Characterization of cellulose pulps and the influence of their properties on the process and production of viscose and cellulose ethers

Peter Strunk
“Cellulose is a system, not a pure individual”
Louis E. Wise

„Für einen Mann des praktischen Lebens ist jede wissenschaftliche Leistung zunächst nur eine brotlose Kunst. Ihre technische Durcharbeitung macht sie zu einer interessanten Möglichkeit. Wichtig wird sie ihm erst, wenn sie in allen Einzelheiten dem Bedürfnis des Lebens völlig angepasst worden ist, wenn aus dem, was einmal eine Entdeckung war, eine Art Ware geworden ist.“
Fritz Haber

„For the practical person, any scientific achievement is but profitless art. What makes it an interesting possibility is its further technical development. It finally becomes important once it has entered the realm of daily usage, when it has turned from discovery into merchandise.”
Abstract

Today’s market offers an ever-increasing range of cellulose pulps (derivative pulps) made from various wood types through different delignification processes. Each pulp segment has its unique characteristics, which makes it difficult for the producer of cellulose derivatives to choose the most suitable pulp for optimum processability and product quality. The objective of this study was to improve knowledge of cellulose pulps and to describe how different pulp properties affect processability and quality in the production of viscose dope and cellulose ethers.

Ten pulp samples were investigated, originating from both sulfite and sulfate processes, with high and low viscosities and with softwood and hardwood as raw material. The pulps were analyzed for their properties and then processed to viscose dope and a cellulose ether in two separate pilot facilities. The intermediates in the viscose process as well as the quality of the viscose dope and cellulose ether were analyzed and the results correlated to pulp properties.

Multivariate regression methods were applied to investigate the dominating physical and chemical properties of each pulp and pulp segment, and to study the use of spectroscopic analyses in predicting pulp origin, concentration and composition of hemicelluloses as well as the content of reducing end groups in cellulose. For the production of viscose dope, the models presented showed the most important pulp properties for good cellulose reactivity and viscose filterability. In addition, the properties affecting gel formation, flocculation, degree of substitution and clarity in the production of a cellulose ether were highlighted. The study also emphasized the need to supplement the use of conventional analyses on pulps and viscose intermediates with other analytical methods, such as molecular weight distribution and carbohydrate analysis, to better predict the quality of both viscose dope and viscose fiber.

The results of the present study could be useful to predict the origin and properties of new pulps, to replace or supplement otherwise expensive pulp analyses, and to assess the impact of pulp properties on the production of cellulose derivatives without extensive pilot-scale trials.
Det finns idag ett allt ökande utbud av cellulosamassor (derivatmassor) tillverkade från varierande vedslag och delignifieringsprocesser. Varje massasegment har sina unika egenskaper, vilket försvårar för producenten av cellulosaderivat att välja den mest lämpade massan för optimal processbarhet och produktkvalitét. Målsättningen för studierna som ligger till grund för denna avhandling var att förbättra kunskapen om cellulosamassor och att beskriva hur olika massor påverkar processbarheten och kvalitéten i produktionen till viskoslösning och cellulosaetrar.

Tio cellulosamassor undersöktes, tillverkade från sulfit- och sulfatprocessen, med höga och låga viskositeter samt med barr- och lövved som råvara. Massorna analyserades med olika metoder med avseende på många av deras egenskaper varefter de förädlades till viskoslösning och en cellulosaetar i värst i pilotanläggning. Intermediärerna i viskosprocessen samt kvalitéten i viskoslösningen och etern analyserades och korrelerades mot massornas ursprungsegenskaper.

Genom användning av multivariata regressionsmetoder visades vilka fysikaliska och kemiska egenskaper som dominerar i massorna och massasegmenten, samt hur spektroskopiska metoder kan användas för att prediktera en massas ursprung, sammansättning och halt av hemicellulosa liksom halt av reducerande ändgrupper i cellulosan. För tillverkningen av viskos visar de framtagna modellerna de mest framträdande massaege skaper för en bra cellulosareaktivitet och viskos- filtrerbarhet. Dessutom visas vilka egenskaper som påverkar gelbildning, flockpunkt, substitutionsgrad samt klarhet i tillverkningen av cellulosaetern. Studien demonstrerar dessutom vikten av att komplettera de konventionella analysmetoderna på massan och viskosintermediärerna med andra analysmetoder, såsom molekylviktsfördelning och kolhydratanalys, för att bättre förutse kvalitéten på både viskoslösning och viskosfiber.

De presenterade modellerna och metoderna bör således kunna användas för att prediktera ursprung och egenskaper av nya massor, för att ersätta eller komplettera annars dybara massaanalyser och för att utan dybara pilotförsök kunna bedöma inverkan av massornas egenskaper på tillverkningen av cellulosaderivat.
List of Papers

This thesis is based on the following papers which are referred to by roman numbers I-IV in the following text.

Paper I
The influence of properties in cellulose pulps on the reactivity in viscose manufacturing


Paper II
Characterization of dissolving pulp by multivariate data analysis of FT-IR and NMR spectra


Paper III
Properties of cellulose pulps and their influence on the production of a cellulose ether


Paper IV
Chemical changes of cellulose pulps in the processing to viscose dope

P. Strunk, Å. Lindgren, B. Eliasson and R. Agnemo
Submitted
Presentation of results other than papers

Characterization of Dissolving Pulps and its Derivatives
**P. Strunk**, B. Eliasson

The Biorefinery Domsjö: From tree to sustainable eco-products
**P. Strunk**
Workshop “Enhanced Technologies in Direct Dissolution of Cellulose”, 16 June 2010, Rudolstadt, Germany.

The influence of properties in cellulose pulps on the reactivity in viscose manufacturing
**P. Strunk**, B. Eliasson, C. Hägglund, R. Agnemo
16th International Symposium on Wood, Fiber and Pulping Chemistry, 8-10 June 2011, Tianjin, PR China.
Abbreviations

α-cellulose  Cellulose with high DP, residue in 17.5% NaOH solution.
β-cellulose  Carbohydrates with DP <200 dissolved in 17.5 NaOH but regenerated in acetic acid.
γ-cellulose  With alcohols regenerated carbohydrates (DP<10) from the β-cellulose filtrate.

DP  Degree of polymerization.
DS  Degree of substitution (0-3).
EC  Ethyl chloride.
EHEC  Ethyl hydroxyethyl cellulose.
EO  Ethylene oxide.
FT-IR  Fourier transform infrared spectroscopy.
MS  Molecular substitution (0-∞).
MVDA  Multivariate data analysis.
Mv  Viscosity average molecular mass.
Mw  Weight average molecular mass.
Mn  Number average molecular mass.

OPLS-DA  Orthogonal projection to latent structures with discriminant analysis (regression analysis).
PLS  Partial least squares (regression analysis).
PCA  Principal component analysis (regression analysis).
PD  Polydispersity (molecular weight distribution).
Q²  Validation of model, goodness of prediction.
R²  Validation of model, goodness of fit.
R10, R18  Cellulosic residue in 10% and 18% NaOH solution.

2D ¹H ¹³C  Two dimensional heteronuclear single quantum coherence nuclear magnetic resonance.

HSQC NMR
Table of Contents

Abstract .......................................................... iii
Sammanfattning (Abstract in Swedish) .............................. v
List of Papers .......................................................... vii
Presentation of results other than papers ......................... viii
Abbreviations ........................................................... ix

Introduction ................................................................ 1
Cellulose ..................................................................... 1
Cellulose derivatives .................................................... 4
Objectives ................................................................... 6
Processes ..................................................................... 7
Pulping process to dissolving pulp .................................. 7
Viscose process ........................................................... 9
EHEC process ........................................................... 13
The reactivity of cellulose ............................................... 15

Experimental ................................................................ 17
Materials ..................................................................... 17
Methods ...................................................................... 18
Choice of pulp analysis and the reason for it ..................... 18
Spectroscopic analyses ............................................... 20
Viscose dope and EHEC analyses .................................. 23
Multivariate data analysis ............................................. 25
   PCA (Principal Component Analysis) ........................ 25
   PLS (Partial Least Square) ...................................... 27

Summary and Discussion of Paper I-IV ......................... 29
Pulp characteristics ....................................................... 29
Pulp characterization by chemical and physical properties 29
Pulp characterization by spectroscopic properties (Paper II) 31
Influence of pulp characteristics on properties of cellulose derivatives 36
Influence of pulp characteristics on viscose dope properties (Paper I) 36
Influence of pulp characteristics on EHEC properties (Paper III) 38
Correlations between pulp analyses and spectroscopic methods (Paper II) 43
Important analyses from pulp to viscose dope (Paper IV) ........ 44

Conclusions and further investigations .......................... 46
Acknowledgements ..................................................... 49
References ................................................................... 50
Appendix – Viscose dope preparation .............................. 52
Introduction

Cellulose
Cellulose is the most common polymer surrounding us. It is found in cell walls of green plants and algae and can be produced by certain types of bacteria. The structure of the polysaccharide chains in cellulose in its morphological, supramolecular and molecular level is well described by Krässig (Krässig 1993), whereas much information on the composition of wood and the wood chemistry containing cellulose can be found in a recent book by Ek (Ek et al. 2009). Unless being used for direct burning, cellulose needs to be refined in order to become a consumer product. Either by a saw mill to planks or boards for the construction industry, or by mechanical and/or chemical pulping to paper- or dissolving grade pulp. Pulps that are primarily intended for the preparation of chemical derivatives of cellulose are often referred to as dissolving pulps or high alpha pulps. Depending on the refinement of those pulps, they can be categorized into pulps for regeneration or cellulose derivatives, each category representing its own demand on quality and reactivity towards the specific chemicals in question. The main characteristics of dissolving pulps contrary to paper pulps are a higher purity in cellulose with low content of hemicelluloses, lignin, extractives and ashes. In addition, they represent pulps with a uniform molecular weight distribution, a pre-determined viscosity, high brightness and a high reactivity towards specific chemicals.

For the production of dissolving pulp, different cellulose sources are being used. About 85% of the total volume uses wood-derived celluloses (Sixta 2006), originating from hardwood (beech, eucalyptus) or softwood (spruce, pine). The most distinct difference between these two wood types is the shape and length of the fibers of each category. The appearance of the fiber, both from its natural state in wood but also how the pulping process has affected the fiber is of outmost importance for the end-user of dissolving pulp. Fiber morphology such as fiber length, fiber length distribution, fiber shape and roughness are vital to the physical properties of many cellulose derivatives. As evident from microscopy images in Fig 1, the state of the fibers in dissolving pulps differs significantly depending on wood- and process type. While a softwood sulfite pulp (Fig 1a, pine and spruce) shows many deformities (twists, bends and compressed areas), yet relatively long fibers, a hardwood sulfite pulp (beech) in Fig 1b shows short and compressed fibers, but with visible vascular tracheids. The sulfate pulps on the other hand show less physical fiber damage compared to the sulfite process. Differences can be seen in the less deformities of the fiber, with long and less defect pine fibers and visible pore openings from a sulfate process in Fig 1c,
and long and non-damaged eucalyptus fibers with only a few fiber bends and breaks from the sulfate process in Fig 1d.

Fig 1. Dyed dissolving pulp samples investigated in this study analyzed by light microscopy, showing softwood a) and hardwood b) from sulfite processing and softwood c) and hardwood d) from the sulfate process.

About 15% of the remaining cellulose source used for dissolving pulp is originating from cotton linters. Here, the shortest fibers closely attached to the cotton seed are being used, giving pulps of the highest cellulose purity and fibers suitable for high viscosity end products. Besides differences in the fiber morphology, dissolving pulps differ also in chemical and physical properties, see Table 1. The amount and different types of hemicelluloses is the most significant chemical variation and have thus different impact on the processability to and quality of end products. Even though related both chemically and structurally closely to cellulose, hemicelluloses differ by the type and amount of monosaccharides. While cellulose is a non-branchend homopolymer, hemicelluloses vary in the degree of branching, have lower molecular masses and exist in amorphous condition only. The monosaccharides can be classified into following groups: Pentose units (xylose, arabinose), hexose units (glycose, mannose and galactose), units of hexuronic acid (glycuronic acid) and deoxy-hexoses (rhamnose and/or fucose), see Fig 2. The structure and composition is dependent on the wood
type used for the dissolving pulp. Hemicelluloses in softwoods have a higher proportion of mannose and galactose than hardwoods, while hardwoods have more xylose units and acetyl groups. Hence, softwood hemicelluloses consist of mainly glucomannan with some acetyl groups in mannose and a glucose mannose ratio of 1:3.5. They also contain short chain xylan, a polymer of xylose, without acetyl groups but substituted with glucuronic acid and arabinose. Hemicelluloses in hardwood consist only to a small extent of glucomannan with a ratio of glucose mannose of 1:1. Xylan is the dominating hemicelluloses with short branches of xylose and highly acetylated compared to softwoods.

Table 1. Typical chemical and physical dissolving pulp properties (Sixta 2006).

