeneous reaction that is catalyzed by heavy metal ions, which are mainly cobalt or manganese. There are different opinions regarding the depolymerisation mechanism: Entwistle et al. (13) are of the opinion that degradation is mainly due to radicals, whereas Mattor (14) suggests an ionic mechanism. Peroxides, however, play an important role in both theories. An average cellulose degree of polymerisation (DP) of 250-300 is sufficient for most of the viscose products that are produced today (11). Earlier, when viscose cord for car tyres was produced, an average DP of 500-700 was required to gain the high tenacity needed. The ageing rate is dependent on time, temperature and composition of the alkali cellulose (see Paper I). Conventional ageing is time-consuming: the normal process time is 4-5 hours at 40-45°C in revolving, open-end drums. It is, of course, possible to speed up the process by increasing the temperature. This is not, however, convenient from a processing point of view because of the amount of energy necessary to cool the alkali cellulose to a suitable temperature prior to sulphidation. An increase in the formation of sodium carbonate in the alkali cellulose caused by a higher temperature could also result in problems in the spinning process: the carbonate could be converted into gaseous carbon dioxide bubbles and disturb the jet stream of the viscose in the spinnerets.

The aged alkali cellulose is then transferred to the sulphidation vessel where carbon disulphide, the derivatisating agent, is added. The alkali cellulose reacts like an alcoholate with the carbon disulphide, producing a compound that is soluble in aqueous sodium hydroxide. This compound is not stable, decomposing very quickly at low pH. All three OH-groups of the cellulose molecule are involved in the substitution process; a degree of substitution (DS) of 0.5 is sufficient.
for a fibre-free xanthate solution. Although the DS normally varies from 0.5 to 0.7 under technical conditions, it is possible to reach a DS of 1.0 under laboratory conditions.

A problem that has economic and environmental repercussions in the manufacture of viscose is the over-charging of carbon disulphide. A typical problem that can occur is clogging of the viscose filters, which can be the result of several process problems, e.g. poorly mercerised pulp, uneven ageing of the alkali cellulose and stirring problems in the dissolution vessels. A simple solution here is to increase the carbon disulphide charge in the sulphidation step but, in the long run, this is not in the best interest of either the environment or the economy of the process.

The viscose dope is transferred to the ripening vessels where the viscose is stirred slowly for 16-17 hours at a temperature of 12-15°C. The ripening process involves a suitable reduction in the number of xanthate groups per glucose unit. Whereas the DS should be relatively high in the dissolving step so that a good solution is obtained, it should be less during spinning so that coagulation of the filament is facilitated in the spin bath (11).

The viscose is then passed through filter presses and de-aerated by means of vacuum to remove air bubbles. These could cause a breakage of the jet rays in the spinning step, thereby leading to an uneven feed of viscose through the spinning nozzles.

The viscose dope is filtered a final time to remove the last fine particles that could have been transferred into the liquid from the piping and various vessels during its transport. Fine gel particles which could have passed the first filtration stage are also removed.

The dope is then pressed through spinnerets which are immersed in an acidic spinning bath. The xanthate cellulose complex is decomposed immediately when exposed to the bath, regenerating the cellulose
which is wound onto bobbins in the form of filaments. Zinc oxide, which is added to the spinning bath, produces a protective shell around the xanthate cellulose of the viscose, thereby inhibiting the reaction between the xanthate to such an extent that it is possible to apply a stretching force on the filament and increase its tenacity.

Spinning is a crucial step in the manufacture of viscose fibre. It is of utmost importance to keep the spinnerets clean or they will clog and cause disturbances in the spinning process. The platinum and gold spinnerets are switched, washed and maintained manually on a regular basis.

The regenerated cellulose filaments are then stretched and cut into shorter fibre fragments (i.e. 5-120 mm). The fibre mat is then de-gassed of carbon disulphide and washed in alkaline and acidic baths. A final bath of fatty components gives the fibre mat a “finishing” before it is homogenised, dried and baled. (A detailed description of the viscose process is presented in the Appendix.)

1.4 Cellulose reactivity in the production of viscose

The anhydroglucose unit, i.e. the monomer that represents the backbone of the cellulose polymer, possesses three hydroxyl groups all of which participate in derivatisating reactions within the cellulose chain. The positions of the groups are on the C-2, C-3 and C-6 atoms (Figure 2). The C-2 position is favoured over the C-6 and C-3 in both homogeneous and heterogeneous reactions for steric reasons (15). The substitution of the primary position at C-6 is thermodynamically more stable than the secondary positions at C-2 and C-3 (16), which can be seen in the study of the effect of ripening on the DS at C-6, C-2 and C-3 in a typical viscose (17). The primary position of a carbon means that it is bound to only one other carbon, which is the case for the atom at position six in the anhydroglucose unit. The secondary carbons at positions two and three are both attached to two other carbons (18).
The most important forms of cellulose are Cellulose I and Cellulose II. Cellulose I exists mainly in nature and is divided into two sub-groups: I_α and I_β. Cellulose I_α is the dominant form present in bacterial and algal cellulose. Cellulose I_β is produced mainly by higher plants, such as cotton and trees. When fibres of Cellulose I are swollen in strong acids, bases or chelating agents, the strong intramolecular and intermolecular hydrogen bonds are broken. The cellulose forms new structures when the swelling agent is removed. The predominant structure formed is known as Cellulose II (19). Cellulose II is formed when pulp is mercerised, and also when cellulose is regenerated in the acidic bath in the viscose manufacturing process. Unfortunately, Cellulose II is less accessible than Cellulose I: the cellulose layers in Cellulose II are mainly held together by hydrogen bonding, whereas the Cellulose I layers interact with much weaker van der Waals bonding. The average bonding length is 2.72 Å in Cellulose II and 2.80 Å in Cellulose I (16). The chain packing is thus tighter in Cellulose II than in Cellulose I, which contributes further to the lower accessibility of the former.

Comparisons between different pulps have shown that dissolving pulp contains more Cellulose II than most other pulps (20).

1.5 Treating cellulose with enzymes

Enzymes have been used in industrial and food processes since the beginning of the last century. The use of proteases in leather making
and beer stabilization, amylases in textile desizing and renin in cheese production has been common knowledge for a long time. Initially, manufacturers were quite satisfied if the enzymes did their job, and were not concerned with the how or why. That attitude has changed during the last fifty years, and particularly over the past ten, when immense progress has taken place in industrial biotechnology.

Active research on cellulases began in the 1950s, when it was discovered that they had the enormous potential of converting lignocellulose into glucose and soluble sugars. Despite the fact that results obtained in the 1970s and 1980s showed that the enzyme-catalysed conversion of lignocellulose into sugars was rather difficult and uneconomical, this was a breakthrough for continuous research in the field of cellulase (21).

New applications for enzymes in areas such as detergents, textile, grain wet milling, pulp and paper, natural polymer modifications, etc. have become possible thanks to the development of molecular biology, protein engineering and fermentation technology (22).

**Cellulases**

Cellulases are a group of O-glycosyl-hydrolases that hydrolyse β-1→4 glucosidic bonds in cellulose (23). A cellulase preparation can contain many different enzymes, depending on the source of the cellulase. Three types of enzymes have been distinguished over years of intensive research on cellulases: exoglucanases (1,4-β-D-glucan cellobiohydrolase) which attack the cellulose from the chain ends, releasing mainly cellobiose and thus decrease the DP of the substrate very slowly (24); endoglucanases (1,4-β-D-glucan 4-glucanohydrolase) which attack the chain randomly at internal sites and thus depolymerise the cellulose to a much higher degree than the cellobiohydrolases (25) and, finally, β-glucosidase which cuts the cellobiose into monomers in the form of glucose units (26), (Figure 3, modified from Teeri (27))
Some cellulase applications:

**The textile industry**

Cellulases are a group of enzymes that are relatively new in the textile industry, where amylases were the only biochemical product used until the late 1980s. The cellulase enzymes, in the form of multi-component or mono-component preparations, are quite common nowadays in the processing of garments and textiles. The most relevant applications for cellulases are: the stone washing of jeans and denim garments, bio-polishing and bio-finishing of piece fabrics and garments, modifications to improve the feel of fabrics and fabric preparation prior to dyeing in order to increase dye affinity (22).

**The laundry industry**

Cellulases have been used in detergents for about fifteen years. The “unnatural” conditions used when washing clothes, such as high pH, hot temperature, bleaching agents, etc. mean that the enzymes used in detergents have to be tailored to withstand rather harsh treatment. There are not many kinds of suitable cellulases available on the market.
at the moment due to the problems associated with the conditions in which the enzymes have to perform. The ones that are available are all endoglucanases that are active at pH 6 to about pH 10 and at temperatures of up to about 60 °C. The difference between cellulases and other detergent enzymes is that the cellulases are not meant to decompose stains. They are instead active on the fibrils where they can achieve one or more tasks such as: stain removal from dirt trapped in the fibrils, cloth softening and defibrillation which improves the colour of the textile (22).

The pulp and paper industry

Commercial enzyme preparations contain several active components, some of which have positive effects on the substrate and others negative. It is therefore very important that the enzymes have been thoroughly examined for the effect they have on the substrate(s). Some cellulase functions of interest are: modifying mechanical pulp properties, improving the bleaching ability of chemical pulps, acting as release agents for ink on fibre surfaces and hydrolysing colloidal materials in paper mill drainage systems (21).

1.6 Endoglucanase V

Endoglucanase V is the sole cellulase component in the enzyme solution called Carezyme®, which makes it suitable for use in most of the enzyme treatment tests of the pulps in this study (Papers II, III and V). A more detailed presentation of the cellulase itself is therefore required.

