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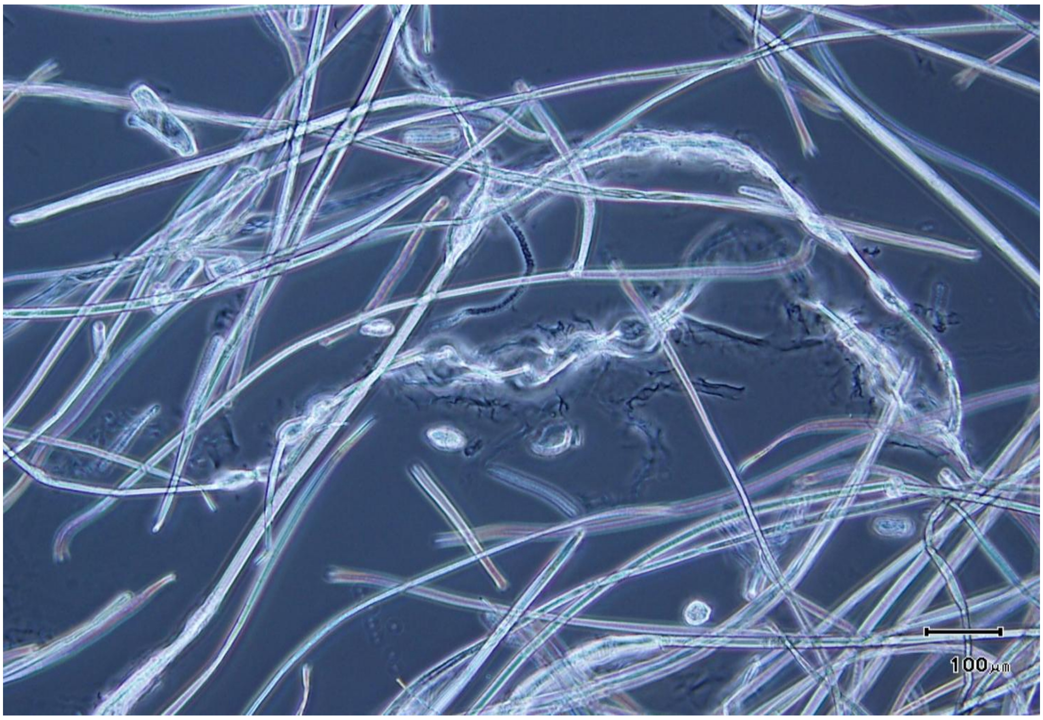

# Preparation of Nanofibers from Pulp Fibers

*Master of Science Thesis in the Master Degree Programme, Materials and Nanotechnology*

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Master thesis in collaboration with Eka Chemicals AB

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Cover figure: **Oxidized fibers**

# Abstract

TEMPO-mediated oxidation is a powerful technique for preparation of highly crystalline, individualized cellulose nanofibers. This regioselective oxidation can be achieved with sodium hypochlorite and catalytic amounts of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) and sodium bromide under aqueous conditions at pH 10 and room temperature. In this master thesis, the TEMPO-mediated oxidation for preparation of nanofibers from hardwood kraft pulp fibers has been examined, with the purpose to find the optimum process conditions. An obvious disadvantage of this oxidation procedure is the use of TEMPO and sodium bromide, which both are associated with environmental issues. Therefore, an important factor was to examine the possibility to reduce the addition levels of these two chemicals. Several methods were used to characterize the oxidized pulp fibers. Total fiber charge, water retention value and intrinsic viscosity were considered most important. The results showed that pH is, undoubtedly, the most important parameter, concerning both the oxidation procedure and the properties of the nanofibers. Moreover, it was shown that it is possible to prepare nanofibers of high quality with low charges of TEMPO and sodium bromide. To set the properties of the nanofibers in relation to dry and wet strength applications, the fibers were evaluated as a binder in paper sheets. The strength properties of the paper sheets can be significantly increased with addition of nanofibers and at a given addition level, the highly charged nanofiber product had the best performance.