<table>
<thead>
<tr>
<th>Preferred Application</th>
<th>Viscose</th>
<th>Ether</th>
<th>Viscose</th>
<th>Acetate</th>
<th>Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Material</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooking Process</td>
<td>Sulfite</td>
<td>Sulfite</td>
<td>PHK</td>
<td>PHK</td>
<td>Linters</td>
</tr>
<tr>
<td>Brightness %</td>
<td>92.2</td>
<td>90.2</td>
<td>90.7</td>
<td>92.2</td>
<td>87.9</td>
</tr>
<tr>
<td>R₁₈ %</td>
<td>93.4</td>
<td>95.2</td>
<td>97.9</td>
<td>98.2</td>
<td>99.0</td>
</tr>
<tr>
<td>R₁₀ %</td>
<td>87.6</td>
<td>93.8</td>
<td>93.3</td>
<td>97.7</td>
<td>97.4</td>
</tr>
<tr>
<td>Xylan %</td>
<td>3.6</td>
<td>3.1</td>
<td>1.5</td>
<td>0.9</td>
<td>0.2</td>
</tr>
<tr>
<td>Carbonyl μmol g⁻¹</td>
<td>18.8</td>
<td>6.0</td>
<td>4.3</td>
<td>4.4</td>
<td>3.7</td>
</tr>
<tr>
<td>Carboxyl μmol g⁻¹</td>
<td>35.6</td>
<td>59.8</td>
<td>32.0</td>
<td>15.0</td>
<td>12.4</td>
</tr>
<tr>
<td>DPₜₗ (°)</td>
<td>1790</td>
<td>4750</td>
<td>1400</td>
<td>2100</td>
<td>1250</td>
</tr>
<tr>
<td>DPₐ (°)</td>
<td>277</td>
<td>450</td>
<td>460</td>
<td>650</td>
<td>700</td>
</tr>
<tr>
<td>PD</td>
<td>6.5</td>
<td>10.6</td>
<td>3.0</td>
<td>3.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>
Consequently, the physical and chemical properties of different dissolving pulps are many. Hence, dissolving pulps can not only be categorized by their origin of wood type or milling type, but also for their purpose of final application since the demand on quality can vary. In extreme cases, they are only suitable for a certain process or plant, meaning that a certain pulp can fit perfectly for one viscose producer, but is unsuitable for a different viscose producer that manufactures the same type of fiber.

**Cellulose derivatives**
The three major pathways of functionalizing cellulose to cellulose derivatives are the reaction types altering the three available hydroxyl groups of the glucose unit, mainly esterification and etherification. A schematic overview of possible products originating from dissolving pulps is given in Fig 3 with dissolving pulp volumes by end-use in Table 2. A slight increase of the volume of each end-use product is expected in 2012 due to an estimate of a total production volume of dissolving pulp of 4.2 MT/a (estimate Domsjö Fabriker AB).
Fig 3. Overview of some important products and processes originating from dissolving pulps.

Table 2. World production of dissolving pulp by end-use in 2003 (Sixta 2006).

<table>
<thead>
<tr>
<th>Cellulose Derivative</th>
<th>End-use</th>
<th>Mio T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regenerated fibers</td>
<td>Staple, filaments</td>
<td>2.20</td>
</tr>
<tr>
<td>Cellophane</td>
<td>Films, sponges, casings</td>
<td>0.10</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>Tow, filament, plastic</td>
<td>0.53</td>
</tr>
<tr>
<td>Cellulose ether</td>
<td>Non-ionic, ionic</td>
<td>0.47</td>
</tr>
<tr>
<td>MCC</td>
<td>Pharmaceutical, molding powder</td>
<td>0.09</td>
</tr>
<tr>
<td>Others</td>
<td>Nitrocellulose, papers</td>
<td>0.26</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>3.65</strong></td>
</tr>
</tbody>
</table>

Esters of cellulose with inorganic and organic acids were the first covalently modified cellulose derivatives on the market. The main derivatives counting to this group are cellulose nitrate, cellulose acetate and cellulose xanthogenate.
Objectives
The main objective for this project was a general investigation of the impact of chemical and physical properties in different dissolving pulps on the processability to and quality of cellulose derivatives, namely viscose dope and a cellulose ether such as EHEC. The study was extended to also include one paper pulp and one semi dissolving pulp to see how their properties affect the manufacturing of cellulose derivatives. An overview of the project and its objectives is given in Fig 4.

Fig 4. Overview of the project objectives. Sampling and analyses of pulps (1), viscose dope preparation and analyses of intermediates (2), viscose dope analyses (3) as well as EHEC preparation and analyses (4). Correlation of analytical results to pulps, viscose dope intermediates, viscose dope and EHEC.

The general objective can be structured into specific objectives:

- To set up a bench pilot unit with high reproducibility and repeatability for the preparation of viscose dope including suitable viscose dope analyses
- To analyze pulp samples, intermediates and final products for chemical and physical properties with conventional and non-conventional methods, and to find and explain correlations between product- and pulp properties
• To investigate to what extent paper grade pulps differ from
dissolving grade pulps with respect to processability and product
quality in the preparation of cellulose derivatives

• To find explanations for the weakness in some well-established
analytical methods for pulps and suggest alternative or
supplementary methods

• To establish multivariate models for the prediction of viscose
dope and EHEC qualities from pulp properties

• To find similarities and dissimilarities in processing behavior to
viscose dope or EHEC in for instance formation of gel particles

Processes

**Pulping process to dissolving pulp**
The two main processes for the production of dissolving pulps are the acid
sulfite process and the caustic pre-hydrolysis sulfate process (also called for
PHK process). Both processes and their possible variations in for example
pulping and bleaching are well described elsewhere (Sixta 2006, Rydholm
1965, Sjöström 1981). Hence, only a brief description of the cooking steps
and their impact on the cellulose will be mentioned here. The selectivity on
lignin and carbohydrates of the Kraft, acid sulfite and two-stage sulfite
pulping process is shown in Fig 5.

![Fig 5. Selectivity of lignin and carbohydrate dissolution during (1) Kraft, (2) acid sulfite and (3) two-stage sulfite pulping of softwood, according to Sjöström (Sjöström 1964).](image)
The Kraft process comprises an alkaline delignification process using sodium hydroxide (NaOH) and sodium sulfide (Na$_2$S) as active delignification chemicals. One of its main advantages is the possible processing of all wood types, while the sulfite process in most cases can not process pine. In general, a pre-hydrolysis stage is utilized to treat the cellulose before the actual Kraft pulping stage. Wood chips are steamed or cooked in water at 140-170ºC for 30-60 min, where acetyl and formyl groups are cleaved from the wood forming acetic and formic acid, thus lowering the pH to 3 to 4. The acids formed in this pre-hydrolysis step in turn promote an acid hydrolysis, depolymerizing wood components and reducing the wood mass by 5-20% depending on hydrolysis time and temperature (Woodings 2001). In the case of softwood up to half of the amount of hemicelluloses can dissolve during this step, while for hardwood also significant amounts of lignin can be removed. By prolonging the hydrolysis step, not only hemicelluloses will be depolymerized to achieve a higher purity in the final product, but also cellulose resulting in a lower overall yield of the process.

The cellulose molecules do not remain stable under these strong alkali conditions and Kraft pulping results thus in considerable carbohydrate losses. The degradation of carbohydrates in the alkali process during 200-400 min cooking time consists of mainly three reactions: peeling at the end of a carbohydrate chain or oxidative peeling randomly in the chain at temperatures over 80ºC and alkaline hydrolysis at temperatures over 140ºC (Sixta 2006). For the peeling reaction, the reduced end groups in the cellulose or hemicellulose chain can undergo a series of keto-enol-formations which will lead to the peel off of one end unit at the end of the chain as one glucoisosaccharinic acid (for cellulose or glucomannans) or as xyloisosaccharinic acid (for xylan). This peeling effect can continue as a new reduced end group is formed until the peeling reaction is finally interrupted because of the competing “stopping” reaction. Consequently, the yield of cellulose is reduced in Kraft pulping although to a much lower extent than for hemicelluloses, as hemicelluloses are degraded more rapidly due to their lower DP, branched chains and amorphous state. However, remaining hemicelluloses will become less branched in their structure, increasing the tendency for crystallization and tendency to associate to the cellulose molecules which in turn can increase the caustic resistance of hemicelluloses in the viscose process. Degradation of cellulose occurs mostly in the final phase of the cooking sequence and even though the DP is decreased, the total yield loss at higher temperatures is fairly small.

The acid sulfite process can vary by the use of different cations, pulping pH and cooking temperature. Depending on the wood, cooking times up to 10 hrs and 145 ºC are applied. The most usual process was initially the
calcium sulfite process (Ca(HSO₃)₂ and SO₂) which due to the regeneration of insoluble calcium sulfate was replaced by more soluble cations such as magnesium, sodium and ammonia. The acidity in the pulping sequence ranges from pH 1-2 in the conventional calcium process, up to pH 5 for the magnesium process, a wide pH range for the sodium process to even alkaline conditions in some rare cases. The sulfite process with two- or three-cooking stages was later introduced to alternate between different pH levels in order to improve the further removal of hemicellulose and lignin. The reaction time during the first stage is up to 2-6 hrs and 2-4 hrs at 140 ºC in the second stage. A major drawback for the sulfite process is the limited use of wood materials. Due to the presence of phenolic compounds in the lignin and a strong concentration of pinosylvine in pine, a lignin condensation at low pH or low concentrations of SO₂ can easily happen. This is why pine is usually not used for the sulfite pulping process. However, in the two- or multistage sulfite process, pH is varied in the different stages allowing for the use of pine. Here, the first step consists of a neutral to slightly acid cooking solution, during which lignin is sulfonated but remains in solid phase where the most reactive groups are protected by sulfonation, and can thus not condensate with pinosylvine in the second stage to form a “black cook”. The acid conditions on the sulfite process promote the cleavage of glycosidic bonds in the cellulose and hemicelluloses. Due to their lower DP and amorphous state, as well as weaker glucosidic bonds, hemicelluloses are depolymerized easier than cellulose and will be dissolved in the cooking liquor as monosugars. Even though the cellulose chains are also affected by acid hydrolysis during the entire cooking process, the major depolymerization of cellulose does not occur until the end of the delignification.

**Viscose process**
The manufacturing of viscose fibers or films (Woodings 2001, Götze 1967, Rath 1972) was discovered by the dissolution of cellulose with caustic and carbon disulfide by Cross, Bevan and Beadle in 1891. An overview of a typical staple fiber production is given in Fig. 6 and can consist of the following steps.
Fig 6. A schematic overview of a typical viscose staple fiber process at the former Svenska Rayon AB in Vålberg, Sweden. Process steps circled in red are included in the bench pilot unit utilized in this project for viscose dope evaluation.

The cellulose pulps are supplied in bale or role and added to a steeping tank where caustic lye reacts with cellulose to form alkali cellulose (Fig 7 (A)). Most of the hemicelluloses and some low weight celluloses will be dissolved by the caustic lye. In addition, the cellulose is “activated” by the swelling of the fibers and the breakage of intra- and intermolecular hydrogen bonds in and between the cellulose chains by caustic lye. Hence, the formed alkali cellulose is more accessible for the introduced chemicals later in the process. Excess of caustic lye and dissolved carbohydrates are removed in the following press, after which the shredding of the pressed and activated cellulose occurs. Shredding of the cellulose cake increases the reactive surface of the alkali cellulose and hence increases the accessibility of chemicals. The next step is aging of the alkali cellulose to a pre-determined intrinsic viscosity by oxidative hydrolysis. This reduction in the degree of polymerization of the cellulose chains is a required step to allow for a better processability of the viscose dope in the later process. In the xanthation step, alkali cellulose is allowed to react with carbon disulfide (CS₂) to form cellulose xanthate (Fig 7 (B)). Side reactions in this step is the formation of bye products such as sodium trithiocarbonate (Na₂CS₃), giving the typical yellow to orange color in the xanthate and viscose dope.
Fig 7. Main reactions involved in the formation of cellulose xanthate. The mercerization or steeping step to form alkali cellulose (A) and the xanthation step, the reaction of alkali cellulose to cellulose xanthate (B).

After the cellulose xanthate crumbs have been formed, water and caustic soda (NaOH(aq)) is added under vigorous agitation for dissolution of the cellulose and the formation of the viscose dope in the dissolving step. For textile viscose, the composition of the dope is about 10w% cellulose and 5w% caustic. The following ripening of the dope fulfills two important steps: i) to remove entrapped air bubbles in the viscose dope which could harm the spinning and quality of the viscose fiber and ii) to facilitate the redistribution of the xanthate groups from the kinetically favored C2 and C3 positions to the more thermodynamically stable C6 position. Even though DS is reduced during this step by a release of some xanthate groups to form bi-products, the rearrangement of the groups to C6 will form a more homogeneous derivatization of the cellulose chain. After filtration, the viscose dope is transported to the spinning step where the dope is pressed through spinnerets (see Fig 8) into an acid spin bath consisting of mainly sulfuric acid (H₂SO₄), sodium sulfate (Na₂SO₄) and zinc sulfate (ZnSO₄), releasing both carbon disulfide and hydrogen sulfide.
Fig 8. Typical shape of a spinneret with 0.5 inch diameter containing 26 holes for 26 filaments in the spun yarn.

The composition of the spin bath determines the rate of cellulose regeneration and hence the stretchability and alignment of the cellulose chain in the viscose fiber (see Table 3). The regenerated cellulose fiber is stretched and prepared for baling in the following stretching, washing and cutting steps.

Table 3. Important parameters for the spinning process and their influence on cellulose regeneration and viscose fiber tenacity (personal reference).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Function</th>
<th>Increase</th>
<th>Decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid (H₂SO₄)</td>
<td>Neutralization of lye, regeneration</td>
<td>Faster regeneration</td>
<td>Slower regeneration</td>
</tr>
<tr>
<td>Salt (ZnSO₄, Na₂SO₄)</td>
<td>Buffer, delay of acid dissociation and regeneration</td>
<td>Slower regeneration</td>
<td>Faster regeneration</td>
</tr>
<tr>
<td>Modifier</td>
<td>Delay of regeneration</td>
<td>Slower regeneration</td>
<td>Faster regeneration</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td>Faster regeneration</td>
<td>Slower regeneration</td>
</tr>
<tr>
<td>Stretch ratio</td>
<td>Molecule chain orientation</td>
<td>Higher tenacity</td>
<td>Lower tenacity</td>
</tr>
<tr>
<td>DP</td>
<td></td>
<td>Higher tenacity</td>
<td>Lower tenacity</td>
</tr>
</tbody>
</table>
**EHEC process**

Descriptions of different processes to different cellulose ethers are in detail described elsewhere (Klemm 1998, Thielking and Schmidt 2006, Majewicz and Podlas 2000). A general overview of the process is shown in Fig. 9 where a possible process for the production of EHEC consists of shredding cotton linters or cellulose pulps in the cellulose grinding step and mixing the cellulose with NaOH(aq) and ethyl chloride (EC) in the reactor.