The saprophytic fungus Humicola insolens produces at least seven different cellulases that have been cloned and expressed in a non-cellulolytic host, five endoglucanases and two cellobiohydrolases. It has also been found that the fungus produces two kinds of xylanases (28).
Endoglucanase V (EGV) consists of a six-stranded β-barrel domain of 248 amino-acid residues with a number of disulphide-bonded interconnecting loops. A 40 Å long active site groove of 210 amino-acid residues, running across the surface of the molecule, contains the catalytic residues Asp-10 and Asp-121. Asp-121 is situated in the centre strand of a three-stranded mixed β-sheet that makes up one side of the cleft. Asp-10 is found on the opposite side of the cleft and a tyrosine residue makes up the floor of the active site cleft at this point. Asp-121 is in a predominantly hydrophobic environment whereas Asp-10 is in a more hydrophilic surrounding. The catalysis of EGV is said to be inverting (Figure 4). Asp-121 acts as a catalytic acid and protonates the glycosidic oxygen between two glucose residues in the cellulose chain. Asp-10 acts as a catalytic base, and a solvent water molecule is activated for nucleophilic attack at the C1 position of one of the glucose residues (Figure 4). Asp-10 and Asp-121 now have protonation states, in direct contrast to those before catalysis, so the initial states therefore have to be restored before catalysis can continue (29).

Figure 4. Likely mechanism for catalysis of cellulose by Endoglucanase V
Optimization studies on carboxy methyl cellulose (CMC) have shown that EGV has a relatively broad optimum pH range (pH 6-9). The enzyme has, for example, the widest pH optimum of all known enzymes from H. insolens (28). Figure 5 shows the topography of Endoglucanase V derived from H. insolens.

*Figure 5. A 3D model of endoglucanase V from H. insolens. The black area represents the cleft-like glycosidic active site.*
2 Materials and Methods

2.1 The fibre materials and enzymes used

Four different wood pulps and one de-waxed, commercially-available fibre grade cotton were used for the tests in the studies (Table 2).

<table>
<thead>
<tr>
<th>Origin of cellulose</th>
<th>Pulp type</th>
<th>Cooking process</th>
<th>Used in Paper No.</th>
<th>Viscosity dm³/kg</th>
<th>Viscosity cP</th>
<th>Alkali resistance R₁₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce</td>
<td>Dissolving</td>
<td>Sulphite</td>
<td>I-IV</td>
<td>510 ± 30</td>
<td>16.0 ± 1.5</td>
<td>&gt;94 %</td>
</tr>
<tr>
<td>Spruce</td>
<td>Dissolving</td>
<td>Sulphite</td>
<td>V</td>
<td>615 ± 10</td>
<td>22.1 ± 0.1</td>
<td>&gt;94 %</td>
</tr>
<tr>
<td>Eucalyptus</td>
<td>Dissolving</td>
<td>Pre-hydrolysed kraft</td>
<td>V</td>
<td>441 ± 10</td>
<td>12.1 ± 0.1</td>
<td>&gt;94 %</td>
</tr>
<tr>
<td>Spruce</td>
<td>Paper grade</td>
<td>Kraft</td>
<td>I, V</td>
<td>828 ± 10</td>
<td>46.3 ± 1.2</td>
<td>&gt;88 %</td>
</tr>
<tr>
<td>Cotton</td>
<td>*</td>
<td>*</td>
<td>V</td>
<td>1674 ± 160</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

The analyses were performed in accordance with ISO 5351:(2004) for viscosity and SCAN-C 2:61 for R₁₈.

Five different enzyme preparations from Novozymes AS, Bagsværd, Denmark were used in the studies. The properties of the enzymes are described in Table 3.

<table>
<thead>
<tr>
<th>Enzyme preparation name</th>
<th>Type of preparation</th>
<th>Enzyme activity in the commercial product</th>
<th>Used in Paper No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celluclast</td>
<td>mix of cellulases</td>
<td>700 *</td>
<td>II</td>
</tr>
<tr>
<td>Carezyme*</td>
<td>mono-component endoglucanase</td>
<td>4500 **</td>
<td>II, III, V</td>
</tr>
<tr>
<td>Celluzyme</td>
<td>mix of cellulases</td>
<td>700 ***</td>
<td>II</td>
</tr>
<tr>
<td>Renozyme*</td>
<td>mono-component endoglucanase</td>
<td>4500 **</td>
<td>II</td>
</tr>
<tr>
<td>Endolase*</td>
<td>mono-component cellulase</td>
<td>3000 **</td>
<td>II</td>
</tr>
</tbody>
</table>

* = EGU/g solution (Endo-Glucanase Units)
** = ECU/g solution (or powder) (Endo Cellulase Units)
*** = DCU/g powder (Detergent Cellulase Units)
2.2 Depolymerising cellulose using pressurized oxygen (Paper I)

The pulp sheets were cut into squares (~1 cm$^2$). Water (500 ml) was added to a 30 g pulp sample and mixed in a blender for 2 minutes at 1000 rpm. The resulting slurry was filtered in a Büchner funnel and the residue weighed. Sodium hydroxide (NaOH) and cobalt sulphate were then added and, finally, water was added to give a final pulp consistency of 20%. The pulp was oxidised in a cylindrical steel autoclave into which oxygen could be applied at pressure through a nozzle in the lid. The autoclave was immersed in a hot oil bath (110°C) where it was rotated during the entire process. Once the set time was reached, the sample was immediately transferred to a beaker containing acetic acid (10 % v/v) to inhibit further depolymerisation of the cellulose. The neutralized sample was then washed with hot water and dried at 105°C.

2.3 Analysis of the reactivity of the pulp (Papers I-V)

The reactivity of the was measured according to the Fock method (31). In this test, the sample is dissolved in an excess of NaOH (9% w/w) and CS$_2$. A certain amount of the dissolved cellulose reacts with the CS$_2$. The excess CS$_2$ is then removed and the cellulose is regenerated with H$_2$SO$_4$. The amount of cellulose that is regenerated is determined by oxidation with potassium dichromate (K$_2$Cr$_2$O$_7$).

In the tests, a 0.50 g sample of the pulp is added to a 100 ml Erlenmeyer flask with a stopcock. 50 ml of NaOH (9% w/w) and 1 ml of CS$_2$ are added to the flask and the mixture is stirred for 3 h with a magnetic stirrer. The sample is then transferred to a tube with a stopcock, and distilled water is added to give a total weight of 100 g. The tube is shaken vigorously until the sample is well mixed. It is then centrifuged for 5 min at 6000 rpm. 10 ml of the liquid phase is pipetted into a 100 ml beaker and neutralized with ca. 3 ml sulphuric acid (20% w/w). The mixture is set to react for 15-20 h, during which time the cellulose is regenerated and degassed to remove CS$_2$. 20 ml of H$_2$SO$_4$ (68 % w/w) is
added and the sample is mixed and stirred with a magnetic stirrer for 1 h. The mixture is transferred carefully to a flask and 10 ml of 1/6 M \( \text{K}_2\text{Cr}_2\text{O}_7 \) is added; oxidation takes place whilst it is reboiled for 1 h. When the oxidised sample has reached ambient temperature, it is poured into a 100 ml volumetric flask and 40 ml of the liquid is removed to react with an excess (5 ml) of potassium iodide (10 % w/v). The iodine produced is then titrated with sodium thiosulphate (0.1 M), using starch as the indicator. The calculations of the pulp reactivity is described in Section 3.1

2.4 Size Exclusion Chromatography (SEC) (Papers II, IV)

A SEC method called Gel Permeation Chromatography (GPC) was used to determine the molecular weight distribution of the samples. The molecules in the sample are separated hydrodynamically in a gel column and eluted at different volumes. A calibration curve can be established by using standards of known molecular weight. Pullulan, which is the only commercial polysaccharide standard currently available, was used to determine the molecule weight distribution of the cellulose(32).

The GPC analysis was performed using a single Styrage™ HT4 column with a pore size of 10 µm and an effective molecular weight range of 5000 to 600,000 Da. The detector was a Waters 410 refractive index refractometer (RI). The operating temperature in the column was 80°C, the mobile phase was 1% lithium chloride in dimethyl acetamide (DMAC), the sample concentration was approx. 2.5 g/l and the sample injection volume was 200 µl.

Five pullulan standards (Shodex Standard P-82) were used to calibrate the column: pullulan is a polymaltotriose, i.e. a linear macromolecular polysaccharide that consists of links of maltotriose. The five standards ranged in molecular weight from 5800 to 380,000 Da. The sample preparation procedure was in accordance with (32) and was as follows: 25 mg of the sample was mixed with 10 ml of distilled water in a test tube. The tube was stored overnight in a refrigerator.
(9°C) to allow the sample to swell. The sample was then transferred to a glass filter and the water was removed by vacuum suction. Methanol was added to the sample to act as a transition agent in order to remove the residual water. The sample was soaked with methanol for 30 minutes before the solvent was removed by vacuum suction. This procedure was repeated 3 times. After the third time, the sample was soaked with DMAC for 30 minutes before the solvent was removed by vacuum suction. This procedure was also repeated 3 times. The sample was then transferred to a test tube with a solution of 1.25 ml 8% lithium chloride in DMAC and was allowed to dissolve for at least 3 days at 9°C. The sample was diluted to 10 ml with DMAC to a concentration of 1% lithium chloride in DMAC solution. Finally, the solution was filtered through a PTFE membrane filter (0.45 µm) to remove any undissolved material before it was injected into the column.

2.5 Determination of the gel content of a viscose dope (Paper I)

The most common way of determining the suitability of a pulp for use in producing viscose is to make the viscose dope according to Treiber (33) and then determine its clogging value. This indicates how well the pulp reacts with the carbon disulphide and how good the viscose preparation parameters are. This analysis requires, however, some special equipment. A simpler way of establishing whether or not a pulp is suitable for use in the production of viscose is to determine the gel content whilst the viscose is ripening. This was done in the following way: a sample (10 g) of the viscose (produced according to (33)) was dissolved in 200 ml of distilled water. It was then poured onto a dried and pre-weighed filter paper (Munktell 00R) in a Büchner-funnel. The filter was air-dried and, finally, weighed. The residue on the filter was considered to consist of undissolved xanthate in the viscose, i.e. gel. Viscose samples were removed at different time intervals.
2.6 Yield and viscosity analyses of the samples (Papers I-V)

The yields were determined using filters of pore size 3 (40-100 µm). The samples were poured onto the dried and pre-weighed filter and then re-washed twice with the drawn off liquid to minimize the filtration error due to fibre losses. The filter was dried at 105 °C, conditioned to room temperature and, finally, weighed. The viscosity of the samples was determined in accordance with ISO 5351:2004.

2.7 Preparation of pulp samples using enzymes (Papers II, III, V)

The pulp samples were cut into squares (~1 cm²) and dropped into a beaker containing distilled water adjusted to the appropriate pH. The beaker was immersed in a water bath for conditioning at the chosen temperature. The pH and temperature were chosen according to Table 4 since different enzymes require different working conditions for optimum performance.