# Table of contents

# Introduction

## Background

Wood has been described as the world's only renewable natural resource, for the reason that a new tree can be grown where another one has been cut (PULP & PAPER RESOURCES & INFORMATION SITE 2010). In terms of chemistry, wood is best defined like a three dimensional biopolymer composite which consists of an interconnected network of cellulose, hemicelluloses, lignin, extractives and inorganic compounds (Dietenberger, et al. 1999).

Cellulose is the world's most abundant organic raw material, which also can be described as a unique biomaterial that presents a huge set of opportunities for the industry. During the past decades, this biodegradable, inexpensive and renewable resource has been widely studied (Carlmark and Malmström 2003). Traditionally, cellulosic fibers have been used to make paper and clothing due to their suitable properties; high stiffness, low density and low cost. Recently, these versatile fibers have been highlighted as nanomaterials (Abe and Yano 2009).

Cellulose possesses many functional properties such as strength, stiffness and toughness, but compared to synthetic polymers it lacks some qualities, for instance hydrophobicity. One way to overcome this lack of certain, desired chemical and physical properties may be by some kind of modification of the cellulosic fibers and its surfaces (Carlmark and Malmström 2003). Today, there is several different modification techniques aimed for this purpose.

Process technologies to prepare nanofibers of natural and synthetic polymers include for instance electrospinning, template synthesis, phase separation, and modified melt-blowing. In general, it is difficult to manufacture highly crystalline nanofibers by these types of techniques.

In 2004, Isogai et al. reported their discovery of individualized cellulose nanofibrils following homogenization of oxidized cellulosic fibers, i.e. the raw material consisted of naturally occurring highly crystalline nanofibers. The cellulose fibers were oxidized by the 2,2,6,6-tetramethyl-piperidine-1-oxyl radical (TEMPO)-mediated oxidation process. This regioselective oxidation can be achieved with sodium hypochlorite (NaClO), sodium bromide (NaBr) and catalytic amounts of TEMPO under aqueous conditions at pH 10 and room temperature (Isogai 2010). The unique chemical and physical properties of these fibrillated oxidized celluloses could offer significant potential to the industry, for instance in the fields of coatings, composites, reinforcement, packaging and drug delivery (Johnson 2009).

The TEMPO-mediated oxidation enables to loosen the adhesion between the cellulose fibrils and thereby generate long, individualized nanofibrils without any significant aggregation (Saito, Kimura, et al. 2007) (Johnson 2009). During this oxidation procedure, only inexpensive sodium hypochlorite is consumed. TEMPO as well as sodium bromide are still present in the spent liquor after the end of the reaction and can be reused (Mao, et al. 2010). TEMPO-mediated oxidation is a powerful technology for manufacturing of nanofibers. However, a very crucial drawback is the use of halide-based reagents, e.g. sodium hypochlorite and sodium bromide as well as TEMPO, which have a negative impact on the environment. Therefore, it is of high importance to optimize the process in order to minimize the environmental effects.

## Objective

The objective of this master thesis is to optimize the process conditions of the TEMPO-mediated oxidation procedure for preparation of nanofibers with high quality.

# Theory

This chapter will give a presentation of major concepts in the master thesis which are useful for a deeper understanding within the research field.

## Wood

Wood mainly consists of hollow, elongated, spindle-shaped cells which are ordered parallel to each other along the trunk of the tree. The usage of wood is to a large extent influenced by its fibrous nature (Dietenberger, et al. 1999).