![Fig 9. Schematic overview of the EHEC process (provided by AkzoNobel Functional Chemicals AB). All steps except mixing are included in the pilot plant trials reported in this study.](image)

Ethylene oxide (EO) is added in temperatures below 100 °C. After the required reaction time for EO, the temperature is then increased above 100 °C for EC to react (Boström et al. 1992). By following these steps, alkali cellulose is allowed to first react by a hydroxyethylation with EO to a specific hydroxy-ethyl MS value, followed by an etherification with ethyl chloride at a higher temperature (Majewicz and Podlas 2000), see Fig 10. A possible structure of an EHEC molecule with its characterization of MS\textsubscript{EO} and DS\textsubscript{Et} is presented in Fig 11.
**Formation of alkali cellulose**

\[ \text{OH} \quad \text{H}_2\text{C} \quad \text{O} \quad \text{H} \quad + \text{NaOH} \quad \xrightarrow{=} \quad \text{OH} \quad \text{H}_2\text{C} \quad \text{O} \quad \text{Na}^+ \quad + \text{H}_2\text{O} \]

**Ethylene Oxide-(poly)-addition**

\[ \text{O} \quad \text{H} \quad \text{H}_2\text{C} \quad \text{O} \quad + \text{H}_2\text{C} \quad \text{O} \quad \xrightarrow{=} \quad \text{O} \quad \text{H} \quad \text{H}_2\text{C} \quad \text{O} \quad \text{H}_2\text{C} \quad \text{O} \quad \xrightarrow{=} \quad \text{O} \quad \text{H} \quad \text{H}_2\text{C} \quad \text{O} \quad \text{H}_2\text{C} \quad \text{O} \quad \]

**Substitution with Ethyl Chloride**

\[ \text{O} \quad \text{H} \quad \text{H}_2\text{C} \quad \text{O} \quad + \text{H}_2\text{C} \quad \text{Cl} \quad \xrightarrow{=} \quad \text{O} \quad \text{H} \quad \text{H}_2\text{C} \quad \text{O} \quad \text{H}_2\text{C} \quad \text{Cl} \quad \xrightarrow{=} \quad \text{O} \quad \text{H} \quad \text{H}_2\text{C} \quad \text{O} \quad \text{H}_2\text{C} \quad \text{Cl} \quad \]

Fig 10. Reaction steps involved in the formation of first alkali cellulose, the EO addition to HEC and the final substitution of EC to form EHEC.

![Diagram](image1.png)

**Fig 11. Possible structure of the EHEC molecule, where the blue colored, circular parts represent hydroxyethyl groups and the brown shaded, oval parts represent ethyl groups. In this example, MS\_{EO} = (2+3+0+2+3)/5 = 2 and DS_{Et} = (0+2+0+1+1)/5 = 0.8.**
For the reaction of EO only catalytic amounts of caustic soda are required in contrast to the reaction of EC, where a stoichiometric amount of caustic soda is consumed according to the Williamson ether synthesis. After neutralization, the raw product passes the after-treatment steps such as washing, dewatering, drying and grinding. Side products generated are mainly different types of glycols and NaCl.

The reactivity of cellulose
Reactivity is defined as the degree of ability for the three hydroxyl groups to react with chemicals, an ability different for different processes and depending on accessibility, the relative ease by which the hydroxyl groups can be reached by the reactants (Sjöström 1981).

However, the term “reactivity” of dissolving pulps is often used in many different ways, sometimes even equivalent with the term “accessibility”, “yield” or “processability”. For the pulp producer and pulp customer, reactivity is sometimes referred to as the yield of the added substituents and thus including even the purity of the cellulose, since also hemicelluloses react with the chemicals. For the viscose producer, reactivity can also mean a shorter time of pre-aging, which in turn is dependent of DP, cellulose density and degree of mercerization. Reactivity is also mentioned in connection with gel formation, DS, MS or as the formation of by-products. Reactivity is thus applied in many different measurements of explaining the ability of cellulose to react to cellulose derivatives. A clear definition of the terms involved is thus missing. In this study, reactivity is used as a chemical term, which is the degree of ability of reactants to access to the free hydroxyl groups in a cellulose chain and to form covalent bonds. Accessibility, on the other hand, is the physical ability of reactants to reach those hydroxyl groups, to overcome steric hinders. In this way, reactivity could be expressed as a function of accessibility, temperature and concentration of chemicals. Accessibility, however, could be described as a function of degree of swelling, available active surface, pore size and absorption. Analogously, analyses for reactivity are methods involving chemical interactions such as Fock (Fock 1959) or DSxanthate while analyses for accessibility are methods involving sorptive actions, such as Hg-porosimetry, caustic absorption or water retention. In practice, the term reactivity would therefore be misused when comparing different pulps for interaction with ionic liquids or NMMO for dissolving purpose, whereas it is correctly used for the manufacturing of ethers and esters where cellulose reacts with the reactants by covalent bonding.

An often required pre-treatment for the manufacturing of cellulose derivatives is the activation of the cellulose. The purpose of this activation is
to increase the reactivity and accessibility of the hydroxyl groups in cellulose towards the reactants involved by for example reducing the amount of intra- and intermolecular hydrogen bonds for more available hydroxyl groups. This can be done by either chemical or mechanical treatment of the pulp. These treatments can open or widen the inner pore structures, disrupt fibrillar aggregation and increase accessible surface or reduce crystallinity to increase available hydroxyl groups. It is necessary to distinguish between activation methods that

i) open and widen existing capillaries, voids and pores,

ii) split up fibrillar aggregates and

iii) disrupt crystallinity and/or change the crystal modification.

Activation methods used are either degradative treatments (hydrolysis, oxidation or radiation), mechanical treatments (steam explosion, wet and dry milling) or swelling treatments (mercerization, DMSO, DMF) or combinations thereof (Krässig 1993). In recent years, enzymatic treatment of cellulose has been introduced as a novel path of increasing reactivity (Köpcke 2010). Most important in an industrial scale is the swelling of cellulose with inorganic acids or metal hydroxide solutions, in particular the use of NaOH solution. Here, the impact on the physical and chemical properties of the cellulose depends on the concentration, temperature, time and choice of metal ion used within the alkalization step. It is suggested that the order of swelling capacity is increased by the order LiOH>NaOH>KOH>RbOH>CsOH (Heuser and Bartunek, 1925). However, for many of the activation methods mentioned, a reduction of the degree of polymerization is a side effect and needs to be considered in further processing steps.

Some positive and negative influences on affinity of reactants towards the cellulose chain are listed by Krässig (Krässig 1993):

- The restrictive swelling effect of the lamellar layer structure
- The effect of fibrillar aggregations, or “hornification”
+ The effect of capillaries, voids and fibrillar interstices
+ The effect of exposed, easy accessible internal fibrillar structure by means of a less ordered, amorphous form of cellulose chains
+ The availability of reactive hydroxyl groups not occupied by intra- and intermolecular hydrogen bonding.

Reactivity is also influenced by the presence of cellulose II, a more stable allomorph with more intermolecular hydrogen bonds and a more dense packing of the cellulose chains due to its antiparallel positioned molecules compared to native cellulose I with parallel arrangement. Since cellulose II is already formed by the treatment of cellulose with NaOH concentrations between 6-7w% at ambient temperature (Sixta 2006), the influence of this
allomorph on reactivity is of special interest in refining process steps involving caustic, such as bleaching, pulping or mercerization.

**Experimental**

**Materials**
Since the main objective of this project was to understand the properties in pulps from different wood species, type of pulping process and viscosity, three conditioning factors had to be established (see Table 4). Producers providing sulfate samples manufactured the cellulose pulps by either a pre-hydrolysis Kraft process (highest cellulose purity), a modified Kraft (medium cellulose purity) or a Kraft process (lowest cellulose purity). The selection of the pulps was done according to a $2^3$ factorial design (Eriksson et al. 2008) without center points. For each pulp type, a sample from the highest and lowest commercially available viscosity was chosen. However, a low viscosity sample from producer A was not available. Also, an intermediate viscosity sample from producer B was included. Even though producers B and C’s samples were similar regarding design factors, samples from both manufacturers were still included to evaluate differences between them. This resulted in a set of ten pulp samples of which seven originated from the experimental design, see Table 4 and Table 5. In Paper III, pulp from producer A could not be included in the pilot production of EHEC, since the samples were delivered in small sheets and could thus not be fed into the pilot grinder.

Table 4. Conditioning factors for raw material selection.

<table>
<thead>
<tr>
<th>Wood type</th>
<th>Process type</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-) SF, hardwood</td>
<td>(-) Sulfite</td>
<td>(-) Low</td>
</tr>
<tr>
<td>(+) LF, softwood</td>
<td>(+) Sulfate</td>
<td>(+) High</td>
</tr>
</tbody>
</table>

Table 5. Design matrix of investigated samples. Process type showing the cation used in acid sulfite process, prehydrolysis Kraft (PHK), modified Kraft (MK) or Kraft (K) in sulfate process.

<table>
<thead>
<tr>
<th>Producer</th>
<th>Designation in Paper I-IV</th>
<th>Wood type</th>
<th>Viscosity</th>
<th>Process type</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, SF sulfite</td>
<td>1 or 1A</td>
<td>- (Beech)</td>
<td>+</td>
<td>- (Mg)</td>
</tr>
<tr>
<td>B, LF sulfite</td>
<td>2 or 2B</td>
<td>+ (Spruce, Pine)</td>
<td>-</td>
<td>- (Na)</td>
</tr>
<tr>
<td>B, LF sulfite</td>
<td>3 or 3B</td>
<td>+ (Spruce, Pine)</td>
<td>-</td>
<td>- (Na)</td>
</tr>
<tr>
<td>C, LF sulfite</td>
<td>4 or 5C</td>
<td>+ (Spruce)</td>
<td>-</td>
<td>- (Ca)</td>
</tr>
<tr>
<td>B, LF sulfite</td>
<td>5 or 4B</td>
<td>+ (Spruce, Pine)</td>
<td>+</td>
<td>- (Na)</td>
</tr>
<tr>
<td>C, LF sulfite</td>
<td>6 or 6C</td>
<td>+ (Spruce)</td>
<td>+</td>
<td>- (Ca)</td>
</tr>
<tr>
<td>D, SF sulfite</td>
<td>7 or 7D</td>
<td>- (Eucalyptus)</td>
<td>-</td>
<td>+ (PHK)</td>
</tr>
<tr>
<td>E, LF sulfite</td>
<td>8 or 9E</td>
<td>+ (Pine)</td>
<td>-</td>
<td>+ (MK)</td>
</tr>
<tr>
<td>D, SF sulfite</td>
<td>9 or 8D</td>
<td>- (Eucalyptus)</td>
<td>+</td>
<td>+ (PHK)</td>
</tr>
<tr>
<td>F, LF sulfite</td>
<td>10 or 10F</td>
<td>+ (Pine, Loblolly)</td>
<td>+</td>
<td>+ (K)</td>
</tr>
</tbody>
</table>
Methods

Choice of pulp analysis and the reason for it
An extensive set of analysis tools had to be applied on all pulps to find relevant correlations between pulp properties and final product qualities. Analyses for both wet chemical properties and physical properties performed in this study are listed in Table 6. Traditionally, the most important parameters describing a cellulose pulp for the purpose of derivatization are analyses describing the polymeric properties and pulp purity. Mercury porosimetry and nitrogen adsorption (the BET method) are two methods widely used to characterize the pore structure and accessible surface area of pulp samples (pore area, pore diameter and permeability). In this study, mercury porosimetry gave results with good repeatability while BET did not, an observation which was explained by a lower degree of affinity of nitrogen to the pulps than mercury. Porosimetry studies are important since the specific surface of pulps gives an indication of the accessibility of the cellulose and hence a key factor for monitoring the swelling properties and chemical reactivity of the pulps (Sixta 2006). While pores and voids are generated during the pulping process due to the removal of lignin and hemicelluloses and the mechanical treatment (Maloney and Paulapuro 1999), the water that fills those pores is evaporated during drying, bringing the pores to collapse and in worst case leading to “hornification”. Even though limited to pore diameters of 3 nm-14 µm (Sing et al. 1985) and mostly restricted to pores available at the surface of the pulps, mercury porosimetry is yet a good indicator for a pulps behavior in viscose dope or EHEC manufacturing.

One very common property describing the chain length and weight is intrinsic viscosity, where cellulose is dissolved in cupri-ethylene-diamine solution and efflux times noted through a capillary-tube viscometer. A more specific method is the determination of molecular weight distribution by size exclusion chromatography (SEC), yielding the weight average molecular weight (Mw), number average molecular weight (Mn), viscosity average molecular weight (Mv) and z average molecular weight (Mz). For any molecular weight distribution obtained by SEC, the different and most used average molecular weights always come in the following order:

\[
M_n \leq M_v \leq M_w \leq M_z \leq M_{z+1}
\]

Different other techniques often measure only one of them, where for example Mv is obtained from viscosimetry, Mn by osmometry, Mw by light scattering and Mz by sedimentation. The polydispersity (PD) of a pulp sample is defined as the ratio of Mw and Mn, giving an indication on the broadness of the molecular weight distribution curve. Due to the vast
amount of different methods available, comparing the average molecular weights in pulps or any other polymeric material for that matter, the definition of which method used and what average molecular weight referring to is of outmost importance!

Pulp purity can be determined by different analyses. The most common method is the alkali resistance based on determination of the residue (R18, R10) or solubility (S18, S10) of the pulps at ambient temperature. The solubility is determined by titration of the dissolved organic matter in the filtrate oxidized by potassium dichromate. The 18% caustic lye dissolves the shorter hemicellulose fraction whereas 10% caustic lye dissolves both hemicelluloses and short chain cellulosics. In general, the S10 fraction contains those polymers with less than 25000 g/mol (log Mw=4.4) while the S18 fraction contains polymers less than 8000 g/mol (log Mw=3.9), see Fig 12. To achieve a viscose fiber with the highest strength, the viscose producer should hence utilize a pulp with high R10, low S10-S18 and low S18 (Hinck et al. 1985).