The pulp sample was homogenized with a mechanical stirring device to form a slurry. The enzyme was then added to the slurry; stirring was set to 150 rpm throughout the reaction time.

<table>
<thead>
<tr>
<th>Enzyme preparation</th>
<th>pH</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celluzyme</td>
<td>6.0</td>
<td>50</td>
</tr>
<tr>
<td>Endolase</td>
<td>7.5</td>
<td>40</td>
</tr>
<tr>
<td>Renozyme</td>
<td>7.5</td>
<td>40</td>
</tr>
<tr>
<td>Carezyme</td>
<td>7.5</td>
<td>40</td>
</tr>
<tr>
<td>Celluclast</td>
<td>4.5</td>
<td>50</td>
</tr>
</tbody>
</table>

2.8 Preparation of viscose dope and determination of the clogging value (Papers III-V)

A laboratory viscose dope has to be produced and characterized in order to thoroughly investigate whether or not a pulp, or a certain
treatment condition, is suitable for the production of viscose. Micro-scale laboratory equipment was used to accomplish this according to (33). The procedure is as follows: 25 g of the pulp sample is immersed in 800 g of NaOH (18% w/w and with a Co concentration of 0.4 ppm) and stirred for 20 minutes at 45°C. The resulting slurry is then poured into the pressure vessel (Figure 6) and a vacuum applied to remove the liquid present from the slurry.

Figure 6. The pressure vessel

The vessel is placed in the pneumatic pressing device (Figure 7) and a pressure of 60 kg/cm² is applied for 75 sec. The alkali cellulose (AC) cake produced is then weighed to establish the pressure factor, which is important for the future processing of the sample. According to Treiber (34), there is a direct relation between the pressure factor and the clogging value of the viscose dope. The value of the factor is determined by dividing the weight of the pressurized cake by the weight of the starting material.
The cake is torn into small pieces and placed in the milling apparatus (Figure 8) where the AC is processed for 35 minutes.

50 g of the ground AC is then transferred to a glass vessel immersed in a water bath at 40°C, where the sample is pre-aged for five hours to reduce the viscosity of the cellulose. A sample of about five grams is also taken from the mill to determine the cellulose content of the AC. The pre-aged AC is placed in a round-bottomed flask mounted in a rotating device. A vacuum is applied in the flask and a calculated amount of carbon disulphide (CS₂) is added. The temperature is held at 29°C and the reaction time is 2.5 hours.
The sodium xanthogenate that is produced in the reaction between the AC and CS$_2$ is placed in a jacketed steel vessel and weak NaOH (2 % w/w) is added to the sample. The vessel is then placed in the stirring device for dissolution (Figure 9). The mixture is stirred for 3 hours at a temperature lower than 10°C; the temperature is kept constant by running cooling liquid through the jacket of the vessel. It is very important to maintain a low temperature throughout the dissolution step, as a high temperature speeds up the decomposition of the xanthate, giving a much poorer dissolution result.

![Figure 9. The stirring equipment.](image)

The viscose dope produced (Figure 10) is then set to ripen at room temperature for 15-16 hours whilst being gently stirred. The side reactions between sodium hydroxide and different sulphuric compounds are partly responsible for the viscose dope being red in colour.

![Figure 10. The viscose dope.](image)
The clogging value of the viscose can be measured only if the viscosity of the dope is known. This is usually measured as the “ball-fall” time, which is defined as the time it takes for a steel ball of diameter 1/8 inch to fall 20cm through a cylindrical phase of viscose (Ø 20mm) at 20°C (35).

Once the ball-fall time has been established, the viscose is transferred to a cylindrical filtration vessel (Figure 11), which is prepared with a filter (Munktell, viscose filter No.702 with controlled porosity according to Kolos and Treiber (36)) and two pieces of nylon cloth at the bottom of the vessel. The apparatus is sealed at the top and a pressure of 2kg/cm² (N₂) is applied. A beaker is placed under the nozzle to catch the viscose drips during filtration. When the filtration time is over, the amount of viscose is weighed and the clogging value calculated (Section 3.2).

![Figure 11. The filtration unit.](image)

### 2.9 Analysis of the fibre (Papers IV-V)

A Bauer-McNett apparatus was used for the analysis of the fibre length distribution, which was performed according to SCAN-CM 6:05 (2005). The fraction plates used in the studies had the filtration density of 30 and 200 mesh.
2.10 Preparation of viscose dope after treating the pulp with enzymes (Paper V)

The enzyme treated sulphite dissolving pulp slurry (Section 2.7) was dewatered by vacuum suction to a dryness of ~30%. 25 g of the pulp, calculated as bone dry pulp, was then mercerized in sodium hydroxide (NaOH, 18% w/w) at 45°C for 20 min in a steel vessel. The remaining process steps for producing a viscose dope were in accordance with Section 2.8.

2.11 Treatment with oxygen and preparation of viscose using the pulp produced (Paper IV)

The pulp sheets were cut into squares (~1 cm²). 25 g of the pulp sample was mercerized in sodium hydroxide (NaOH, 18% w/w) at 45°C for 20 min in a steel vessel. The resulting slurry was dewatered in a hydraulic press to 50% dry solids, corresponding to ~30% cellulose in the sample. The alkali cellulose cake was torn into smaller pieces and milled for 35 minutes in a shredder. The alkali cellulose was then oxidized in a cylindrical steel autoclave (Figure 12) where pressure could be applied through a nozzle in the lid. The autoclave was immersed in a polyethylene glycol bath where it was rotated for the duration of the process. When the set time was reached, 50 g of the depolymerised alkali cellulose was transferred to a glass vessel equipped with a stirrer. A vacuum was applied in the vessel (pressure in the vessel: ~0.2 bar) before CS₂, calculated from the amount of cellulose in the alkali cellulose, was added. The rate of stirring was set at 250 rpm. The temperature of the sulphidation process was held at 29°C and the reaction time was 2.5h. The sodium xanthogenate produced was placed in a jacketed steel vessel and a low concentrated solution of NaOH (2% w/w) was added to the sample. The vessel was placed in a stirring device for dissolution; the mixture was stirred for 3h. The temperature was held below 10°C to minimize side reactions between the NaOH and the CS₂. The viscose dope produced was then left to ripen at room temperature for 15-16h whilst being stirred gently.
2.12 Measurement of the Dynamic Contact Angle (DCA) (Paper IV)

Measurement of the DCA was performed using a Radian DCA 322 contact angle analyzer (Cahn Instruments Inc.). The fibre samples were prepared by mercerizing the pulp and treating it with oxygen (Section 2.11). The resulting alkali cellulose was then air dried to remove any moisture from the fibres, as this would interfere with the DCA analysis. Single fibres were chosen randomly from the oxygen-treated alkali cellulose samples and mounted, with one end free, on a piece of adhesive tape. This was, in turn, attached to the sample holder which was suspended from a microbalance in the instrument. A beaker with the wetting liquid (distilled water) was placed on a platform under the fibre sample. The beaker was moved towards the fibre at a constant velocity (advancing mode) until the sample came into contact with the liquid surface (Figure 13, taken from (37)). The movement of the beaker was then continued in the same direction, submerging the fibre in the liquid to a specified depth (1 mm in this study). It was then withdrawn from the fibre (receding mode) until the fibre was completely out of the wetting liquid. It was important that the fibre sample was placed perpendicular to the water surface to avoid distorted measurements caused by curved fibres. The force exerted on the cellulose fibre was related to the contact angle of the fibre surface by the Wilhelmy plate technique equation (Section 3.3). At least 30 fibre samples were analysed for every data point in the study.
2.13 Sulphidation mixing techniques (Paper V)

**Sulphidation A**

An evaporator-like device that rotates the xanthogenate inside a glass bulb is shown in Figure 14.

![Sulphidation device comprising a rotating glass bulb (Sulphidation A).](image)

**Sulphidation B**

A glass vessel equipped with a stirring rod that mixes the xanthogenate thoroughly is shown in Figure 15.

![Sulphidation vessel equipped with a stirring rod (Sulphidation B).](image)
3 Calculations

3.1 Pulp reactivity (according to Fock)

The calculation of the reactivity is based on the amount of unreduced Cr\textsuperscript{6+} that remains after the oxidative reaction between potassium dichromate and cellulose:

\[ 4 \text{Cr}_2\text{O}_7^{2-} + 32 \text{H}^+ + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 8 \text{Cr}^{3+} + 6 \text{CO}_2 + 21 \text{H}_2\text{O} \]  \[1\]

The unreduced Cr\textsuperscript{6+} in reaction [1] is reduced by iodide to Cr\textsuperscript{3+}:

\[ 14 \text{H}^+ + 6 \text{I}^- + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} + 3 \text{I}_2 + 7 \text{H}_2\text{O} \]  \[2\]

and the iodine is then titrated with sodium thiosulphate:

\[ 6 \text{S}_2\text{O}_3^{2-} + 3 \text{I}_2 \rightarrow 3 \text{S}_4\text{O}_6^{2-} + 6 \text{I}^- \]  \[3\]

Finally, the addition of reactions [2] and [3] gives:

\[ 14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 6 \text{S}_2\text{O}_3^{2-} \rightarrow 2 \text{Cr}^{3+} + 3 \text{S}_4\text{O}_6^{2-} + 7 \text{H}_2\text{O} \]  \[4\]

The amount of oxidised cellulose is indirectly calculated as follows:

The amount of reacted dichromate moles, A:

\[ A = V_1 \cdot C_1 - (V_2 \cdot C_2 \cdot a) \cdot \frac{1}{6} \]  \[5\]

where \( V_1 \) = dichromate added (ℓ), \( C_1 \) = dichromate conc. (mol/ℓ), \( V_2 \) = used sodium thiosulphate (ℓ), \( C_2 \) = sodium thiosulphate conc. (mol/ℓ) and \( a = 100/40 \) (the dilution of the sample in the volumetric flask (100 ml) and the amount used for titration (40 ml)). \( \frac{1}{6} \Rightarrow \) each dichromate ion consumes 6 thiosulphate ions (Reaction [4]).