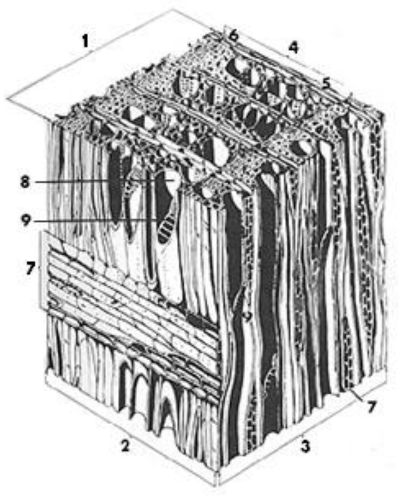
All wood is composed of cellulose, hemicelluloses, lignin and minor amounts of extractives.  These components are contained in a structurally complex hierarchical structure, where the cellulose fibers are embedded in a matrix of lignin. Like many other biological tissues, wood is a hierarchically structured composite which offers maximum strength with a minimum of material (Wegner and Jones 2009).

The chemical composition varies depending on factors such as tree part, type of wood, geographic location and soil composition. Therefore, the chemical composition of wood cannot be defined exactly for a given tree species (Pettersen 1984).

At the dimensions of nanometers, wood is a cellulosic fibrillar composite. About 30-40 % by weight of wood consists of cellulose; approximately 50 % in nanocrystalline form and the rest is amorphous (Wegner and Jones 2009).

### Hardwood

Wood is classified into softwoods and hardwoods. Softwood is produced by gymnospers (plants having seeds with no covering) whereas hardwood is produced by angiosperms (plants that produce seeds with some sort of covering). Hardwoods have a more advanced and complex structure than softwoods. Additionally, hardwoods have a larger number of different cell types including vessels, the most characteristic cell type in hardwoods (Gellerstedt 2004). Thus, the major structural difference between the classes is the types of cells used in support and conduction (John Wiley & Sons, Inc. 2010). The complex structure of a typical hardwood is depicted in figure 1. The libriform cells, often named fibers, give support, i.e. they are highly rigid and have thick walls in relation to their diameter. The vessels function as fluid transport elements and occupy approximately 25 % of the total volume. These specialized cells are evident as pores, i.e. wood cells with open ends. Finally, the pith ray cells are placed perpendicular to the other fibers, which can be clearly seen in figure 1.



1. Horizontal cross section
2. Radial cross section
3. Tangential cross section
4. Growth ring
5. Earlywood
6. Latewood
7. Pith ray cells
8. Vessel
9. Libriform cells

**Figure 1 Schematic structure of hardwood (Norman 1991).**

Hardwood fibers are generally shorter than softwood fibers. In average, fibers from hardwoods are 1 mm whereas the length of softwood fibers ranges from 3 to 8 mm (Dietenberger, et al. 1999). In addition, hardwood fibers have thicker cell walls and smaller cell lumina. Another difference between hardwood and softwood fibers is the shape; hardwood fibers are rounded in cross section while the softwood tracheids are rectangular to squarisch. Examples of hardwoods are aspen, birch, elm, maple and poplar. Most of the imported tropical woods are hardwoods (Gellerstedt 2004).

### *Birch*

The three most important species within the birch family are yellow birch, sweet birch and paper birch (Dietenberger, et al. 1999). Birch, mixed with aspen and other hardwoods, is the preferred hardwood raw material in Scandinavia for paper manufacturing.

The proportions of the major cell types present in birch are shown in table 1.

**Table 1 Proportion of different cells in birch. The values are given in % of total volume (Gellerstedt 2004)**

| Fibers | Vessels | Rays | Parenchyma (longitudinal) |
|---|---|---|---|
| 64.8 % | 24.7 % | 8.5 % | 2.0 % |

Approximately 45 % of the cell wall in birch wood contains cellulose. These cellulose microfibrils have a cross section formed almost like a square with lateral dimensions of 4-5 nm. The side length of the square equals 7-9 cellulose polymer chains (Gellerstedt 2004).

## Chemical composition of wood

Wood is primarily composed of cellulose, hemicelluloses and lignin. In general, cellulose contributes reinforcing fibers, hemicelluloses surround cellulose microfibrils and lignin provides rigidity as well as plastic character.