A closely related and widely used analytical method in viscose manufacturing is the determination of the α-, β-, and γ-cellulose in the pulp. Here, α-cellulose is the fraction of the pulps not soluble in caustic lye containing cellulose chains with a high DP, β-cellulose the carbohydrates with DP <200 soluble in caustic lye but regenerated in acetic acid. γ-cellulose is defined as the fraction of a pulp with carbohydrates having a DP generally below 10 which can be regenerated with alcohols from the β-cellulose filtrate.
For a viscose producer, the content of β-cellulose in a pulp should be kept at its minimum since it will regenerate in the acid spin bath and plugging the spinneret or weakening the fibers.

A more exact analysis of purity is the determination of carbohydrates by ion chromatography, detecting the hemicelluloses in the pulps as monosugars. Different hemicelluloses in the pulp have different impact on the quality and processability to cellulose derivatives. As some of them get dissolved and extracted with the mercerization lye, the remaining hemicelluloses will lead to irregularities in product quality since hemicelluloses tend to consume chemical substituents in the process before they actually can react with the cellulose polymers, reducing the availability of chemicals for the cellulose derivatization. Hence, a qualitative and quantitative determination of hemicelluloses in pulps is crucial for the manufacturer of cellulose derivatives.

Extractives are compounds in pulps soluble in different organic solvents such as for example chloroform, hexane and acetone. In this project, acetone was used as organic solvent. Extractives consist of waxes, fats, resins and non-volatile hydrocarbons. Even though the amount of extractives in dissolving pulps should be kept to a minimum, some of the compounds have shown to have a positive impact in the production of viscose. This can be compared to addition of man-made surfactants to the pulps to increase reactivity.

The reactivity or accessibility of a pulp to viscose chemicals can be measured by the Fock method (Fock 1959, Köpcke 2010). It is by no means a method determining the pulps behavior in a viscose plant, but rather a comparison of different cellulose pulps with each other in their tendency to react with caustic and carbon disulfide. The pulps sample is mixed and stirred with 9 w% caustic lye and carbon disulfide (CS₂). The formed cellulose xanthate solution is collected and regenerated in sulfuric acid (H₂SO₄), after which the regenerated cellulose is oxidized by dichromate sulfuric acid (K₂Cr₂O₇, H₂SO₄). Potassium iodide (KI) is added, the iodide ions are oxidized (I⁻) to iod (I₂) by the remaining dichromate ions (Cr₂O₇²⁻) and reduced again by titration with sodium thiosulfate (Na₂S₂O₃). The recorded volume of sodium thiosulfate determines the amount of regenerated cellulose.

Spectroscopic analyses
Many of the wet chemical analyses discussed above are time consuming and costly. It is therefore of great interest to utilize faster and simpler means to replace or complement some of the chemical analyses by spectroscopic methods provided that the same accuracy can be obtained. Several spectroscopic methods can be utilized, of which Fourier transform infrared
(FT-IR) and nuclear magnetic resonance (NMR) are two successful methods for pulp characterization used in Paper II. NMR provides the possibility to analyse cellulose in both liquid and solid state. The difference in spectra obtained between the two states is that in solid state the free molecular motions are limited giving rise to broader resonance signals, limited resolution and large linewiths.

*FT-IR spectroscopy* has today widespread use in the pulp and paper industry, ranging from off-line applications in the laboratory (characterization of lignocellulosic material, extractives, contaminants, additives) to on-line process control. An FT-IR spectrometer simultaneously collects spectral data in a wide spectral range (in Paper II the mid infrared region 400-4000 cm$^{-1}$ was used) and applies a mathematical algorithm, Fourier transform, to convert the raw data into the actual spectrum. Apart from the industrial applications, basic scientific analyses also apply FT-IR frequently to study lignocellulosic materials, for instance with the purpose to explain structural features of cellulose. A typical spectrum for a cellulose pulps is shown in Fig 13, excluding the spectral range over 1600 cm$^{-1}$ to avoid contributions from remaining atmospheric intrusion and moisture.

Fig 13. FT-IR spectrum of sample 8, showing the spectral range 400 – 1600 cm$^{-1}$, prior to baseline correction and normalization to illustrate quality. Some of the important descriptive bands are highlighted for clarity (Paper II).

FT-IR is a versatile, non-destructive technique that can probe various compositional changes in pulp samples with minimum to no sample
destruction, especially in attenuated total reflectance (ATR) mode where the sample is placed on a reflecting crystal without pre-treatment. Even though ATR FT-IR has only a small depth of penetration of the IR beam into the sample, it is when coupled with multivariate analysis a powerful tool to analyze differences among various classes of pulp samples.

Solid-state cross polarization/magic angle spinning nuclear magnetic resonance ($^{13}$C CP/MAS NMR) spectroscopy has been used extensively for cellulose and pulp analysis and is particularly useful for the analysis of cellulose morphology, such as crystallinity or the presence of Cellulose I and II (Krässig 1993). Here, proton-carbon cross polarization increases the sensitivity of the experiment while the magic angle spinning technique, where the solid sample is rotated at high speed around an angle of 55° with respect to the magnetic field, provides higher resolutions resulting in well resolved $^{13}$C-spectra. To further enhance the spectral resolution, samples were moisturized with 50% water before packing into a 4 mm rotor. For a typical solid-state NMR cellulose spectra, see Fig 14.

![Figure 14](image)

**Fig 14.** A typical solid state $^{13}$C NMR spectrum from a dissolving pulp sample. C$_1$-C$_6$ represent the different carbons in the glucose unit. Peaks from crystalline and amorphous cellulose are denoted cr and am, respectively (Paper II).

For liquid-state NMR, the newly developed method for analysis of wood material in solution using two-dimensional heteronuclear single quantum coherence nuclear magnetic resonance ($^1$H-$^{13}$C HSQC NMR) was employed. This method is used frequently in NMR spectroscopy of organic molecules, particularly in the protein analyses. The obtained spectrum is two-
dimensional with one axis for $^1$H and the other axis for a different nucleus, in Paper II the $^{13}$C nucleus (for an example, see Fig 15).

Fig 15. A typical 2D $^1$H-$^{13}$C HSQC spectrum as an example from pulp sample 3 (Paper II).

The spectrum contains a peak for each unique proton attached to the nucleus being considered. Thus, if the chemical shift of a specific proton is known, the chemical shift of the coupled nucleus can be determined, and vice versa. This method has been shown to yield a detailed chemical fingerprint of all major secondary cell wall components where both the chemical structure and the relative amounts of cellulose, hemicelluloses and lignin can be determined. Paper II is to our knowledge the first publication where 2D HSQC spectra and multivariate analysis were combined to study the composition of dissolving pulps. The sample preparation is more tedious than for solid-state NMR as it includes activation of the finely ground pulp samples by dimethyl sulfoxide (DMSO) and N-methylimidazole (NMI), acetylation with acetic anhydride and dissolution in deuterated chloroform (CDCl$_3$).

**Viscose dope and EHEC analyses**
Analyses performed on viscose dope and on intermediates to viscose dope, such as cellulose content, ball fall time, filterability and gamma number reported in Paper I and Paper IV, are in detail described in the appendix.

The most important properties of EHEC are the characteristics of this cellulose ether in a water solution.
The cloud point is defined as the temperature at which an increase of turbidity in the EHEC solution can be detected. As the temperature is slowly increased, the EO side chains change to a water insoluble conformity and turn gradually into more hydrophobic side chains. Consequently, the polymers are water soluble at low temperatures while at high temperatures the sample separates into one polymer-rich phase and one water-rich phase leading to increased turbidity.

Table 6. Properties for pulps, viscose dope and viscose intermediates as well as EHEC analyzed in this investigation.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pulp analyses</strong></td>
<td></td>
</tr>
<tr>
<td>α-, β- and γ-cellulose</td>
<td>%</td>
</tr>
<tr>
<td>Caustic absorption amount</td>
<td>g/cm²</td>
</tr>
<tr>
<td>Caustic absorption rate</td>
<td>cm/min</td>
</tr>
<tr>
<td>Hemicelluloses⁴</td>
<td>g/kg</td>
</tr>
<tr>
<td>Pore area</td>
<td>m²/g</td>
</tr>
<tr>
<td>Pore diameter</td>
<td>mm</td>
</tr>
<tr>
<td>Permeability</td>
<td>mdarcy</td>
</tr>
<tr>
<td>Polydispersity: ratio of Mw/Mn</td>
<td></td>
</tr>
<tr>
<td>Mw, Mn, Mv: weight,number and viscosity average molecular weight</td>
<td>g/mole</td>
</tr>
<tr>
<td>R18, R10: alkali resistance in 18 and 10% caustic lye</td>
<td>%</td>
</tr>
<tr>
<td>Extractives: acetone soluble compounds</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Viscosity</td>
<td>ml/g</td>
</tr>
<tr>
<td>Uronic acids⁵</td>
<td>g/kg</td>
</tr>
<tr>
<td><strong>Viscose dope analyses</strong></td>
<td></td>
</tr>
<tr>
<td>Fock reactivity: residual cellulose or cellulose yield</td>
<td>%</td>
</tr>
<tr>
<td>Kr: filterability of viscose dope corrected by viscosity</td>
<td>%</td>
</tr>
<tr>
<td>γ-number: degree of substitution of cellulose in viscose</td>
<td>%</td>
</tr>
<tr>
<td><strong>EHEC analyses</strong></td>
<td></td>
</tr>
<tr>
<td>Cloud point</td>
<td>°C</td>
</tr>
<tr>
<td>Clarity</td>
<td>%</td>
</tr>
<tr>
<td>Gel</td>
<td>%</td>
</tr>
<tr>
<td>Viscosity EHEC</td>
<td>cP</td>
</tr>
<tr>
<td>DSₘEt</td>
<td></td>
</tr>
<tr>
<td>M₂BO</td>
<td>mole/AGU</td>
</tr>
</tbody>
</table>

⁴ total amount of hemicelluloses, expressed as sum of xylose and mannose unless specified otherwise; ⁵ sum of hexenuronic acid, glucuronic acid, galacturonic acid and methylglucuronic acid in pulps with low EHEC clarity or high hemicellulose content.

The degree of substitution for ethyl chloride (DSₘEt) and the molecular substitution for ethylene oxide (M₂BO) are two important characteristics determining the property of the EHEC molecule, in particular the hydrophobicity. While in general DS denotes the average number of
cellulosic hydroxyl groups per cellulose molecule involved in the reaction, \( \text{DS}_{\text{Et}} \) denotes the average number of ethyl chloride molecules added per cellulose unit. \( \text{MS}_{\text{EO}} \) denotes the average amount of ethylene oxide molecules added per cellulose unit. The higher the amount of reacted ethyl chloride, and thus the higher \( \text{DS}_{\text{Et}} \) of the EHEC product, the less hydrophilic the EHEC molecule becomes, lowering the cloud point in water solution. 

\textit{Clarity} is a measure of colorization and/or un-dissolved particles in the product, determined by the transmittance of the EHEC solution at 550 nm. 

\textit{Gel particles} can be caused by un-dissolved cellulose chains where cellulose chains are tightly pressed together by either a high degree of crystallinity or by hornification. Being that tight, no substituents can penetrate this section to react with cellulose and hence leads to non-dissolved parts in EHEC solution. Determination of gel particles was done by a photo analyses.

\textbf{Multivariate data analysis} 
In the presented study a high amount of spectral data and analyses data was collected, leading to a complex data set with large data tables that would be difficult to overview without special methods. The conventional approach of linear regression to find correlations and dependences of variables \( x \) to responses \( y \) only resulted in an abundance of \( x \) vs. \( y \) plots, impossible to find any relationship between observations (samples) or variables. Instead, multivariate projection methods such as PCA, PLS and OPLS were found to be useful tools to get an overview of the data. These methods are used in order to detect outliers or deviating trends in the set of observations of the different cellulose pulps and analysis performed on them. These methods were also applied to find groups or similarities/dissimilarities among observations and to determine the important variables influencing the behavior of observations. A more detailed description of multivariate data analyses than the one given below can be found in literature (Eriksson et al. 2006, Eriksson et al. 2008, Jackson 1991) and the application of these methods in the field of dissolving pulp and paper in other papers (Christoffersson et al. 1999, Christoffersson et al. 2001, Wallbacks et al. 1991). For data calculation and visualization of the models, the software SIMCA-P+11 (Soft Independent Modeling of Class Analogy) supplied by Umetrics AB, Umeå, Sweden was used for Papers I-III.

\textit{PCA (Principal Component Analysis)} 
This tool provides for a general overview of the collected multivariate data in an X-matrix. The variables in the X-matrix do not need to be independend and can contain errors. PCA introduces new variables, also called latent variables or principal components, to describe the variation within the investigated system. The latent variables consist of \textit{scores} \( t_i \) describing the samples and \textit{loadings} \( p_i \) describing the original variables. The number of
latent variables is always fewer than the number of original variables but still describing a large amount of the variation in the data set. An additional term is the residual $E$. This is the variation in the data not explained by the model. The first principal component represents a vector, describing the largest variation of the observations in the data set. The second principal component describes the remaining largest variation of the observation. Additional principal components can be added containing an increasing amount of noise. For example, in a three-dimensional case, two latent components span a window in the original variable space $x_1$, $x_2$ and $x_3$ (see Fig 16). By projecting all points down to a plane, the former three dimensional space has been reduced to a two dimensional one. Here, the relationship between the samples can be seen in a score plot ($t_1/t_2$) and the relationship between original variables in a loading plot ($p_1/p_2$). The score plot reveals (dis-)similarities between samples while the loading plot reveals (dis-)similarities between the original variables. If the loading and score plots are combined one can see which variables are the causes for the position of each sample. Or, simplified, which variables have more or less impact on a sample. This combination is done by the use of a loadings bi plot in Paper I and Paper III.

Fig 16. Two principal components forming a “window” on which each observation (grey dot) is projected to (black dot). The distance from each projection point on each PC to the origin represents the score value ($t_i$) of the observation. The cosine angle between the original variable to each PC ($p_i$) describes the variables importance to each PC. (Figure kindly provided by Umetrics AB, www.umetrics.com).
In addition, extreme outliers or unexpected behaviour can be detected in the score plot and explained by the loading plot.