The conversion from dichromate to cellulose, B, is given by:
B = A*(M*\(1/4\)) \[6\]

where \(M\) = molecule weight of a glucose unit (g/mol); \(1/4\) => cellulose consumes 4 dichromate ions (see reaction [1]).

The amount of cellulose that has reacted with the carbon disulphide (%), \(C\), is then given by:

\[C = \frac{(100*b)/y}{y} \times B\] \[7\]

where \(b = 100/10.4\) (The first dilution to 100 g and the used amount of 10.4 g (10 ml)); \(y\) = weight of sample (o.d.) (g).

### 3.2 Filter value determination of viscose

The filtration law was stipulated by Hermans and Bredée in 1935 (38),

\[\frac{k_w t}{2} = \frac{t}{M} \times \frac{1}{S_o}\] \[8\]

where \(k_w\) = clogging constant, \(t\) = time, \(M\) = amount of filtrate and \(S_o\) = a constant, depending on the filter material and the viscose viscosity. As \(k_w\) is a very small figure, it is common to use the expressions:

\[K_w = k_w \times 10,000\] \[9\]

where \(K_w\) is the filter clogging value, or:

\[F_w = \frac{2}{k_w}\] \[10\]

where \(F_w\) is the filter value to describe the filterability of the viscose. The filterability value is determined in an apparatus described in Section 2, where the viscose that passes the filter during different time
intervals is collected and weighed. The filterability is then calculated according to Hermans and Bredée’s filtration law and is presented as either $K_w$ or $F_w$.

Besides the filterability of the viscose, the filtration value is dependent on the porosity and the surface of the filtration material and on the viscose viscosity. Re-calculation from one filter material to another can be difficult, as no simple proportionality exists. Since it is hard to keep the viscose viscosity at an absolutely constant value, Vosters introduced a reduced filtration value, $R_v$, (39) where:

$$R_v = \frac{F_w}{\sqrt{S_0}} \quad [11]$$

The $S_0$-constant is however influenced by different factors and it cannot be determined with great reliability. For this reason, Kolos and Treiber investigated the empirical connection between $F_w$ and the viscose viscosity ($\eta$, ball-fall time (Section 2)) and found that for several different filtration materials:

$$R_v^* = k^* F_w^* \eta^{0.4} \quad [12]$$

where the proportionality constant, $k$, could be determined to a value of 0.6 (36). This was later confirmed by Philipp et al. (40). $k_w$ is calculated as the slope of the straight line in a diagram based on the Hermans and Bredée’s filtration law, as shown in Figure 16.
The filter clogging value, $K_w$, can thus be calculated from the expression:

$$K_w = \frac{10,000 \times ((t_2 / M_2) - (t_1 / M_1))}{(t_2 - t_1) \times 0.6 \times \eta^{0.4}}$$

Equation [13]

The expression indicates that the viscose filterability (or quality) increases with decreasing $K_w$ value.

### 3.3 Calculation of the Direct Contact Angle (DCA) by the Wilhelmy plate technique

The Wilhelmy plate technique equation:

$$F = \gamma \times P \times \cos \theta + W - \sigma \times g \times y \times A$$

Equation [14]

where $F$ is the measured force, $\gamma$ the surface tension of the wetting liquid, $P$ the wetted perimeter of the fibre at the liquid/air interface, $\theta$ the contact angle of the fibre surface, $W$ the weight of the fibre, $\sigma$ the density of the wetting liquid, $y$ the immersion depth of the fibre and $A$ the cross-sectional area of the fibre. As the weight of the fibre was zeroed before the measurement, and the expression $\sigma \times g \times y \times A$ (the buoyancy term) was equal to zero when the fibre was precisely at the liquid’s surface, Eq. [14] could be reduced to:
$F = \gamma \times P \times \cos \theta$ \hspace{1cm} [15]

Eq. [15] could be divided into expressions for both the advancing ($\theta_A$) and the receding ($\theta_R$) contact angles, Eqs. [16] and [17] (43).

$F_A = \gamma \times P \times \cos \theta_A$ \hspace{1cm} [16]

$F_R = \gamma \times P \times \cos \theta_R$ \hspace{1cm} [17]

Only the advancing contact angle ($\theta_A$) was investigated in this study, however, since there was a risk that the receding contact angle ($\theta_R$) could have been distorted due to the water influencing the crevices in the fibres during the measurement of the advancing contact angle.
4 Summary of Papers

4.1 Paper I: The effect of modifying the oxidative pre-aging conditions in the manufacture of viscose from wood pulp

The production of viscose fibres from cellulosic pulps involves the conversion of cellulose into alkali cellulose by dissolution of the cellulose with sodium hydroxide of mercerisation strength, i.e. about 18% (w/w). This is followed by an oxidative depolymerisation of the alkali cellulose, called aging, and a conversion of the aged alkali cellulose into sodium cellulose xanthate with carbon disulphide. The xanthate is then dissolved in weak sodium lye to give a viscous liquid (viscose) and, after filtration, de-aeration and ripening of the viscose, the liquid is pumped through an acidic spinning bath where the carbon disulphide is removed chemically and the cellulose is regenerated and spun onto bobbins to produce a (theoretically) infinitely long fibre filament. The tow is then cut, washed and treated with finishing products. Finally, the fibre is dried and baled for storage or sale.

In the aging of the alkali cellulose, where the depolymerisation of the cellulose is most effective, it is important that the mean DP (Degree of Polymerisation) of the cellulose is reduced to a suitable level for viscose manufacture or the viscose will become too stringy and impossible to process. The conventional way to lower the DP is to expose the alkali cellulose to atmospheric oxygen at temperatures of 40-45 °C in revolving drums (see Figure 45 in the Appendix). The mercerisation lye is prepared with small amounts of cobalt (approx. 0.4 ppm) which enhances the depolymerisation of the cellulose, but it is still a time-consuming process where the mean process time is 4-5 h.

The first part of the study focused on the alteration of various parameters for the pre-aging of the alkali cellulose, to investigate which parameter had the greatest impact on the cellulose depolymerisation. The parameters considered were the sodium hydroxide and cobalt charge in the mercerisation lye and the
temperature in the pre-aging drum. Two types of pulps were used in the study; a dissolving sulphite softwood pulp and a conventional kraft softwood pulp (Section 2.1).

The tests showed that an increase in the temperature contributed significantly to the lowering of the viscosity of both the pulps, as shown in Figure 17. An increase from 45 to 60°C reduced the viscosity from 2.6 to 1.8 cP for the dissolving pulp and from 4.6 to 2.7 cP for the kraft pulp. These viscosity values are however lower than what is considered to be preferable from a manufacturing point of view. The viscosity values are lowered due to the optimal analysis conditions of the laboratory, as opposed to industrial conditions.

![Figure 17. Viscosity obtained after pre-aging at different temperatures. Reaction time: 5 h.](image)

The net NaOH-charge was varied between 250 and 310 kg/t pulp and Figure 18 shows that optimum charge for the lowest viscosity was reached at 290 kg NaOH/t pulp. This level is at a normal NaOH net charge of an industrial mercerisation. The second x-axis in Figure 18 shows the actual concentration of NaOH in the mercerisation lye at different net NaOH charges/t pulp. A higher or lower charge resulted in an increase in the viscosity, probably due to the more disadvantageous mixture of NaOH and water that lowers the swelling of crystalline parts of the cellulose matrix. The tests with various
cobalt-charges between 0.4 and 1.0 ppm (calculated on the NaOH charge) did not show any significant change in the viscosity, indicating that the lowest charge was sufficient.

Although it was possible to depolymerise even the high viscosity kraft pulp to a viscosity level suitable for viscose manufacture by increasing the temperature, the gel formation test clearly showed that the gel formation was much higher when a conventional non-dissolving pulp was used (Figure 19 and Figure 20). These figures show the gel particle formation in a viscose dope made from a dissolving pulp and a conventional kraft softwood pulp, respectively. A significantly longer reaction time, or a significantly higher CS$_2$ charge, was necessary to achieve a suitable gel content in the conventional pulp than in the dissolving pulp. The viscoses were produced according to Treiber et al. (33).
A new approach to reduce the viscosity of the cellulose prior to the viscose process was also tested. The principle was that the cellulose was mixed with NaOH to a total dryness of 15% and placed in a pressurized vessel under an oxygen pressure of 6 bar. The reaction was then carried out at 110°C for 2 h (Figure 21).
The figure shows that at 6 bar it was possible to reach the viscosity goal of about 5 cP for a dissolving pulp within the 2 hour set time. An even more interesting result was that a major reduction in the NaOH charge was possible compared with the standard condition. A level of 300 kg/t pulp is usually used in the manufacture of industrial viscose but, in this case, a significantly lower charge was sufficient. A charge of 50 kg NaOH/t pulp was almost as effective as a charge of 300 kg NaOH/t pulp. The main factor of importance for reducing viscosity seems therefore to be the oxygen pressure and not the NaOH charge.

The reactivity test confirmed that a relatively low NaOH charge of 50 kg/t pulp seemed to be sufficient at 6 bar oxygen pressure for derivatisation of the alkali cellulose. This showed that the lower NaOH charge resulted in a higher reactivity than the higher NaOH charge (Figure 22).
The main conclusion of the study was that it was possible to lower the NaOH charge and the reaction time for the depolymerisation of the cellulose using pressurized oxygen treatment instead of conventional pre-aging treatment in an open revolving drum at atmospheric pressure. The lower NaOH charge and the shorter reaction time mean that the operating costs and the investment needed for pre-aging can be reduced considerably. However, a new pressurized oxygen reactor is necessary, and this requires an investment. Although this method makes it possible to reduce the viscosity of the cheaper conventional kraft pulp reasonably rapidly, it is still not sufficient to enable conventional kraft pulps to be used in the manufacture of viscose due to the formation of large amounts of gel particles.

4.2 Paper II: Enzymatic treatment to increase the reactivity of a dissolving pulp for viscose preparation

The aim of the second study was to investigate how five types of enzymes affected the yield, viscosity and reactivity of a softwood sulphite dissolving pulp. The molecule weight distributions of the pulp samples were also determined after enzyme treatment.