### *Cellulose*

Cellulose has the chemical formula $(C_6H_{10}O_5)_n$. The simple glucose unit is the basic unit in cellulose, the tough organic fibrous compound which gives structure and tensile strength to plant and wood fibers (Gellerstedt 2004) (Rowell, et al. 2005). Cellulose is one of many possible polymers made up of glucose but the only one that forms structural fibers. The glucose residue contains three hydroxyl groups enabling intra- and intermolecular hydrogen bonds, and many possibilities for chemical derivatization. In all cellulosic materials a complex microstructure of cellulose deriving from extensive hydrogen bonding is found (Elices 2000).

Cellulose is the major component in wood and accounts for approximately 50 % of the wood substance by weight. It is a linear polysaccharide which is composed of β-D-glucopyranose units linked with (1→4)-bonds, which is depicted in figure 2. The glucose units are arranged in a linearly manner so that adjacent glucose units share an oxygen atom (Gellerstedt 2004) (Rowell, et al. 2005).

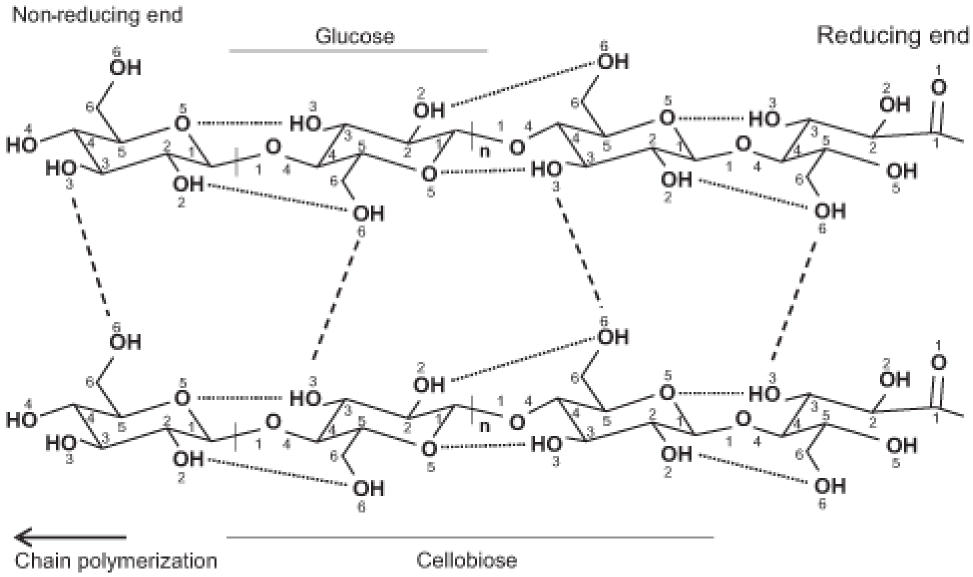


**Figure 2 The structure of cellulose, glucose units, cellobiose, reducing- and non-reducing ends, and intra- and intermolecular hydrogen bonds (Festucci-Buselli, Otoni and Joshi 2007).**

The number of glucose units within a cellulose molecule is referred to as the degree of polymerization (DP). The molecular weight of cellulose is high, hence the average degree of polymerization is at least 9000 (Rowell, et al. 2005). The glucose units of the cellulose chain are often called anhydroglucose units, because the unit can be schematically considered as a glucose molecule with a water molecule lacking. The cellobiose unit consists of two D-glucopyranoses linked by a β-(1→4)-bond, and is produced from partial hydrolysis of cellulose. The ends of the cellulose chains can be of two different natures, more exactly reducing and non-reducing ends. The hemiacetal situated at the reducing end, see figure 2, can open up to form an aldehyde (Gellerstedt 2004).

## Structural hierarchy of cellulose fibers

The hierarchical structure is spanning over six orders of magnitude and involves well-defined levels of hydrogen-bonded substructures. The assembly sequence can be seen in figure 3.