Before applying PCA, one should consider scaling of all variables in X. This is particularly of importance when variables have different units or ranges. Scaling is normally applied by mean centering all data $(x_i - \bar{x})$ and normalizing it by dividing the mean centered data by the standard deviation so that all original variables get the same weight despite having different units. This approach is called unit variance. However, caution should be applied to data where all variables have the same unit, which is the case for spectroscopic data since the risk of losing important information and misinterpretation is imminent. Here, only centering is to prefer. In Paper I-III, all collected variables were centered and scaled to unit variance.

**PLS (Partial Least Square)**

This multivariate tool is used to find relationships between blocks of variables in X and responses in Y. With the difference of applying a second data space in Y besides the one in X, the geometric interpretation and scaling requirements corresponds to the ones explained for PCA. While in PCA correlation between the variables in X is to be found only, PLS helps to find correlations between the original variables in X and the selected responses in Y. Analogous to the PCA approach, a *loading plot* and *weight plot* can be defined, where the loading plot consists of all original variables $x$ and response $y$ and their relationship towards each other. The weight plot presents both variables and responses in one, explaining which $x$-variables are important for $Y$. In order to determine the importance, a line is drawn through the response point $y$ and the origin of the plot. All original variables can then be perpendicularly projected down to the line and the importance of the variable in question is determined by the distance from the plot origin. The further away from the origin the projection is the more influence the variable has on the response. $X$-variables which are situated on the same side as the response relative to origo influence the response positively while variables being on the opposite side relative to origo influence the response negatively. This can be visualized in SIMCA by the regression coefficient plot for each variable and its standard deviation.

In PLS, a model is validated by the “goodness of prediction”, $Q^2$. Introducing more and more components, $Q^2$ reaches a certain optimum and decreases. This can be explained by the inclusion of more and more noise to the model. The point where $Q^2$ reaches its maximum corresponds to the optimal amount of components. A more geometrical approach to determine the optimal amount of components is the size of each components “eigenvalue”. If the length of the vector gets to small, meaning that mostly noise is described, the eigenvalue falls below 2 and the vector in question can be discarded. The validation in PLS is done by excluding data in X and Y row
wise, generating a model with the remaining data and predicting the excluded values by the model. $Q^2 Y$ is calculated and the amount of significant components determined by the maximum size of $Q^2$ (see Fig 17). This approach for model validation was used in Paper II and Paper III. Another approach for validation is response permutation, where the response data in $Y$ is scrambled and for each scrambled set a PLS model is fitted, cross validation is applied and $Q^2 Y$ is calculated. This approach for model validation was used in Paper I.

![Fig 17. Determination of significant components $A_{\text{sig}}$ where $Q^2= \max$ by cross validation. Figure kindly provided by Umetrics AB (www.umetrics.com).](image)

OPLS (orthogonal projections to latent structures) is a refined method of PLS regression and separates two different types of variations, systematic variations where the original variables in the data set influence the responses and systematic variation by noise. It is widely used method in multivariate calculations of spectroscopic data, where undesirable systematic variation is present as noise. OPLS extracts and removes these undesired systematic contributions and was used in Paper II for the treatment of FT-IR and NMR data.

To evaluate the importance of each variable on the responses chosen in PLS/OPLS, a VIP (Variable Importance for the Projection) plot and a coefficient plots can be used. In the coefficient plots, the PLS models are being re-calculated to a regression model represented by the equation $y = k \times x + m$. Thus, the plot visualizes all involved variables $k$, sorted by their importance, and their impact on the chosen response $y$. Variables with a confidence interval (error bars) not passing the x-axis are considered
significant and influence a high value of the response positively if greater than zero and negatively if below zero.

Summary and Discussion of Paper I-IV

All investigated cellulose pulps were chosen according to availability and fulfilling the design conditions for the three selection criteria process type, wood type and intrinsic viscosity. The pulps were analyzed to their chemical and physical properties as well as by FT-IR, liquid and solid state NMR and the outcome correlated to the original design criteria. The same set of pulps was then used to produce viscose dope and EHEC to find important correlations between the properties in the cellulose pulps and the viscose dope and EHEC properties. In addition, samples were taken of the different intermediates from pulp to viscose dope to follow the chemical changes of the different pulps in the process. This provided for a unique chance to follow the different steps to viscose dope and investigate the relevance of important analytical methods to final viscose dope and in extension to the quality of viscose fiber. A similar evaluation of different process steps in the production to EHEC was unfortunately not possible since the reactor is a closed system during the whole reaction. Correlation and evaluation of the collected data was done by multivariate data analyses (Paper I-II) or by linear regression (Paper IV).

It has to be pointed out that the validity of the obtained results in the presented models are limited to pulps that fulfill the design criterias for the pulps investigated. In the evaluation of multivariate data results, it is also important to note that all data points within the model are needed and that variables should not be analyzed one by one. Hence, single variables should not be selected on their own to explain certain results even if a variable shows a good fit.

Pulp characteristics

Pulp characterization by chemical and physical properties

For a better understanding of the pulps selected and to see which parameters in the pulps are more or less pronounced for each selection criteria, a PCA model was calculated. In Fig 18 a combined loading and score plot is presented, showing the characteristics of each pulp to the investigated variables. The model consisted of two significant latent components and ten samples, giving the models accuracy by the goodness of fit in x, R²x= 48% in the first component and R²x= 24% in the second component.
It is evident that sulfite pulps (both long- and short fiber) are separated from the sulfate pulps in both components due to a strong influence by variables such as the amount of extractives, polydispersity, caustic absorption rate and pore area. Sulfate short fiber and sulfate long fiber are highly separated from each other even though only one of them represents a paper grade pulp. The selected samples of sulfate long fiber are characterized by, for example, big pore diameter, high hemicellulose content and low amount of extractives. They can also be described by high permeability and low pore areas. A possible reason for the big pore diameter can be found in the use of pine in the sulfate process, having fibers and cells with generally more and wider pore openings compared to spruce or softwood (Daniel 2009). Sulfate short fiber samples on the other hand can be explained by high alpha cellulose content, low beta and gamma cellulose content and
hence higher values of R18 and R10. This separation also coincide with the origin of sulfate pulping type, separating the pre-hydrolysis Kraft (sample 7 and 9) from the modified and standard Kraft process (sample 8 and 10) indicating that the modified and standard Kraft type are resulting in similar pulp properties and in pulps of higher hemicelluloses content.

**Pulp characterization by spectroscopic properties (Paper II)**

For the characterization of the pulps, both FT-IR, solid-state and liquid-state NMR were used. The spectral data obtained were treated by means of multivariate data analysis to correlate differences in the dissolving pulp samples to the choice of raw material (softwood, SW or hardwood, HW), process type (sulfate or sulfite) and pulp viscosity.

FT-IR spectroscopy has today widespread use in the pulp and paper industry, ranging from off-line applications in the laboratory (characterization of lignocellulosic material, extractives, contaminants, additives) to on-line process control. Apart from the industrial applications, basic scientific analyses also apply FT-IR frequently to study lignocellulosic materials, for instance with the purpose to explain structural features of cellulose.

A PCA model calculated on all spectra, base line adjusted and normalized, did not indicate any outliers and all spectra were hence included in the following calculations using OPLS-DA (discriminant analysis) as regression method. No correlation between differences in the spectra and differences in viscosity could be found, but high predictability ($Q^2 = 0.93$) could be found where the samples were classified according to process type (see Fig 19a and Fig 19c) showing a clear separation of samples originating from the different process types sulfate and sulfite. The main reason for this separation in the first component are positive peaks (sulfate) in the corresponding loadings at 810, 870, 1030, 1050 and ca. 1150 cm$^{-1}$ and negative peaks (sulfite) at 509, 667, 740, 1310 and 1450 cm$^{-1}$.
Fig 19. OPLS-DA models, obtained from FT-IR data where samples were classified according to either process type or wood type. a) Score plot with samples classified to the sulfate or sulfite process. b) Score plot where samples were classified to wood type, hardwood (HW) and softwood (SW). c) Loading plot for the predictive component in a). d) Loading plot for the predictive component in b) (Paper II).

High correlation ($Q^2 = 0.76$) and a good separation between samples could also be reported for OPLS-DA on wood type (see Fig 19b and Fig 19d). Here, separation into two classes could be explained by peaks more intense in softwood including those at 438, 500-545, 810, 875-1050, 1084, 1308 and 1360 cm$^{-1}$ and those for hardwood at 630, 690-760, 1150 and 1200-1280 cm$^{-1}$. Besides the band at 810 and 870 cm$^{-1}$ being assigned to glucomannan and 1200 to 1280 cm$^{-1}$ to possible vibrations in –COO groups in xylan and in acetyl groups in glucomannan, no bands could directly be assigned to specific vibrations from cellulose or hemicelluloses other than the type of hemicelluloses represented in the different pulps contribute to the class separation in both cases. These two OPLS studies could not pinpoint a single property of the pulps that explain why the models distinguish between pulps from sulfite and sulfate, as well as hardwood and softwood. In the two present cases, the hemicelluloses composition appears to be of significance.
Solid-state $^{13}$C NMR spectroscopy has been used extensively for cellulose and pulp analysis and is particularly useful for the analysis of cellulose crystallinity. A PCA study on the pulps revealed no outliers but shows that the major source of variation comes from the different producers rather than from raw material or process type (see Fig 20a and Fig 20b). The PCA plot in Fig 20a shows the two first principal components describing 71.8% of the variation in the data (60.8% in the first component and 11% in the second). Along the first component, samples 9 and 10 differ the most from the mean and have more of the negative peaks and less of the positive peaks in the corresponding loading plot (Fig 20b).

![Fig 20. PCA model plots from solid state $^{13}$C NMR data. a) t₁-t₂ score plot from a mean centered PCA model. b) Loading plot of the first component, p₁.

The positive peaks with the largest contributions to the model are the cellulose peaks with ppm values of 105.0 (C₁), 88.8 (C₄cr), 74.9 (C₂₃₅) and 72.4 (C₂₃₅). The negative peaks in the same loading plot are located at 101.75, 81.2, 78.8, 77.2, 63.6, 60.3 and 59.5 ppm and are contributions from different hemicelluloses. Hence, samples 9E and 10F have higher hemicelluloses content than the others. The main contribution to the separation in the second component can be explained by the high positive peaks in the corresponding loading plot (not shown) at 105.8, 88.8, 75.0, 71.5 and 65.1 ppm and the high negative peaks positioned at 107.7, 84.0, 76.9, 73.0 and 70.1 ppm. While the peak at 71.5 ppm might be from a hemicellulose, the chemical shifts of the remaining positive peaks are in good agreement with literature values found for the crystalline cellulose structures of cellulose I. The peak at 84.0 ppm may be assigned to C₄ in amorphous cellulose, and the chemical shift of the peak at 107.7 ppm is in good agreement with published values for cellulose II. Hence, sample 1A has
a lower degree of crystallinity and a higher amount of cellulose II than the other dissolving pulp samples. OPLS-DA on solid state NMR with wood type or viscosity as discriminants did not give any model. A model could be obtained with process type as discriminant ($Q^2 = 0.60$), where the main reason for a good model predictability is the composition of hemicelluloses. However, since there is a large amount of overlap in the regions where hemicelluloses signals appear in the solid-state $^{13}$C NMR spectra, differences in hemicelluloses composition are more suitably studied with 2D-NMR.

The newly developed method for analysis of wood material in solution using two-dimensional (2D) $^1$H-$^{13}$C HSQC NMR was also employed. This method has been shown to yield a detailed chemical fingerprint of all major secondary cell wall components where both the chemical structure and the relative amounts of cellulose, hemicelluloses and lignin can be determined. A PCA on all spectra showed no outliers and high goodness of fit in two components, $R^2 = 84.6\%$, see Fig 21, and coincides with the PCA results from solid state $^{13}$C NMR analysis where sample origin, with respect to the producer, is the main discriminant.

Fig 21. PCA model calculated from 2D NMR data. a) Score plot from PCA model. b) Loading plot for the first component. $G =$ glucose, $X =$ xylose and $M =$ mannose. Positive loadings are shown in red and negative in black (Paper II).

Positive peaks (in red) are assigned to glucose units and appear at $^1$H/$^{13}$C ppm values of 3.59/72.6 (G5), 3.76/75.9 (G4), 4.12/61.7 (G6), 4.43/61.9 (G6), 4.46/100.2 (G1), 4.85/71.5 (G2) and 5.13/72.4 (G3). Negative peaks (in black) at 3.35/62.1 (X5), 3.82/74.3 (X4) 3.96/62.1 (X5), 4.52/99.8 (X1), 4.78/70.4 (X2), 5.08/71.4 (X3), 5.39/68.2 (M2), 4.24/62.4 and 4.36/62.4 ppm (M6) are assigned to either xylose or mannose residues. Interpretation
of the variation along the first component, $t_1$, shows that samples with positive values along $t_1$ have higher cellulose contents at the expense of hemicelluloses compared to, for example, sample 10. An OPLS-DA on wood type ($Q^2 = 0.40$, see Fig 22b and Fig 22d) showed a separation of softwood in the first component due to strong positive peaks in the loading plot, mainly peaks from mannose, namely M2 (5.38/68.4), M1(7.72/97.3), M4 (3.94/72.6) and M6 (4.24 and 4.36/62.4).

Fig 22. OPLS-DA models, calculated from 2D NMR data, with sample classification according to either process type or wood type. Positive peaks are colored red and negative peaks are colored black, and only loadings with p-values above 0.5 are plotted in c) and d). a) Score plot where samples were classified according to process type. b) Score plot where samples were classified according to wood type. c) Loading plot for the predictive component in a). d) Loading plot for the predictive component in b) (Paper II).
It confirmed the fact that softwood has more glucomannan than hardwood and that this higher level of mannose remains in the refined pulp.