The enzymes had different fungal origins, having either a multi or a mono-component composition. Four of the enzymes are used
commercially in the laundry industry and one is normally used to
degrade cellulose into sugar monomers.
The pH and temperature conditions used were based on the enzyme
manufacturer’s recommendation for optimum activity on CMC
samples (Section 2.7). The amount of enzyme charged on the pulp was
based on the slurry mixture instead of the activity units given by the
manufacturer, due to the difficulty in relating the different activities to
each other. The enzyme amounts chosen were 0.1 % and 1.0 %
calculated on the Volume of the slurry mixture.

It is a well-established fact that mixtures of endoglucanases and
exoglucanases produce synergistic effects in cellulose degradation; the
yield results in Figure 23 show that the multi-cellulase mixtures
(Celluclast ®, Renozyme ® and Celluzyme ®) reduced the cellulose into
short chain fragments to a greater extent than the mono-component
cellulases (Carezyme ® and Endolase ®). Most of the short fragments are
soluble in water and they are therefore lost when the sample is filtered
and washed.

![Figure 23. Yield of a sulphite dissolving pulp treated with different types of enzymes.
Reaction time: 2 h. Enzyme concentration: 1.0 %. Temperature: (see Materials and
Methods) and pulp consistency: 1.0 %.

Analysis of the viscosity (Figure 24) showed conformity with the yield
results, at least for the samples at 1.0% enzyme charge. At this level of
enzyme content, the multi-component enzyme preparations seemed to
depolymerise the cellulose to smaller fragments to a greater extent
than the mono-component enzymes, lowering both the viscosity as
well as the pulp yield. The 0.1% samples of all the enzyme preparations
reached more or less the same level of viscosity, suggesting that this
enzyme charge was too low for the given reaction time of 2 h,
regardless of the kind of cellulase mixture used.

Figure 24. Viscosity reached with 0.1 % and 1.0 % enzyme dose for the five enzyme types
studied. Reaction time: 2h. Pulp consistency: 1.0 %. Temperature: see Materials and
Methods.

The sole component of the enzymes Endolase® and Carezyme® is an
endoglucanase which attacks the cellulose chain internally, mainly in
the amorphous regions of the cellulose matrix. This could mean that
when the accessible parts of the cellulose are degraded, the enzyme is
inactivated due to the lack of assistance of an exoglucanase capable of
attacking more crystalline regions in the cellulose. Thus, the reduction
in viscosity is halted not because of too low an enzyme charge or too
short a reaction time, but due to a lack of reaction sites in which the
enzyme can act. An indication that this is the case is the similarity in
the level of viscosity for the 0.1 % and 1.0% charges of these two
enzymes (Figure 24).

In contrast to the comparison of viscosity, the results of the reactivity
test showed only very small differences between the enzyme charges
(Figure 25); there seemed to be no correlation between the drop in
viscosity and reactivity. One example of this is the multi-component
mixture of Celluzyme®, which did not show any positive results in reactivity even though the viscosity was reduced considerably with a charge of 1.0%. It could be assumed that shorter cellulose chains should react more easily with the enzymes, due to less hydrogen bonding between the cellulose chains. This was not the case, however, as the Carezyme® treatment, with its relatively poor depolymerisation rate, resulted in a very high reactivity value.

![Figure 25. Reactivity after enzyme treatment with charges of 0.1 % and 1.0 %. Time: 2h. Temperature: (see Materials and Methods). Pulp consistency: 1.0% .](image)

The conclusion drawn from this study was that it seemed possible to use enzymes to increase the reactivity of dissolving pulp and thus reduce the demand of carbon disulphide in the viscose manufacturing process. The most promising enzyme was the mono-component endoglucanase Carezyme®, which gave a pulp with a high level of reactivity and a low yield loss. The reduction in viscosity was not, however, completely satisfactory.

**4.3 Paper III: Optimization of the enzymatic activation of a dissolving pulp before viscose manufacture**

In this study, the enzyme preparation Carezyme® was selected on the basis of the results obtained in Paper II: an optimization survey where the parameters of the enzyme considered were the temperature, concentration of the charge and length of time of the treatment. The
parameters of the pulp tested after treatment with enzyme were the pulp yield, reactivity (according to Fock (31)) and viscosity. Viscose dopes were also made from dissolving pulps treated with enzyme and then tested. The parameters considered were the filter clogging value, $K_w$, and viscose viscosity, determined here as the ball-fall time.

The yield analysis at different temperatures showed that the treatments at low temperatures (5-20°C) gave a slightly higher yield than the rest of the samples (30-70°C), which is probably indicative of a relatively low level of activity of the enzyme at the lower temperatures.

The yield studies at different concentrations of enzyme showed that there was no significant difference in yield loss, although the treatments were carried out over a large concentration range. The highest concentration of enzyme was 45,000 ECU (endoglucanase units)/g pulp, which was 10,000 times higher than the lowest (4.5 ECU/g pulp). The reason for this is probably that the endoglucanase enzyme only cuts the cellulose chains internally, leading to a low formation of water-soluble sugars. These are lost in the washing process, holding the yield loss at a minimum regardless of the degree of enzyme concentration.

The yield loss at different reaction times was also determined. Two different enzyme charges were used in the study: 450 ECU/g pulp and 4500 ECU/g pulp. The lower enzyme charge did not lower the yield significantly regardless of the reaction time: the charge that was ten times higher, on the other hand, showed a greater yield loss, especially at the longest reaction time of 24h (Figure 26).
Figure 26. Yield of a pulp treated with enzyme at two enzyme concentrations and for different lengths of time. The reaction temperature: 40 °C.

The reason could be that the enzyme had enough time to degrade very small cellulose fragments that would not normally be attacked to any great extent during a short time period. The enzyme would then produce a greater amount of soluble sugars that are removed in the washing process.

Treating the pulp with enzyme resulted in a depolymerisation of the cellulose chains that seemed to stop at a viscosity of about 10 cP, regardless of the temperature, charge or reaction time of the enzyme. This suggests that the enzyme primarily attacks amorphous regions of the cellulose and that when this is degraded, the enzyme is unable to attack the more crystalline parts of the cellulose matrix. This could mean that there is no, or very little, substrate accessible to the enzyme for further depolymerization. Figure 27 shows the similarities of the viscosity at different reaction times.
Figure 27. Pulp viscosity versus reaction time in the enzyme stage at 450 and 4500 ECU/g pulp. Reaction temperature: 40 °C.

The most important parameter in the optimization study is the reactivity of the pulp, which was determined according to (31). The tests showed that reactivity increased with treatment temperature up to 40°C, and levelled out at higher temperatures. This meant that a temperature of 40°C was sufficient for the enzyme reaction, as a higher temperature did not contribute to its enhancement. The enzyme concentration could also be held at a low level, according to the tests: an enzyme charge of only 4.5 ECU/g pulp gave as good reactivity as a charge of 4500 ECU/g pulp. It would thus probably be possible to use the enzyme on an industrial scale. The reaction time proved to be quite critical, as the results showed a rather fast decline in reactivity after 2h (Figure 28).
The study included two trial series with enzyme charges of 450 ECU/g pulp and 4500 ECU/g pulp. The fact that the curves have the same form is a good indication that it is the time parameter which is decisive and not the concentration. The reason for the drop in reactivity with a longer enzyme reaction time could be that the opened cellulosic matrix collapses slightly due to the extended mechanical influence of the fibres, leading to lower accessibility of the carbon disulphide (Figure 29).

When the optimal enzyme treatment parameters had been established, the pulp treatment was extended to include the manufacture of viscose. This, along with its characterization, is of immense importance for the evaluation of the enzyme treatment of the pulp. The parameters
of interest were the filter clogging value, $K_w$ (Section 3) and the viscosity of the viscose (ball-fall time (34)).

The pre-aging step is usually a time-consuming process, taking about 4-5 h in the conventional production of viscose. However, Figure 30 shows that enzyme treatment of the pulp prior to sulphidation meant that the pre-aging time could be shortened to approximately 1 h. This shorter pre-aging time is probably the result of a more open cellulose structure, which exposes the cellulose chains to the depolymerising oxygen radicals.

As can be seen in Figure 31, the clogging values for the enzyme-treated viscoses were better than the references, which is a good indication that the reactivity is enhanced by treating the pulp with enzyme. Prior to this production of viscose, the parameters of the enzyme treatment were: pH 8, temperature 40°C, concentration 450 ECU/g pulp and reaction time 2h. Reference viscoses were also produced based on pulps that were treated in the same way but with no enzyme. Viscose samples were then prepared according to Treiber et al. (33) using different levels of carbon disulphide charges.
However, the viscoses did not reach sufficiently good quality according to the clogging value characterization derived from Sixta et al. (44), and was probably due to small fibre fragments in the dopes. The reason for the relatively poor clogging value results was probably that the laboratory method used was not optimized for the enzyme-treatment step implemented. This can be seen in Figure 32, where viscose dopes were produced either in the conventional way according to (33), or by pre-treating the pulp as in the enzyme-treatment step, but with no enzyme added to the pulp slurry.

It is important to note that the ball-fall time is highly dependent on the viscosity of the viscose. According to (45), a viscose with a ball-fall time of e.g. 300 seconds has a viscosity that is about 0.5 cP higher than one
with a time of 70 seconds. Keeping the ball-fall time within the industrial range is therefore not easy. The results of the study showed that it was possible to use the Carezyme enzyme to enhance pulp reactivity at temperatures, concentrations and time levels that are within reasonable economic limits. Furthermore, characterization of the viscose dope in the samples treated with enzyme showed that enzyme treatment could make it possible to lower the carbon sulphide charge in the xanthation step. The analysis method for the viscose must, however, be optimized in order to investigate this conclusion further; such an optimization was performed in Paper V.

4.4 Paper IV: Pressurized oxygen treatment of alkali cellulose prior to the preparation of viscose dope

This study investigated the possibility of making viscose dope from pressurized oxygen and dissolving pulp treated with NaOH as a continuation of the results achieved in Paper I. The hypothesis was that it would be possible to use a much lower charge of NaOH in the pressurized oxygen step, since it was shown that reactivity was not only increased to a greater extent with the lower NaOH charge than in the conventional mercerisation stage (Figure 33): it could also produce a high quality viscose dope.
Figure 33. The reactivity* of a dissolving pulp after treatment with pressurized oxygen at different net NaOH charges. Temperature and treatment time in the oxygen stage: 110°C and 2 h. * = according to Fock

The good results achieved for the reactivity of the pulp treated with oxygen allowed a hypothesis to be postulated: that it would be possible to replace the conventional cold (40°C) mercerization stage with hot (110°C) alkali treatment with a lower charge of NaOH (50 kg/t pulp), but where the oxygen pressure was high (>6 bar). If this were possible, it could reduce the usage of NaOH significantly as well as the total reaction time. However, when the CS$_2$ was added in the sulphidation step after such an oxygen treatment stage, no xanthogenation of the alkali cellulose seemed to occur. Tests with much greater charges of NaOH were also performed, but still no viscose dope was produced (Table 5). The poor result was therefore not caused by the addition of alkali being too low.

Table 5. Sulphidation tests carried out on pressurized oxygen-treated cellulose using two different charges of NaOH. Oxygen treatment time: 2h.

<table>
<thead>
<tr>
<th>O$_2$ pressure (bar)</th>
<th>Temperature (°C)</th>
<th>NaOH charge kg/ton pulp</th>
<th>CS$_2$ charge (% on AC)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>110</td>
<td>50</td>
<td>30</td>
<td>No viscose dope could be produced</td>
</tr>
<tr>
<td>6</td>
<td>110</td>
<td>300</td>
<td>30</td>
<td>No viscose dope could be produced</td>
</tr>
</tbody>
</table>
It was proposed that the reason for the poor xanthogenation results in the oxygen treatment step could be either that the high concentration of oxygen was detrimental to the reaction, or that the temperature was too high. The fact that a high temperature can be problematic during the transformation of cellulose into alkali cellulose has indeed been certified by Woodings (46), where it was shown that the temperature used in the oxygen step (110°C) is not very suitable for mercerising pulp at any NaOH concentration.

The results obtained in the viscose preparation tests meant that the approach to the mercerisation and oxygen treatment steps had to be altered: two steps were chosen instead of one for pre-treating the pulp prior to sulphidation. In the first step, the pulp was mercerized in the conventional way at 40°C and with a high alkali charge (net charge of 300 kg /t pulp) and, in the second step, the alkali cellulose formed was exposed to pressurized oxygen at 110°C for 2h. The result was sticky, doughy, dark brown and unprocessable alkali cellulose. Tests were therefore performed to investigate whether or not a reduction in temperature during oxygen treatment could enhance the situation. It was thereby speculated that oxygen treatment at a temperature of 110°C was too intense for a successful reaction.

A study of how different temperatures influence the alkali cellulose during pressurized oxidation was performed; the results are shown in Figure 34.
It was found that a temperature of 40°C in the oxidation vessel and a treatment time of 1h were sufficient to produce good, depolymerised alkali cellulose. Higher temperatures and longer treatment times discoloured the alkali cellulose and depolymerised the cellulose chains too much.

A graph of viscosity versus oxygen treatment time was produced to ensure that an excessive pressurised oxygen treatment time at 40°C would not depolymerise the cellulose too rapidly. It was found that viscosity dropped rapidly to the preferred level of around 4-5 cP during the first hour of oxygen treatment; thereafter, extended oxygen treatment time decreased the cellulose viscosity only very slightly (Figure 35).
A molecular size exclusion analysis of the alkali cellulose treated with pressurized oxygen for four different lengths of time (45 min, 1h, 2h and 5h) was carried out to investigate the impact of the treatment on the cellulose molecules. Figure 36 shows that the molecular size distribution becomes narrower and more homogenous with increasing time. Earlier studies have shown that conventional mercerisation and pre-aging (4-5h) of the alkali cellulose produces a Gaussian-shaped molecular size distribution curve (Paper II). This indicates that the quality of a viscose dope made from alkali cellulose treated with pressurized oxygen increases with time. Thus, the conclusion to be drawn here is that treating alkali cellulose with pressurized oxygen for a long period of time increases the quality of the resulting viscose dope.

Figure 36. Molecular weight distribution of alkali cellulose treated with oxygen for different lengths of time. The curves are shifted upwards in an arbitrary order for the sake of clarity.

Figure 37 shows filter clogging values of viscose samples produced from alkali cellulose treated with pressurized oxygen for different lengths of time. The filter clogging values decreased for treatment times up to 1h, which meant that the quality of the viscose dopes increased. At longer treatment times, however, the quality of the viscose samples not only decreased, but also varied greatly. The results presented in Figure 37 contradicted the hypothesis that prolonged treatment of alkali cellulose with pressurized oxygen has an entirely positive effect on the
quality of the viscose dope. This indicated that the increasing filter
clogging values for viscose samples made from alkali cellulose treated
for longer than 1 h in the oxygen stage originated at the fibre level
rather than at the molecular level.

Figure 37. Clogging values of the viscose dope versus the length of time the alkali
cellulose has been treated with oxygen at a CS₂ charge of 20%, calculated on the cellulose
content of the alkali cellulose. The reference viscoses were prepared according to the
conventional method (mercerisation 45°C and ageing time 5 h). Each bar represents one
sample.

A contact angle analysis of the fibre surface was performed to
investigate whether the uneven viscose quality for oxygen treatment
times exceeding 1 h depended on the uneven diffusion of carbon
disulphide into the fibres. The hypothesis was that prolonged oxygen
treatment of the alkali cellulose would disrupt the cellulosic matrix,
which could lead to an internal collapse of the fibre and thereby render
it more dense and inaccessible to chemicals.

The same theory was applied to extended enzyme treatment times in
Paper III, although oxygen treatment seemed to attack and disrupt the
cellulosic structure more aggressively than enzyme treatment, which
probably leads to a greater collapse of the cellulose matrix (Figure 38).
If this were the case, the contact angle between the fibre and the liquid in the analysis would increase with increasing pressurized oxidation time of the alkali cellulose: increasing contact angles mean that the surface becomes more even and contains fewer crevices through which carbon disulphide can enter into the fibre. The result can be seen in Figure 39, which shows an increase in contact angle with increasing oxidation treatment time, indicating that the hypothesis regarding the fibre surface could be true.

Figure 38. Schematic diagram of the cellulosic matrix collapsing due to either extended enzyme or oxygen treatment time.

Figure 39. Measurement of the dynamic contact angle (advancing mode) of alkali cellulose treated with oxygen at different time intervals. Conditions used: oxygen pressure 10 bar and temperature 40°C. The error bars represent a confidence interval of 90%.
An interesting feature was found when the viscose dopes produced from alkali cellulose treated with pressurized oxygen (time: 1h) were compared with viscoses produced conventionally. The DP (degree of polymerisation) of the cellulose in the viscoses treated with pressurized oxygen was slightly higher than in those produced conventionally. This was found for all of the carbon disulphide charges (Figure 40). A cellulose with a high DP usually produces a stronger viscose fibre when spun.

An alkali cellulose with a high DP usually demands a higher charge of carbon disulphide in the sulphidation stage than one with a low DP. This could be due to the fact that the longer cellulose chains, which obviously contain more glucosidic groups than cellulosics with a low DP, need more carbon disulphide for sufficient substitution of the hydroxyl groups. The longer cellulosic chains could also be less accessible since there are more hydrogen bindings between them. Treatment with pressurized oxygen seemed to influence the matrix of the high DP cellulose chains by breaking the hydrogen bonds between
them. This would make the structure more accessible to chemicals, and thereby enable the production of high quality viscose dope by reducing the carbon disulphide charge from 30% to 20% and maintain, or even increase, the DP of the cellulose. The increased cellulosic DP would thus lead to an increase in the strength of the viscose fibres.

The conclusions drawn from the studies of treating alkali cellulose with pressurized oxygen were that it was possible to lower the carbon disulphide charge compared to conventionally produced viscoses, and to maintain or even increase the quality of the viscose dopes. The temperature and time in the pressurized oxidation stage were, however, critical and should not exceed 60°C and 1h. A correlation was found between the dynamic contact angle of the alkali cellulose fibres treated with pressurized oxygen and the filter clogging value of the viscose dopes.

4.5 Paper V: Modification of the viscose process for enzymatically pre-treated dissolving pulps

The studies in Paper V were a continuation of Papers II and III, i.e. enzyme treatment of dissolving pulps prior to the production of viscose dope. Most of Paper V was concerned with modifying the viscose process in order to implement the use of enzymes, such as dewatering the pulp after mercerisation and using different mixing techniques in the sulphidation step. A reactivity and viscosity study of different cellulosic substrates treated with enzymes was also carried out as the basis for further investigations into suitable cellulosic materials for the manufacture of viscose fibre.

The enzyme used in the studies (Carezyme®) is a good agent for enhancing pulp reactivity: the one crucial drawback is that it shortens cellulosic fibres. This is not really surprising, however, as the enzyme was originally used in the laundry industry as a defibrillating agent for textiles with protruding fibres. A study of the length of fibres in sulphite dissolving pulp was performed, using two different enzyme charges and various pulp concentrations, to investigate the way in
which they are affected by the enzyme. As expected, the higher enzyme charge shortened the fibres more than the lower charge. It was also found that defibrillation reached a maximum at a pulp concentration around 8% (w/w) (Figure 41). This was in accordance with Cao and Tan (47), who has found that a pulp concentration higher than 8% (w/w) lowers the enzyme activity for steric reasons.

Figure 41. Long fibre fraction (fibres collected on >30 mesh frames) of enzyme treated pulp vs. pulp concentration.

It was found that the difference between the enzyme charges was about 25% units at a pulp concentration of 5% (w/w), i.e. the pulp concentration used in all of the studies.

The rate at which carbon disulphide diffuses into the cellulosic fibres in the sulphidation stage is a very crucial parameter for the outcome of the quality of the viscose dope. The mixing process becomes even more critical for pulps treated with enzyme as the fibres have been shortened, which promotes both their ability to agglomerate easily and a more uneven diffusion of carbon disulphide. Two different ways of mixing carbon disulphide and alkali cellulose were tested in the sulphidation stage: Sulphidation A and Sulphidation B (Section 2.13). Sulphidation B proved to be the significantly better method (Figure 42). Sulphidation A (used in Paper III) was replaced by Sulphidation B.
in Paper V for producing viscose dopes from enzyme treated and non-enzyme treated dissolving pulps.

Figure 42. Filter clogging value vs. charge of carbon disulphide in the sulphidation stage (calculated on the cellulose content in the alkali cellulose) for Sulphidations A and B. The quality of the viscose dope increases with decreasing filter clogging value.