An interesting result was revealed by the OPLS-DA model on process type ($Q^2=0.64$, see Fig 22a and Fig 22c). The most important peaks are the negative peaks from the reducing end of cellulose, $C_{\text{red}}$. These are located at 5.69/91.31 and 6.28/88.6 ppm. Since observations from the sulfite process are negative in $t_1$, these samples have a relatively large proportion of reducing ends of cellulose. The positive peaks in red at 4.53/80.3, 4.96/76.8, and 5.01/80.7 ppm originating from hemicelluloses have not been assigned and are only visible in the spectra from samples 9 and 10, both being the only samples where arabinose and galactose were detected by chemical analysis. However, since the positive peaks do not contribute as much to the model as the peaks originating from the reducing ends in cellulose, it can be concluded that the major contribution to the model is the high amount of reducing ends in sulfite pulps. It was found earlier that a high value of reducing end groups (high copper number) corresponds well with a high amount of low molecular weight polysaccharides (Sixta et al. 2004). The spectra thus show that sulfite samples have a higher degree of reducing ends and hence a higher proportion of short cellulose chains compared to the sulphate pulps. These spectroscopic findings can also be seen in the distribution plots of the original pulps (not included), where all sulfite pulps have a hump at low molecular weights and is also in agreement with results from wet chemical analysis with sulfite pulps were found to have a higher fraction of low molecular weight cellulose and a higher level of reducing end groups (Sixta 2000).

**Influence of pulp characteristics on properties of cellulose derivatives**

**Influence of pulp characteristics on viscose dope properties (Paper I)**

For the production of viscose dope, several methods are available for the determination of pulp reactivity or to see the influence on pulp characteristics on the quality of viscose dope. In this study, pulp reactivity is defined as filter clogging value of the viscose dope ($K_r$) and yield of regenerated cellulose determined by the Fock method. The collected data of all investigated pulps, as mentioned in the previous chapters, were treated by the multivariate regression method PLS with $K_r$ and Fock reactivity as response. To investigate the impact of cellulose properties on Fock reactivity, a PLS model with Fock reactivity as response was established consisting of three latent variables with a cross validation of $Q^2=0.72$. The loading bi plot of the model with two latent variables is shown in Fig 23a and a VIP plot
(variable importance for the projection plot) is shown in Fig 23b. The VIP plot represents all variables sorted in order of importance to explain the chosen response Fock reactivity. Variables are considered to be important with a calculated VIP value above 1.0 and a confidence interval not passing the x-axis; or unimportant if assigned a value below 0.5.

![Fig 23. a) Loading bi plot with two components for the PLS model with Fock reactivity as response (♦) and b) the model’s VIP plot showing all variables having an impact on Fock reactivity, sorted by their importance (Paper I).](image)

As shown in Fig 23b, Fock reactivity can be explained, in order of importance, by low values of caustic absorption rate, pore diameter, filter clogging value and permeability as well as a high value of total pore area. In earlier reports investigating sulfite pulps only (Christoffersson et al. 2002), the amount of extractives, R18 or intrinsic viscosity were found to have a significant influence on Fock reactivity. This is interestingly not the case in the presented model where pulps with different origin were included.

A similar PLS model was generated with Kr as response (Q²= 0.92, see Fig 24a).
Fig 24. Loading bi plot with two components for the PLS model with filter clogging value Kr as response (♦) and b) the model's VIP plot showing all variables having an impact on Kr, sorted by their importance (Paper I).

The VIP plot of the PLS model (Fig 24b) shows that variables with most impact on a good filterability (low Kr) are low permeability, small pore diameter, low hemicelluloses content, low absorption rates as well as low beta cellulose content. Low filter clogging value is also promoted by high values for variables such as pore area and R18.

Consequently, the most pronounced variables explaining good filterability of the viscose dope and high Fock reactivity of the pulps are the ones describing the morphology and the microfibrillar properties of the cellulose structure. A smaller pore size in the cellulose pulp is related to slower penetration of chemicals (caustic) into the fibers due to a higher pressure drop, resulting in an overall better effect of the chemicals to react with the hydroxyl groups of the cellulose chains. This effect of slower penetration is perhaps in conjunction with an increased removal of air from the pulp voids, resulting in a better filterability of the viscose dope since entrapped air pockets will result in pieces of unreacted cellulose. Many small pore diameters in contrast to fewer big ones lead to a higher total pore area of the cellulose, hence providing a bigger active surface. Both a lower number of entrapped air pockets and an increased active surface area can result in a better reaction of the chemicals with the cellulose. This would result in fewer unreacted cellulose particles (gels) to give better filterability, and higher Fock reactivity (that is, reactivity towards viscose chemicals) due to a higher degree of dissolved cellulose.

Influence of pulp characteristics on EHEC properties (Paper III)
To find correlations between properties in pulps to EHEC, an EHEC quality without methyl groups or hydrophobic modifications was produced from each of the pulps in a pilot plant reactor, after which the final product was
analyzed. The impact of pulp properties and their origin (wood type, process type and pulp viscosity) of the pulps on EHEC quality parameters was studied by means of multivariate data analysis. EHEC quality parameters were cloud point, clarity in solution, presence of gel particles as well as the average degree of substitution ($DS_{Et}$) and average molecular weight substitution ($MS_{EO}$). A separate PLS analysis over all data with respect to each EHEC quality parameter was performed.

A PLS regression with “gel” and “clarity” as response gave models with two latent variables and accumulated cross validation values of $Q^2 = 0.84$ and $Q^2 = 0.89$ respective (see Fig 25a and Fig 25b), where variables affecting each of the two responses are shown in order of importance in the model’s coefficient plot, see Fig 26a and Fig 26b.

![Fig 25. Loadings bi plot with two components of the PLS model with a) gel formation and b) clarity as response (Paper III).](image-url)
Fig 26. Coefficient plots with two components of the PLS model with a) gel formation and b) clarity as response (Paper III).

High gel concentration in EHEC can be explained by pulp properties such as a high intrinsic viscosity and high molecular weight molecules (Mw) in combination with a high concentration of hemicelluloses, also expressed as xylose. In addition, a high absorption rate and absorption amount of caustic will contribute to a higher gel formation in the product. An interpretation of the achieved results can be that hemicelluloses are more reactive towards EC and EO due to their branched and amorphous structure, local deficits of chemicals originally intended for the cellulose chains can occur. The longer the cellulose chains leading to a high Mw, the more important the need for evenly distributed substituents for dissolution of the cellulose. Given a high content of hemicelluloses, more chemicals intended for the cellulose chains are consumed by hemicelluloses instead, leaving spots of non-substituted, non-dissolvable glucose strains particularly in the long cellulose chains, thus resulting in a higher degree of gel formation. The importance of caustic absorption rate was discussed earlier in respect to gel formation for the viscose dope preparation (Paper I). Correspondingly, a pulp with the property of absorbing caustic soda too fast could lead to entrapment of air pockets within the fibrous pulp structure, preventing the formation of mercerized cellulose, a required intermediate step for further ethylation and
ethoxylolation, leading to unreacted parts of the cellulose and the formation of gel particles.

No relevant or useful model could be obtained for the quality parameter clarity due to that producer D had the highest impact on the model for its extreme low value of clarity. Without including producer D, no model could hence be achieved. The dominating impact of producer D to the model could be explained by the extremely low bulk density of the pulp observed after grinding and the presence of chromophores. A low bulk density after grinding can be explained by bigger cellulose particles, resulting in a lower available surface area in comparison to the other samples and hence lower available surface and lower efficiency for the caustic-cellulose interaction, leading to more unreacted fibrous parts and low clarity. The contribution of uronic acids to discoloration and hence low clarity was excluded for producer D as only small traces were found in the samples. However, a possible explanation could be found in the presence of carboxyl groups, or xylan with high molecular weight. PHK pulps bleached by an elementary chlorine free process, such as producer D, are reported to have a higher amount of carboxyl groups (Sixta 2006) promoting heat induced yellowing (Buchert et al. 1997). In addition, the typical higher molecular weight of the PHK xylan causes more intense yellowing than the xylans in acid sulfite pulps in acetate solution, where the color is assumed to be caused by undissolved particles in the range of 1 µm (Sixta 2006). The latter observation could be a possible reason even in caustic processes.

For all samples, a model calculated for cloud temperature could confirm earlier reports (Nilsson et al. 1995, Thuresson et al. 1995) on the correlation of a high MS\textsubscript{EO} and a low DS\textsubscript{Et} to a high cloud point and vice versa (model 1, one component with Q\textsuperscript{2} = 0.85). The influence of cellulose properties on MS\textsubscript{EO} and DS\textsubscript{Et}, and hence on the cloud point, was investigated by a different model (model 2) with two components and Q\textsuperscript{2} = 0.35. Despite a fairly low Q\textsuperscript{2} for model 2, the results are still presented as they give a good indication of the importance of some pulp properties on MS\textsubscript{EO} and DS\textsubscript{Et}. Here, a high pore area, a high PD and a low caustic absorption rate is required for achieving a high MS\textsubscript{EO}. For a high DS\textsubscript{Et}, the most significant cellulose parameter is a high hemicellulose and xylose content and a low R18. These parameters could be confirmed when establishing a model with cellulose properties directly correlating to cloud point (model 3, two components with Q\textsuperscript{2} = 0.84). Fig 27 demonstrates the investigated impact of MS\textsubscript{EO}/DS\textsubscript{Et} on cloud temperature, the impact of cellulose properties to MS\textsubscript{EO}/DS\textsubscript{Et} and the impact of cellulose properties to cloud temperature directly.
Fig 27. Schematic overview of the presented models showing all significant variables correlating to cloud point.

A detailed description on the impact of the different cellulose properties on \( \text{MS}_{\text{EO}} \) and \( \text{DS}_{\text{Et}} \) is given in Paper III. Notable though is the effect of a low caustic absorption rate on the reaction of EO resulting in a high \( \text{MS}_{\text{EO}} \). This effect of absorption rate could also be seen in viscose dope preparation (Paper I), where a low caustic absorption rate promoted a high filterability of the viscose dope and a high Fock reactivity. Similar reasoning on the effect of this parameter on EO reaction was taken as to the preparation of viscose dope.

EHEC viscosity can be predicted by a model with two components and \( Q^2 = 0.81 \), with both a high pulp viscosity and a high molecular weight (Mw) contributing to a high EHEC viscosity.

To find possible similarities between analyses from the viscose dope and EHEC manufacturing, Fock reactivity and filterability Kr reported in Paper I were correlated to all EHEC quality parameters. It was found that only one EHEC parameter could be predicted by viscose dope properties with acceptable reliability: A high cloud point could be predicted by a high Fock reactivity (\( Q^2 = 0.78 \)) and a low Kr (\( Q^2 = 0.78 \)). A possible explanation could be that cloud point is highly dependent on the amount of reacted EO and EC. Since both Fock reactivity and Kr measure the pulps accessibility for chemicals to react, both analytical methods give thus an indication on how accessible the pulp is for EO and EC to react to determine cloud point.
Correlations between pulp analyses and spectroscopic methods (Paper II)

Spectral data collected for investigation in Paper II were used to correlate FT-IR, solid state NMR and liquid state NMR to common pulp analysis reported in Paper I and Paper III. The purpose was to see if the models achieved could help to predict some of the traditional complex and time consuming analytical methods used for pulp characterization. The results of the findings are summarized in Table 7.

Table 7. Overview of the correlations of all spectra to pulp origin and some analytical methods, and the predictive ability $Q^2$ of the models (Paper II).

<table>
<thead>
<tr>
<th>Method</th>
<th>Discriminant</th>
<th>$Q^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT-IR</td>
<td>Process type</td>
<td>0.94</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Wood type</td>
<td>0.76</td>
</tr>
<tr>
<td>FT-IR</td>
<td>PD</td>
<td>0.64</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Mn</td>
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</tr>
<tr>
<td>FT-IR</td>
<td>Pore area</td>
<td>0.77</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Permeability</td>
<td>0.40</td>
</tr>
<tr>
<td>FT-IR</td>
<td>R10/R18</td>
<td>0.46/0.63</td>
</tr>
<tr>
<td>SS-NMR</td>
<td>Process type</td>
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</tr>
<tr>
<td>SS-NMR</td>
<td>Mn</td>
<td>0.95</td>
</tr>
<tr>
<td>SS-NMR</td>
<td>R10/R18</td>
<td>0.67/0.68</td>
</tr>
<tr>
<td>SS-NMR</td>
<td>Pore area</td>
<td>0.64</td>
</tr>
<tr>
<td>SS-NMR</td>
<td>Permeability</td>
<td>0.48</td>
</tr>
<tr>
<td>2D-NMR</td>
<td>Process type</td>
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</tr>
<tr>
<td>2D-NMR</td>
<td>Wood type</td>
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</tr>
<tr>
<td>2D-NMR</td>
<td>R10/R18</td>
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<td>2D-NMR</td>
<td>Mw</td>
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<td>2D-NMR</td>
<td>Pore area</td>
<td>0.73</td>
</tr>
<tr>
<td>2D-NMR</td>
<td>Permeability</td>
<td>0.48</td>
</tr>
</tbody>
</table>

For all models originating from FT-IR spectra, the amount of hemicelluloses was the most important variable. Solid-state $\text{^{13}C}$ NMR could predict R10 and R18, where the amount of hemicelluloses was the most important variable. For the prediction of Mn, cellulose crystallinity is highly significant, where a high Mn value corresponds to a high crystallinity.