Figure 43 shows that an enzyme charge of 45 ECU/g pulp created a significant decrease in the filter clogging value compared to the non-enzyme treated pulp. It can be seen that it would be possible to decrease the carbon disulphide charge from 30% (calculated on the cellulose content in the alkali cellulose) to 20% using a relatively low enzyme charge on the pulp and still keep the filter clogging value (Kw) below 400, which classifies the viscose dope as “excellent”, in accordance with (44) and (48).
Enzymes catalyse chemical reactions, i.e. they are not expended after the reaction and can therefore be re-used. In theory, the enzymes are active infinitely until they are denaturated due to, e.g. high temperatures or damaging levels of pH. It was consequently of interest to examine the possibility of re-using the enzyme from the spent press water collected after the pulp was treated with enzyme on a new batch of pulp. The assumption was that the entire amount of enzyme was collected in the water phase after the pulp was pressed, and that only make-up enzyme corresponding to the amount of water that was lost with the pulp would be added. The viscosity of the pulp was used as the analysis parameter, since the viscosity is more sensitive to the concentration of enzyme than it is, for example, to the reactivity (according to Fock (31)) (Paper III).

The enzyme charge of the pulp was rather high (450 ECU/g pulp) to ensure that a significant decrease in viscosity would be achieved.

Four recirculation cycles of the spent press water from the enzyme treatment stage were analysed; it was found that the viscosity decreased to approximately the same level for all of the cycles (Figure 44). This indicated that it would be possible to re-use the enzymes
from the spent press water with an addition of make-up enzymes in the enzyme treatment stage.

Figure 44. Recirculation test of press water after the pulp has been treated with enzyme. Initial pulp viscosity: 21 cP. The error bars denote the standard deviation.

Most of the studies (Papers I - V) have been performed on sulphite dissolving pulp, which is a good pulp for producing viscose. It was therefore interesting to investigate whether or not the enzyme treatment used on the dissolving pulp could be effective on other cellulosic substrates. Some different cellulosic materials were tested, ranging from highly crystalline substrates (i.e. cotton) to materials with high amorphous cellulosic structures (i.e. kraft softwood pulp). The viscosity and reactivity were analysed, and the results from the latter analyses are shown in Figure 45. The most interesting result is the reactivity of the kraft pulp treated with enzyme, which increased to the reactivity level of the untreated sulphite dissolving pulp. The reason for this could be that the enzyme, which is an endoglucanase that hydrolyses the glucose units within the cellulosic chains randomly, was able to disrupt the cellulose-hemicellulose matrix to such an extent that the structure became more open and accessible to chemical reactions.
The enzymatic treatment of the cellulosic material only slightly reduced the viscosity of most of the substrates, only the kraft pulp showed a significant depolymerisation (~30 cP-units) of the cellulose, Figure 46.

The conclusion of this study is that the enzyme charge in the enzyme treatment stage must be chosen carefully due to the ability of the enzyme to shorten fibres. Fibres that are too short could cause problems in the de-watering stage. Thorough mixing in the sulphidation stage is very crucial for producing good quality viscoses,
especially when the pulp is to be subjected to pre-treatment with enzymes. The carbon disulphide charge could thus be reduced from 30% (calculated on the cellulose content of the alkali cellulose) to 20% without reducing the quality of the viscose dope. It was also found that the enzymes in the spent press water from the enzyme treatment stage could be re-used in the process, which would lower production costs considerably for viscose produced from pulp treated with enzymes. Finally, some different cellulosic substrates were treated with enzymes to investigate the possibility of using pulps other than dissolving pulps for producing viscose. A kraft pulp showed the most promising results, with an increase in reactivity of approximately 45% units after being treated with enzyme.
5 Process economy

One important aspect related to reducing the amount of carbon disulphide used in the viscose process is economy. An estimation of the process economy for the different process methods was therefore made.

It is unavoidable that investments have to be made in order to adapt to either the oxygen or enzyme treatment process, so capital costs must therefore be included. The oxygen treatment process requires a pressure vessel (Figure 47) and the enzyme treatment process requires a pulper, an enzyme tank and a press (Figure 48). Table 6 shows the investments necessary for both treatment processes when used for a small-scale viscose producer.

![Figure 47. A schematic diagram of the pressurized oxygen treatment method. (Courtesy of Metso Fiber AB, Karlstad, Sweden.)](image-url)
Figure 48. A process flow sheet for an enzyme pre-treatment stage followed by mercerisation, sulphidation and filtration stages prior to spinning. (Courtesy of Metso Fiber AB, Karlstad, Sweden.)

Table 6. Approximate investments necessary for the two process methods when used for a small-scale viscose producer.
(Figures obtained from Metso Paper, Sundsvall, Sweden in October 2007.)

<table>
<thead>
<tr>
<th>Production (t fibre/year)</th>
<th>Process method</th>
<th>Pressure vessel (MSEK)</th>
<th>Tanks + Press (MSEK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25,000</td>
<td>Pressurized oxygen</td>
<td>15.5</td>
<td>-</td>
</tr>
<tr>
<td>25,000</td>
<td>Enzyme</td>
<td>-</td>
<td>8.5</td>
</tr>
</tbody>
</table>

The net consumption of CS$_2$ in a viscose plant has been obtained from industrial sources: a net consumption of 0.17 kg CS$_2$/kg viscose fibre corresponds to a viscose producer with a low level of CS$_2$ recovery, whereas that of 0.09 kg CS$_2$/kg viscose fibre corresponds to a producer with high level of CS$_2$ recovery (production data from (49)). A mean consumption of 0.13 kg CS$_2$/kg viscose was used for the economical calculation given below. The cost of the CS$_2$ was estimated to be 2,600 SEK/t (price in 2007); the enzyme was estimated to 30 SEK/kg enzyme solution (4.5 x 10$^6$ ECU/kg enzyme solution) and the oxygen was 0.60 SEK/kg.
Table 7 shows the total costs estimated for the three different process methods. A charge of 30% CS₂, calculated on the cellulose weight, was used in the conventional method and a charge of 20% CS₂ was used in both the oxygen and enzyme methods. The enzyme charge used was 45 ECU/g pulp and the estimated amount of O₂ used in the oxygen method was 10 kg O₂/t fibre. The environmental cost (i.e. the cost for scrubbing exhaust gases and re-cycling CS₂) was estimated as being 0, 1 and 2 SEK/kg of CS₂ consumed, respectively. The capital cost, including interest and depreciation, was calculated using the common rule of thumb, i.e. 0.2 x investments for the annual capital cost.

<table>
<thead>
<tr>
<th>Process method</th>
<th>Conventional</th>
<th>Oxygen</th>
<th>Enzymatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS₂ (SEK/t fibre)</td>
<td>340</td>
<td>225</td>
<td>225</td>
</tr>
<tr>
<td>O₂ (SEK/t fibre)</td>
<td>-</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>Enzyme (SEK/t fibre)</td>
<td>-</td>
<td>-</td>
<td>37</td>
</tr>
<tr>
<td>Environmental cost (0 SEK/kg CS₂)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Environmental cost (1 SEK/kg CS₂)</td>
<td>130</td>
<td>87</td>
<td>87</td>
</tr>
<tr>
<td>Environmental cost (2 SEK/kg CS₂)</td>
<td>260</td>
<td>174</td>
<td>174</td>
</tr>
<tr>
<td>Cost of capital (SEK/t fibre)</td>
<td>-</td>
<td>124</td>
<td>68</td>
</tr>
<tr>
<td>Total cost (SEK/t fibre)*</td>
<td>340</td>
<td>355</td>
<td>330</td>
</tr>
<tr>
<td>Total cost (SEK/t fibre)**</td>
<td>470</td>
<td>442</td>
<td>417</td>
</tr>
<tr>
<td>Total cost (SEK/t fibre)***</td>
<td>600</td>
<td>529</td>
<td>504</td>
</tr>
</tbody>
</table>

* 0 SEK/kg of CS₂ consumed, ** 1 SEK/kg of CS₂ consumed, *** 2 SEK/kg of CS₂ consumed.

Figure 49 and Figure 50 show the accumulated cost reductions for the oxygen and enzyme treatment methods, respectively. Only the chemical and enzyme costs are included in the estimation of the break-even points for the investments necessary.
Figure 49: The cumulative reduction in operative costs of the oxygen method for three different environmental cost cases. The dotted line indicates the investment cost. The rings denote the break-even point for the different environmental cost cases.

Figure 50: The cumulative reduction in operating costs of the enzyme method for three different environmental cost cases. The dotted line indicates the investment cost. The rings denote the break-even point for the different environmental cost cases.

The figures thus show that the break-even point is between 3 and 5.5 years for the oxygen method and between 2 and 4.5 years for the enzyme method. The methods are therefore very interesting for the industrial production of viscose.
6 Conclusions

This work has shown that it is possible to enhance the reactivity of pulp and produce good quality viscose using two entirely different pretreatment methods, viz. a chemical method based on treatment with oxygen and a biotechnical method based on treatment with enzyme. Both methods enabled the viscosity of the pulp to be lowered to a suitable level more rapidly than with the conventional pre-aging procedure.

It was possible to produce a high quality viscose dope from alkali cellulose treated with pressurized oxygen (at 10 bar) using a carbon disulphide charge of 20% instead of 30%, as is used in the conventional viscose process. The temperature and treatment time in the oxygen treatment stage should, however, not exceed 60°C and 1 h.

The enzyme tests showed the best enzyme preparation to be the mono-component endoglucanase Carezyme®, which was therefore used in the preparation of the viscose dope. The optimization studies of the conditions showed that the working temperature could be held at 40°C and that a concentration of 4.5 ECU/g pulp was sufficient for the enzyme reaction. The reaction time could also be held within reasonable process limits. Modifying the dewatering and sulphidation stages when a cellulosic material was treated with enzyme prior to the preparation of viscose was found to be of importance. If this was performed correctly, then the charge of carbon disulphide in the sulphidation step could be reduced from 30%, calculated on the cellulose content in the alkali cellulose, to 20% and the viscose dope would maintain the same good quality. It was also found that the spent enzyme filtrate could be re-used several times without losing its efficiency, which reduces the consumption of enzyme per ton of viscose significantly. Finally, treating several cellulosic materials with enzymes showed that the reactivity of a paper-grade kraft pulp was increased from 40% to about 80%. Treating non-dissolving pulps with enzymes is therefore of great interest in the industrial manufacture of viscose.
Acknowledgments

Under denna rubrik tänker jag byta språk till svenska minsann!

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Let's switch back to English then...
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APPENDIX

The Viscose Process

Mercerisation

The first step in the treatment of dissolving pulp is mercerisation. The pulp sheets are fed into a tank containing sodium hydroxide (18% w/w) where the cellulose reacts to form alkali cellulose at a temperature of 45°C:

\[ \text{Cell-OH} + \text{NaOH} \rightarrow \text{Cell-O}^- + \text{Na}^+ + \text{H}_2\text{O} \]  

[A.1]

The slurry produced has a dry solids content of about 5% and the retention time in the tank is approximately 20 minutes.

The sodium hydroxide lye is held at about 18% (w/w): due to breakage of the intermolecular hydrogen bonds, the cellulose swells most at this level of sodium hydroxide. This means that the hydroxide ions in the cellulose are more accessible to derivatising agents after mercerisation (50).

Pressing

The slurry passes between two perforated rollers and, under high pressure, is pressed to form a mat (Figure 47). The mat has a dryness of 50%. Most of the sodium hydroxide that is drawn off is returned to the mercerisation stage, and the lye concentration is restored to 18% by the addition of fresh sodium hydroxide.
Shredding

Rotating knives shred the mat to increase the reactive area of the alkali cellulose. The surface area of the resulting shredded pieces is between 10 and 100 mm$^2$.

Ageing

The alkali cellulose is transported to a rotating drum that is 20 m long and has open ends (Figure 48). The cellulose is degraded by oxidation at atmospheric pressure prior to xanthation. It is necessary to shorten the cellulose chains to a certain degree; the viscose solution will otherwise become too stringy and extremely difficult to process. The reaction is catalyzed by heavy metal ions, mainly cobalt or manganese. A mechanism for this is suggested by Nevell is presented in Figure 48. The carbonyl intermediates formed under alkaline conditions are transformed into hydroperoxides that can decompose into either alkoxy radicals or peroxy radicals. The cellulose is then depolymerised via radical-chain reactions (15).
Figure 53. Conversion of cellulose into an alkoxy radical or a peroxy radical using oxygen in an alkaline environment (Nevell, 1985).

The number of oxygen atoms consumed per glucose unit is between 1 and 1.5. The oxidative ageing reaction is a homogeneous process. The ageing rate depends on the temperature, alkali-to-cellulose ratio and amount of catalytic metals. Ageing normally takes place at 40-45°C.

**Xanthation**

Sulphidation, or xanthation, is the step in which alkali cellulose reacts with carbon disulphide, the derivatisation agent in the viscose process:

\[
\text{Cell-NaO} + \text{CS}_2 \rightarrow \text{Cell-OCS}_2\text{Na} \quad \quad [A.2]
\]

The xanthate is soluble in aqueous sodium hydroxide. The compound produced is unstable and decomposes very quickly at low pH. Although all three hydroxyl groups are involved in derivatisation, the C2 and C3 positions are sterically favoured. Under technical conditions the DS is somewhere between 0.5 and 0.7. A DS of 0.5 is sufficient for a fibre-free xanthate solution (11). Side-reactions in the xanthation process consume 25% of the carbon disulphide, mainly in the form of
trithiocarbonate, which give the xanthate (or viscose solution) its orange colour (45).

\[ 3 \text{CS}_2 + 6 \text{NaOH} \rightarrow 2 \text{Na}_2\text{CS}_3 + \text{Na}_2\text{CO}_3 + 3 \text{H}_2\text{O} \]  
(trithiocarbonate)  

\[ 2 \text{CS}_2 + 6 \text{NaOH} \rightarrow \text{Na}_2\text{CS}_3 + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{S} + 3 \text{H}_2\text{O} \]  

[Sulphidation takes place in a reactor in a nitrogen atmosphere. Air is removed from the reactor and nitrogen is added to diminish the risk of explosion. The pressure is lowered whilst the carbon disulphide and alkali cellulose are reacting with each other. Sulphidation is complete when the pressure has decreased from 6 kPa to about 2 kPa. The reaction time is about 2.5 h.

**Dissolving**

The yellow crumbs (i.e. the xanthate) are dissolved in a weak sodium hydroxide solution (2% w/w) and are subjected to vigorous mechanical agitation to obtain the viscose composition desired: this is a crucial step in the process. Faulty viscose preparation (or a pulp with a low level of reactivity) can clog the filters to such an extent that the whole batch must be discarded. A typical viscose liquid contains 10% cellulose and 5% sodium hydroxide but, depending on the end product, the composition of the viscose can vary slightly.

**Ripening**

The viscose is stirred gently for about 15-16 h in chilled storage tanks, where it is said to “ripen”. The DS decreases steadily with time, which is necessary for further processing of the viscose. An important feature of the ripening process is the redistribution of the xanthate groups. Under given conditions, the xanthate groups on C2 and C3 (which are favoured kinetically) are hydrolysed 15-20 times faster than the group on C6, although the latter is more thermodynamically stable. The carbon disulphide that is released can thus either react with a C6
hydroxyl group or disappear as a by-product. The redistribution of the xanthate groups causes a more homogeneous derivatisation of the cellulose chain. The viscose is then de-aerated and filtered a final time before being pumped to the spinning bath.

**Spinning**

A jet of viscose fluid leaving the aperture in a spinneret is coagulated and decomposed into regenerated cellulose in a bath of sulphuric acid and sodium sulphate (Figure 49). The spinnerets are made of chemically-resistant precious metals or alloys (mostly gold-platinum) containing as many holes in a circular arrangement as the number of filaments per thread. The diameters of the holes lie between 40 µm and 200 µm. The numbers of openings are of the order of 10,000 to 40,000 for the production of staple fibre. A head comprising several spinnerets is often used rather than just one large, single spinneret (Figure 50). The material, the geometry of the capillaries and the hardness of the spinnerets have a great influence on the quality of the fibre produced. The regeneration process must be retarded so that the molecule chains obtain the stretchability and alignment desired. The simplest way of delaying regeneration is to decrease the acid concentration, increase the salt concentration and add zinc oxide. It is assumed that, due to the interaction between Zn$^{2+}$ and CS$_{32}^{2-}$ ions, a relatively stable layer consisting of compounds containing S and Zn is formed on the surface of the filaments. The rate at which the H$_3$O$^+$ ions diffuse into the filaments decreases as all the more water is precipitated from the spinning dope into the spin bath. Thus, the filaments can be stretched by over 100%, depending on the fibre product desired.
Once the cellulose filament has reached the desired stretch, it is cut into appropriate lengths depending on the type of end-product desired (Figure 51). The fibre must then be washed to remove unwanted substances such as dihydrogen sulphide, zink oxide, carbon disulphide, zink sulphide and other residues from the spinning bath.

Figure 51. The filaments are collected into one single fibre tow, which is stretched before being fed into the cutting machine.
Excess carbon disulphide is removed by treating the fibre mat with hot steam; the gaseous carbon disulphide is condensed using liquid nitrogen and reused in the process. The fibre mat is then washed in acidic and alkaline baths to remove various impurities. Depending on the end product, the fibres are treated with different fatty agents to enhance glossiness and other surface parameters.

**Drying**

When the fibre mat is treated in the washing baths, it is pressed between two rollers to remove as much water as possible (Figure 52). The mat is transported to a “comb” that moves across the fibres in a vertical direction to separate any fibre bundles. The homogenized fibre mat is then lead into the dryer.

![Figure 52. The fibre mat is dewatered.](image)

**Baling**

The dried fibre is homogenized once more and pressed into bales of approximately 220 kg in weigh.
"Fearlessly the idiot faced the crowd; smiling"

(Waters, Gilmour, 1971)

"The sun is the same in a relative way, but you're older; shorther of breath and one day closer to death"

(Waters, 1973)

"Harmlessly passing your time in the grassland away; only dimly aware of a certain unease in the air."

(Waters, 1977)

"Du fångar mig vad kärlek är men jag vet inget om det där, bara samt som man kan mäta kan jag förstå."

(J. Berg, 2007)

"Vi ger upp till slut, vi abdikerar nu och förutnelsen börjar precis när vi fyllt 37"

(J. Berg, 2007)

"There is no dark side of the moon - matter of fact, it's all dark"

(Jerry Driscoll (Doorman at Abbey Road studios), 1973)
Activation of dissolving pulps prior to viscose preparation

The conventional viscose manufacturing process is a mature process that needs to be improved with respect to its environmental impact and its production cost structure. Therefore a research study has been done with the aim to improve the reactivity of the dissolving pulp used, in order to reduce the chemical demand in the viscose process and thus reduce the cost and indirectly the environmental impact.

The work described in this thesis has shown that it is possible to enhance the pulp reactivity and to use less carbon disulphide in the production of viscose, while maintaining a good quality viscose dope, by two entirely different pretreatment methods, one chemical and one enzymatic.

The chemical method used pressurized oxygen after the mercerisation step, which increased the reactivity of the alkali cellulose. The viscose dopes produced from the pressurized oxygen treated alkali cellulose had lower filter clogging values, Kw, compared to conventionally produced viscoses. The temperature and the oxygen treatment time of the alkali cellulose were however crucial for the viscose quality.

The best performing enzyme of several tested was a cellulase of the mono component endoglucanase preparation Carezyme®. This enzymatic treatment was optimized with respect to viscose dope preparation. The study showed that the enzyme treatment could be carried out under industrially interesting conditions with respect to temperature, enzyme dose and reaction time. A re-circulation study of the enzyme showed that it was possible to re-use the spent press water from the enzymatic treatment step several times, and thus lower the production cost. Some of the viscose process stages were modified to properly fit the enzymatically treated dissolving pulp and a comparison between viscose made from enzyme-treated pulp and viscose made from conventional pulp, showed that the enzyme-treated samples had a lower filter clogging value, Kw. This indirectly indicates that the enzyme pretreatment could reduce the carbon disulphide charge in the viscose manufacturing process. An initial study of how the Carezyme® influenced different cellulosic sources was also performed.