2D-NMR could not predict Mn, which is obvious since Mn was shown to correlate to cellulose crystallinity that cannot be detected in solution. For the
prediction of R10/R18, hemicelluloses and the content of reducing end
groups are most important. Permeability and pore area models confirm
results from solid-state NMR, that the amount and nature of hemicelluloses
is the most contributing factor for the prediction of those properties. The
good model for Mw was shown to correlate with high viscosity in the pulp.
Hence, a higher value of Mw corresponds to a higher viscosity. The
correlation between Mn with crystallinity and Mw with viscosity was highly
interesting. The difference between Mn and Mw is a measure of the each
sample’s monodispersity. The closer the two values become, the more
monodisperse the cellulose chains become, resulting in more chains with
similar DP values. It is assumed that cellulose with a larger fraction of
uniform long chains tend to form more crystalline regions (perhaps by a
“zipper” crystallization process) if the crystallization is not terminated by
shorter chain molecules. Since Mn is the more varying descriptor in
molecular weight distribution among the samples, it is thus the most
significant variable in determining crystallinity. Both Mn and Mw did not
correlate to intrinsic viscosity, neither in the achieved models nor in a
correlation between Mv (as a function of intrinsic viscosity) and Mw/Mn.
This is a very interesting result, since both Mn and Mw in viscose dope are
described as important parameters for the strength in final viscose fiber, but
only intrinsic viscosity is measured in industrial applications.

The presented methods have shown to also be useful in the prediction of
the degree of reducing end groups and the xylose:mannose ratio among a set
of samples, two important pulp properties in the production of cellulose

Important analyses from pulp to viscose dope (Paper IV)
One way to determine the accessibility of a pulp is the rate of oxidative
degradation during the pre-aging step in the viscose dope manufacturing,
that is the speed of which the cellulose polymers depolymerize to a set
viscosity. The rate of degradation for each pulp was determined and it was
found that pulps with low amount of hemicelluloses, low viscosity and hight
pore area tend to show high rates of degradation. As previously shown in
Paper II on pulps, intrinsic viscosity on pre-aged pulps did not correlate to
Mn, Mz or Mw. Deviations and variations from the intrinsic viscosity
measurements to molecular weight analyses by SEC show clearly the need
for a total molecular weight analysis by molecular weight distribution of pre-
aged samples prior to xanthation.

High levels of hemicelluloses in viscose dope have a strength reducing
effect in the viscose fiber or disturbing the spinning process (Götze 1967).
That is why the viscose producer often requires pulps with high R18 and high
content of α-cellulose. However, carbohydrate analysis of pre-aged pulps
showed different levels of hemicellulose reduction independent of starting
R18 values in the pulps, a result explained by the existence of caustic resistant hemicelluloses in particular PHK pulps. This indicates that in some cases even cheaper pulps with higher viscosity and hemicelluloses content can still be reduced to the same amount in the viscose dope under same process conditions. This resistance to caustic extraction is fatal as it is effecting R18 values and the pulps purity numbers derived therefrom. These hemicelluloses can mistakenly be included in R18 results, indicating higher cellulose purity than there actually is in the pulp sample. It could be shown that even though the content of hemicelluloses in some pulps is remarkable lower than others in the raw material, the total amount of hemicelluloses in general and the xylose content in particular in the pre-aged cellulose of these pulps had not been extracted to the same extent as for the pulps with high initial hemicelluloses. Hence, the results obtained suggest the following statements: i) some hemicelluloses, and in particular xylose in PHK pulps, are resistant to caustic extraction and can follow the viscose stream all the way to fiber spinning, ii) the original composition in the pulps do not reflect the composition in the pulps after pre-aging and iii) R18/S18 is not a sufficient quality parameter in pulps to determine pulp behavior in the viscose process but is rather a process yield indicator.

The study of molecular weight distribution in viscose dope is essential, since an optimal pulp candidate for a strong viscose fiber is a pulp that results in a viscose dope showing a uniform, monodisperse distribution curve with a small fraction of molecular weights below 20,000 g/mole, a weight representing the β- and γ-celluloses (Rath 1972, Staudinger et al. 1937). The results on molecular weight distribution from pulp to viscose dope in Paper IV indicate that some pulps show a greater reduction of PD and of the low-molecular-weight fraction, compared with others. To some extent, the reduction of PD and Mw goes hand in hand with the reduction of cellulose and hemicelluloses after treatment with caustic lye, but this was not applicable to all pulps and is explained by the cooking and bleaching process for each pulp, keeping the morphological structure of the pulp fibers more or less rigid and preventing the formation of celluloses of lower weight during mercerization and aging.

Hence, it is of extreme importance to not only investigate the raw material, but also to follow the carbohydrate composition and molecular weight distribution all the way to viscose dope to ensure lowest contents of β- and γ-celluloses as well as a uniform molecular weight distribution during all process steps as all pulps react differently to the process steps in viscose dope manufacturing.
Conclusions and further investigations

This thesis describes research on cellulose pulps, their physical and chemical properties and the impact of those properties on the processability and product quality in the manufacturing of viscose dope and cellulose ether.

The pulp samples were chosen according to their origin, produced by different pulping processes and from different wood types with different intrinsic viscosities, and were analyzed with both chemical and spectroscopic methods. The analytical results were investigated by multivariate data analysis. It could be shown that pulps belong to certain groups, not only by their origin (process and wood type) but also by their analytical properties. Furthermore, the models obtained constitute a predictive system for future sample characterization of unknown pulps within the design parameters. By utilizing the achieved models, only a few of the involved analytical methods are sufficient to predict other analytical properties and to classify the new unknown pulp to the originating pulping process and wood type.

Many of the analytical methods used today in pulp characterization are both time consuming and costly. Spectroscopic methods, with the development of faster and more reliable instruments and with simplified sample preparation, could predict and to some extent replace many of these costly analytical methods. This thesis shows that spectroscopic methods such as FT-IR and NMR could be a future alternative for the prediction of pulp properties determined today by wet chemical analysis. Models with high predictive ability were presented, that showed correlation between spectroscopic data and some important analytical methods and pulp origin.

For the purpose of investigating the impact of the pulp characteristics on the intermediates to viscose dope and the final quality of the viscose dope, a bench pilot unit with suitable viscose analyses was erected. Investigations in this study on the intermediate steps to viscose dope stressed the importance of in particular molecular weight distribution and carbohydrate analyses in each individual step to select an optimal pulp for best properties in dope (high filterability, high $\gamma$-number and low ball fall time) and fiber qualities (high tenacity and high fatigue). In other words, common analytical methods such as caustic extraction or intrinsic viscosity on pulps could be shown to be insufficient for the determination of pulp behavior in the viscose process and to predict dope or fiber quality. Moreover, models generated by multivariate data analysis could well predict filterability $K_r$ and Fock reactivity by the pulp properties. Interestingly, for both responses physical pulp properties such as caustic absorption rate, pore area and pore diameter as well as
permeability were dominating in the prediction. Only for the prediction of filterability, also the amount of hemicelluloses and R18 had an important influence.

The ether ethyl hydroxyethyl cellulose was produced in a pilot plant from the same cellulose pulps as for the viscose dope studies, and was analyzed for cloud point, clarity in solution, presence of gel particles as well as the average degree of substitution (DS$_{Et}$) and average molecular weight substitution (MS$_{EO}$). The pulp properties were correlated to the EHEC quality responses by means of multivariate data analysis, and the models obtained showed a high predictability for gel but not for clarity. For the formation of gel particles in EHEC solutions, the most contributing pulp parameters were found to be intrinsic viscosity, the weight average molecular weight, the amount of hemicelluloses and caustic absorption rate. In addition, important predictive models could be presented for cloud point by MS$_{EO}$ and DS$_{Et}$, were the former is predicted by pulp properties such as pore area, polydispersity and caustic absorption rate and the latter is predicted by R18, amount of hemicelluloses and xylose content. Furthermore, a direct prediction to cloud point from pulp parameters could be presented. The two parameters Fock reactivity and filter clogging value, which are specific parameters for the viscose process, also correlated with one EHEC quality, namely cloud point.

The formation of gel particles is a common problem in viscose dope and EHEC manufacturing. The investigations in this study revealed that the gel formation in viscose dope, measured by filterability Kr, and the gel formation in EHEC, has only one common cellulose property correlating to both responses, namely caustic absorption rate. The explanation for this can possibly be found in the difference of analytical methods in determining gel content and the different process conditions.

In conclusion, the presented models can be utilized to predict the investigated final product qualities when considering the use of a new pulp. After analysis of the new pulp with the analytical methods used in this study, and application of its models, costly and time consuming pilot or full scale trials can thus be reduced. It has to be pointed out though that the achieved models and predictions in this study are only applicable for pulps that are related to the investigated pulps in process type and wood type, and that all data points within the model are needed for the prediction of one property. Single variables should not be selected on their own to explain certain results even if a variable shows a good fit.
The striving for the manufacturing of cellulose pulps with improved qualities with distinct properties for each specific cellulose derivative will have to continue. The presented study constitutes for another contribution to a better understanding of pulp properties and their impact on the refinement of pulps to cellulose derivatives. However, much is left to be done. More pulp samples from different producers or from different pulping processes such as for example the Organosolv process (Sixta 2006) could be added to the range of pulps. Additional pulp analyses, for example the measurements of cellulose crystallinity with Raman, IR or X-ray or with a method for the determination of fibrilar hornification of cellulose, could be included in future studies and would hence increase the sample set of the models to better predict the quality of cellulose derivatives. More analyses on viscose dope, such as the chemocolloidal maturity (Hottenroth index, Götze 1967) or a combined degree of substitution with molecular weight distribution could reveal more correlations between pulp and viscose properties. With the establishment of a bench pilot plant for spinning viscose fibers, a direct correlation from pulp to fiber properties, such as tenacity and fatigue, is a necessity.
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References


Appendix – Viscose dope preparation

Workflow for viscose dope preparation and description of pilot facility. An excerpt of the manual written for this project.

1. Introduction
Due to the variety of qualities and unknown de-polymerization time of each sample, the aging time of each sample has to be determined prior to a continuation to xanthation, see Fig 1.

![Workflow of viscose process](image)

Fig 1. Work flow of viscose process

Viscose production

2.1 Preparation

Tear sheets of dissolving cellulose into smaller pieces of approximately 1cm². Make sure that the sheet is also torn along its length to get one fresh, new surface. Dry the flakes in an oven with air circulation of 105 °C. Prepare
a solution of 18w% NaOH by dissolving 540 g of NaOH in 2460 g water. Start the heating of the water bath for both the mercerisation vessels and the press by setting the temperature to 40ºC. Start also the heating of the water bath for the mill to the same set point. Set the water temperature for the ageing bath to 50ºC. Depolymerisation of the cellulose chains will take place as soon as the cellulose is mixed with caustic in presence of oxygen. Since no nitrogen will be used in any step, depolymerisation starts already before the aging step. Thus, the time for each step has to be recorded for recording the total depolymerisation time. **Note: Ageing time is measured and reported from the time of pressing, including both pressing, shredding and ageing bath.** This eliminates the factor of variation in time for shredding and pressing with different employees. Store the rubber plugs used for xanthation in a closed glass containment with some ml of CS\(_2\) to saturate the rubber material with the chemical. A saturated plug will ensure that all amount of CS\(_2\) added during the xanthation step will entirely being used for the reaction with cellulose. Start the heater of the water bath for xanthation to 30ºC. Start the cooling cycle for the dissolving unit and set to 5ºC.

### 2.2 Mercerisation

Fill the steel vessels at the mercerisation station with 800 g of 18w% caustic. Weigh 20 g of dried cellulose flakes (approx. 21.5 g original flakes) and insert into the tempered caustic solution. Close the plastic lid. After 5 min of agitation, change rotation of the motor a few times to avoid lumping of fibres. Total agitation time is 20 min. According to [Treiber], the mercerisation process is less depending on reaction time than concentration of NaOH. Tests in Karlstad have shown that a reaction time of 20-30 min is sufficient.

⇒ 6.1 Sample preparation after mercerisation
3 Pressing

Place one filter cloth in the bottom of the press tube. Start applying vacuum on both tube and press bolt. Empty thoroughly the steel vessels from the mercerisation step into the press tube and place another filter cloth on top of the slurry. Place the bolt into the steel tube and apply a constant pressure of 70 kp/cm² during pressing. The press time depends on the desired press factor. After pressing, release the pressure and open the press bolt. Apply caution so no liquid is dripping back into the tube onto the sample. Remove the cake by using a pair of tweezers and determine its weight. Calculate the press factor and repeat the press cycle if needed (SP 2.8).

⇒ 6.2 Press factor
3.1 Shredding

After pressing, the alkali cellulose (AC) cake is torn into smaller pieces and placed into the tempered shredder. This step breaks all knots and reduces the fibre density to facilitate the penetration of chemicals later. To ensure an even processing of the AC, the mill is run in three periods of 13 min forward and 2 min backwards, resulting in a total shredding time of 45 min.

⇒ After shredding, collect a sample of about 5 g AC
⇒ 6.3 Determination of caustic content in AC
⇒ 6.4 Determination of cellulose content in AC
⇒ 6.6 Determination of CS$_2$ amount
3.2 Aging

The aging process is done in 1 litre glass bottles rotating in a tempered water bath of 50°C. Collect 50 g of shredded AC and transfer into the glass bottles. Cover the bottles with perforated Para film. Shake each bottle after 30 min of aging. The purpose of aging is to reduce the degree of polymerization (DP) by oxidative hydrolysis to a constant number for all samples investigated. For a better comparison of the samples, a set aging temperature of 50°C is chosen and a final DP of about 300 (approx. 240 ml/g). Before proceeding with xanthation, a correlation between time and DP needs to be established for each new cellulose quality. Once aging time to DP 300 is determined for all samples, xanthenation can be performed.

⇒ 6.5 Determination of aging time
⇒ Send sample to lab for carbohydrate, MWD and R₁₈, R₁₀
3.3 Xanthation

While handling CS₂, stay within a fume hood with sufficient ventilation, wear suitable gloves. Remove the Para film and insert the rubber plug consisting of the stainless steel xanthation device connected with a stopcock on top (see Fig 5a). Ensure that the rubber plug has been saturated with CS₂. Place the bottle in the water bath in a fume hood, keeping 30°C. Tighten the plug to the bottle with Para film. Start the vacuum pump and note the final vacuum level after evacuation of the bottle. Add the calculated amount of CS₂ by a 50 ml closed flask with stopcock under vacuum. Due to the vacuum in the bottle, CS₂ will be sucked into the xanthation device, evaporated and slowly led in gas phase into the bottle containing AC. Start agitation by rotating the bottle in the water bath for 150 minutes, after which the final pressure is measured. Note the pressure difference during the reaction. Maintain vacuum in the bottle!

⇒ 6.7 Calculation of amount of NaOH for dissolving step
Fig 5. Left: Xanthation device on bottle, picture by [Treiber]. Right: Xanthation unit consisting of water bath with rotating jars. Picture shows the adding of carbon disulfide to the alkali cellulose in a jar with vacuum and the typical yellow crumbs of cellulose xanthate.

4 Dissolving of cellulose xanthate

The cellulose xanthate is now mixed with sufficient alkali and water to produce a final viscose dope containing 9.5% cellulose and 5.0% NaOH. The resulting xanthate from the previous step has to be dissolved by adding a weak NaOH solution. To avoid any side reactions by oxygen and to maintain a CS₂ environment within the bottle, the solution is added with vacuum maintained. As mentioned by [Götze], a maximum swelling and thus a better dissolving of the viscose dope, is obtained when the dope is allowed to be treated with first a 10% solution of NaOH and later dissolved in pure water. Stop the rotation of the bottle and add the calculated amount of 10% NaOH by a 50 ml closed flask with stopcock under vacuum. There will be some remaining NaOH liquid in the xanthation device, which will be added later when removing the plug. Start the rotation of the bottle again and let react for 10 min. After 10 min, stop the rotation of the bottle, release all remaining vacuum and unplug the rubber plug. Make sure that the xanthation device is drained from all NaOH liquid into the bottle. Transfer the viscose dope to the pre-cooled jacketed steel vessel. Make sure the shell
has been cooled beforehand and maintain 5°C during the whole process by pumping cooling liquid through the jacket of the vessel. A low temperature is important since it will ensure that no xanthate is decomposed prior to dissolution of the cellulose. Inspect the blades prior agitation. During the forward agitation, the bigger, S-shaped, blades are to rotate clockwise whereas the small ones rotate counter clock wise for optimal agitation and to move the dope to the centre of the bottle (see Fig 6). Mount the vessel to the agitator and start agitation. Add the remaining volume of dissolving water after 30 min of stirring. Total agitation time is 180 min in intervals of 25 min forward and 5 min reverse direction.

Fig 6. Above: Dissolving unit with jacketed steel vessels for cooling and agitation. Below: Agitation by [Treiber]: 1) scraper, 2) agitator, 3) cooled wall of steel vessel. Note the main agitation direction.
5 Ripening

Stop agitation and cooling of the water bath. Dismantle the vessel from the agitation unit and place in a fume hood at room temperature while with the opening covered with perforated Papa film. Ripening is taking place for at least 16 hrs.

⇒ Send sample to lab for determination of MWD and carbohydrate content.
⇒ 6.38 Determination of caustic content in viscose
⇒ 6.49 Determination of cellulose content in viscose
⇒ 6.410 Viscosity determination of viscose
⇒ 6.611 Filter value determination of viscose
⇒ 6.612 Gamma number determination of viscose
⇒ 6.613 Salt point determination of viscose

6 Analytical methods and descriptions

An overall picture of samples and analytical methods are given in Fig 7 below. These methods are both for the purpose of process control as well as additional information on the changes of different cellulose properties during the treatment to viscose.

![Analytical process scheme](image)

Fig 7. Overall analytical process scheme.
6.1 Sample preparation after mercerisation

Prepare samples for determination of carbohydrate content, viscosity, MWD (molecule weight distribution) and \( R_{18}, R_{10} \). Samples are washed rigorously with distilled water and neutralized with 5w\% acetic acid. Store the samples in closed tubes until all analyses can be performed.

6.2 Press factor

It is of outmost importance to keep the correct press factor since it will determine the cellulose and caustic content in the sample. According to [Treiber], the pressure factor of the treated AC is directly related to the clogging value of the produced viscose and thus the spinning properties. [Broms] has also observed that a higher degree of pressing results in a decrease of degree of substitution measured by the gamma number, due to a lower amount of free water in the sample. A lower amount of water leads to a lower transport of chemicals into the cellulose sample. However, too much of liquid in the cellulose leads to gel layers or barriers, preventing the chemicals to penetrate. Hence, there is a relation between the press factor and \( K_w \), showing that there is an optimal range of pressing. The press factor is calculated as following.

\[
\text{Press factor} = \frac{\text{Weight of cake (g)}}{\text{Weight of dry cellulose (g)}}
\]

6.3 Determination of caustic content in AC

Place the 5 g AC sample from the mill in a 150 ml flask and mix with 25 ml 0.5M \( \text{H}_2\text{SO}_4 \). Dilute the sample by adding deionised water to the 150 ml level. Ensure a homogenous sample by mixing with a magnetic stirrer for at least 10 min. Add some drops of the indicator phenolphthalein and determine the caustic content by titration with 1.0M \( \text{NaOH} \). Calculate the caustic content, where \( a1 = \) volume of \( \text{H}_2\text{SO}_4 \)(ml), \( a2 = \) volume of \( \text{NaOH} \)(ml),
n1, n2 = normality of H₂SO₄ and NaOH respectively and G = amount of AC(g).

\[
Caustic\ content\ (\%) = \frac{(a1 \times n1 - a2 \times n2) \times 100 \times 40}{G \times 1000}
\]

6.4 Determination of cellulose content in AC

Neutralise the pinkish solution in 6.3 with some drops of H₂SO₄ and filtrate the liquid with a glass filter to collect all insoluble compounds. Wash the insoluble remaining with deionised water. To speed up the drying process and more accurate determine the amount of required CS₂, the insoluble remaining is also washed with acetone and dried in oven for 60 min in 105 °C.

\[
Cellulose\ content\ (\%) = \frac{\text{Mass of dried sample from oven (g)}}{\text{Mass of AC sample from milli (g)}}
\]

6.5 Determination of aging time

Samples are collected during the aging process in pre-defined periods, measured from the time of mercerisation. Samples are washed rigorously with distilled water and neutralized with 5w% acetic acid. Store the samples in closed tubes until DP can be analysed. Sample time for low viscosity material is suggested to be 2, 3 and 4 hrs and for high viscosity 3, 5 and 8 hrs. The aging time is determined if DP reaches 300.

6.6 Determination of CS₂ amount

For the production of spinning viscose, the amount of 36w% CS₂ based on the cellulose content in the AC is considered to be sufficient.

\[
CS₂\ amount\ (ml) = \text{Sample weight (g)} \times \frac{\text{Cellulose content (\%)}}{100} \times 0.36 \times \text{density}^{-1}\left(\frac{g}{ml}\right)
\]
6.7 Calculation of dissolving solution

A NaOH solution is used to dissolve the xanthate cellulose crumbs in water. The caustic concentration of the dissolving solution can vary, but is chosen to result in a desired final caustic concentration in the viscose dope to around 5%. Two steps will be performed, the adding of higher concentrated caustic solution to promote swelling and the adding of remaining water to dissolve the xanthate.

\[
m_{\text{Xanthate}} = \text{xanthate (g)}.
\]

\[
m_{\text{Viscose}} = \text{viscose amount (g)}.
\]

\[
c_{\text{cellulose,viscose}} = \text{cellulose content in viscose (%), about 9.5%}.
\]

\[
m_{\text{NaOH}} = \text{amount of 100% NaOH (g)}.
\]

\[
c_{\text{caustic,AC}} = \text{caustic content in AC prior xanthation (%)}.
\]

\[
c_{\text{cellulose,AC}} = \text{cellulose content in AC prior xanthation (%)}.
\]

\[
m_{\text{NaOH,40g/l}} = \text{amount of NaOH at 40g/l for further swelling/dissolving (g)}.
\]

\[
m_{\text{H}_2\text{O}} = \text{amount of water for dissolving after 10% caustic (g)}.
\]

\[
c_{\text{caustic,viscose}} = \text{desired caustic content in the final viscose (%), here 5%}.
\]

\[
m_{\text{viscose}} = \frac{m_{\text{AC}} \times c_{\text{cellulose,AC}}}{c_{\text{cellulose,viscose}}} [g]
\]

\[
m_{\text{Xanthate}} = m_{\text{AC}} + m_{\text{CS}} [g], \quad m_{\text{H}_2\text{O}+\text{NaOH}} = m_{\text{viscose}} - m_{\text{Xanthate}} [g]
\]

\[
m_{\text{NaOH,viscose}} = \frac{c_{\text{caustic,viscose}} \times m_{\text{viscose}}}{100} [g], \quad m_{\text{NaOH,AC}} = \frac{m_{\text{AC}} \times c_{\text{caustic,AC}}}{100} [g]
\]

\[
m_{\text{NaOH}} = m_{\text{NaOH,viscose}} - m_{\text{NaOH,AC}} [g]
\]

\[
C_{\text{NaOH}} = \frac{m_{\text{NaOH}} \times 1000}{130.706} [g/l]
\]

\[
m_{\text{NaOH,40g/l}} = \frac{130.706 \times C_{\text{NaOH}}}{40} [g], \quad m_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}+\text{NaOH}} - m_{\text{NaOH,40g/l}} [g]
\]
6.8 Determination of caustic content in viscose

Collect about 2g of viscose and note the exact weight. Dissolve the sample in 100 ml deionised water by a magnetic stirrer for about 30-40 min. Bring the solution to boil and add 10 ml sulphuric acid, 0.5M H₂SO₄ (1N). Wait until the solution has cooled down to room temperature. Titrate the sample with 1.0M NaOH (1N) after having added some drops of phenolphthalein. The caustic content is calculated as for the AC case according to the following formula

\[
\text{Caustic content (\%)} = \frac{(a1 \times n1 - a2 \times n2) \times 100 \times 40}{G \times 1000}
\]

6.9 Determination of cellulose content in viscose

Collect about 1.5 g of viscose and note the exact weight. Press the viscose between two glass plates as thin as possible. Ensure that no viscose is pressed outside the plates. Remove one plate and place the viscose film attached to one plate in a hydrochloric acid bath (42 ml/l) until the film loosens from the plate. Wash the film rigorously with pouring fresh water for 10 min and dry by squeezing all moisture with a filter cloth. Treat the film with acetone for 3 min after which it is placed in an oven at 105°C to constant weight. Calculate the cellulose content by using the formula below.

\[
\text{Cellulose content (\%)} = \frac{\text{Weight of sample after drying (g)}}{\text{Weight of viscose sample (g)}}
\]

6.10 Viscosity determination of viscose

The viscosity of viscose is in this work determined by the falling sphere viscometer. A ball bearing sphere of steel with a size of 1/8 inch in diameter is allowed to fall through a column of viscose 200 mm deep and the time of fall (sec) is observed. Make sure that the viscose is properly settled in the column and that no bubbles occur. Three tests are performed and the average
is the falling sphere viscosity $K_F'$, comparable to the one described by [Götze]. If needed, $K_F'$ can be expressed in Poise by using
\[ \eta \text{ [cP]} = 1.23 \times K_F' \times 0.001 \]

Fig 8. Typical brown colored viscose dope in a plastic column for determination of ball fall time. Note the two markings indication the 200 mm distance.

6.11 Filter value determination of viscose

The filter value is determined by use of a cylindrical filtration unit, prepared with a filter and two pieces of nylon cloth at the bottom of the cylinder. The choice of filter paper and its porosity is of utmost importance when comparing filter values between different units [Kolos and Treiber]. For this project, the filter value was determined with the filter apparatus modified with one sheet of steel filter Bekaert BekiporST 15FP. Drain the viscose dope from the column above into the filtration device and seal it by locking the top on the cylinder. Mount the cylinder to the stand and slowly apply a nitrogen pressure of 2 kg/7cm$^2$. Place a small beaker under the unit and start taking time when the first drop is collected in the beaker. Weigh the total amount of viscose ($M_1$, $M_2$) in the beaker after 50 ($t_1$) and 150 ($t_2$) min, after
which the clogging value of the viscose ($K_r$) is determined. The constant $\eta$ represents the falling sphere viscosity in seconds, determined earlier.

$$K_r = \frac{10^5 \times 2 \times \left\{ \left( \frac{t_2}{M_2} \right) - \left( \frac{t_1}{M_1} \right) \right\}}{(t_2 - t_1) \times \eta^{0.4}}$$

Note: The equation above stipulates that the quality of filterability of the viscose dope increases with decreasing $K_r$ value. The above equation is derived from Hermans and Breede general filtration law in 1935 and all steps resulting in the final equation above are well explained by [Kvarnlöf] or [Treiber] to include the reduced filtration value and filter paper dependency.

![Fig 9. Pressurized filtration unit, consisting of steel cylinders filled with viscose dope, a filter in the bottom and plastic beakers for collecting the filtered viscose.](image)

### 6.12 Gamma number determination of viscose

The gamma number is defined as the amount of xanthonate groups per 100 anhydro glucose units (AGU) and describes the level of degree of substitution (DS). Since three hydroxyl groups are available, the highest DS achievable is 3 corresponding to a gamma number of 300%. The gamma
number is measured after the ripening process. Many methods are available, where the fastest and easiest way is spectrophotometrical. A viscose sample of about 1g is collected and its exact weight noted. The viscose is dissolved in 50 ml, 1w% NaOH by stirring for 30-40 min. After the viscose is dissolved, the solution is transferred into a 100ml volumetric flask and filled with 1w% NaOH to the graduation mark. Shake the flask rigorously and directly transfer 5 ml to a bottle containing 1.8 g of ion exchange resin (Amberlite, IRA 402). Leave the solution to react with the resin for 10 min after which the solution is filtered by a filter paper (Munktell 5) into a 250 ml volumetric flask. Dilute with deionised water to the graduation mark and shake rigorously. Measurements are done with an UV spectrophotometer at $\lambda=303$ nm within 20 min after filtration. For reference, fill a 1cm quartz cuvette with deionised water and calculate the gamma number according to the equation below.

$$\gamma - \text{number} = \frac{A \times 546.48}{B \times C}$$

where $A=$ absorbance at 303 nm, $B=$ viscose amount (g) and $C=$ cellulose content (%) according to 3.9.

7 References

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