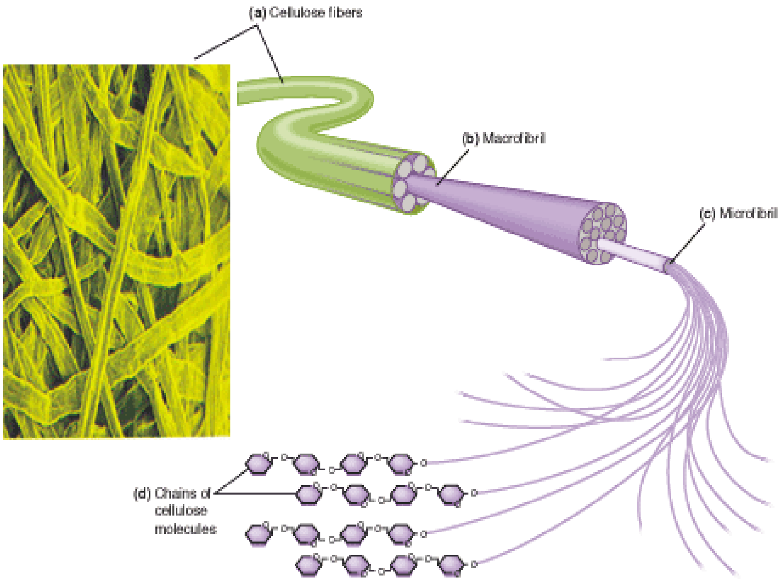


Figure 3 Hierarchical structure of cellulose (Nutrition Resources 2006).

In higher plants, during the biosynthesis of cellulose, lots of cellulose polymer chains are polymerized and aggregated, i.e. synthesized, into cellulose microfibrils. In the microfibrils, the cellulose chains are forming sheets. These sheets are tied together with hydrogen bonds, which in turn form a layered structure with several sheets on top of each other. The layers are held together by van der Waals bonds and hydrophobic interactions. Hence, the cellulose microfibrils are ordered three dimensional crystals (Gellerstedt 2004). The microfibrils are then further grouped into aggregates, called macrofibrils or fibrils, which are integrated into the cell wall.

The orientation of cellulose molecules is of a random character. As the cellulose molecules are denser packed, crystalline regions are formed. The majority of cellulose derived from wood is highly crystalline, as much as 65 % of the cellulose may be crystalline regions. The residual zones, i.e. the amorphous or non-crystalline cellulose, have a lower packing density (Rowell, et al. 2005). The cellulose crystal lattice is slightly disturbed in these regions. The surfaces of the microfibrils account for a large percentage of the amorphous cellulose (Gellerstedt 2004) (John Wiley & Sons, Inc. 2010).

In wood, there are several types of cellulose present. In addition to crystalline and amorphous cellulose, there are also accessible and non-accessible cellulose, which refer to the availability of the cellulose to water, microorganisms etc. Concerning the crystalline cellulose, its surfaces are accessible to water but the residual regions are non-accessible. Most of the non-crystalline cellulose is accessible, but some parts become non-accessible due to coverage of both hemicelluloses and lignin. This concept of availability to water is of great importance to, for instance, pulping and chemical modifications (Rowell, et al. 2005).

### *Hemicelluloses*

Cellulose and most of the hemicelluloses are structural carbohydrates since they form the cell wall, i.e. the bulk of the plant cell's supporting structure. The hemicelluloses are found in the matrix between cellulose fibrils in the cell wall (Gellerstedt 2004).

Hemicelluloses from wood generally consist of a group of polysaccharide polymers with a lower degree of polymerization than cellulose. The main constituents are the sugars D-glucopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, D-glucopyranosyluronic acid and D-galactopyranosyluronic acid with minor amounts of other sugars (Rowell, et al. 2005).

The components in lignocellulose, i.e. a combination of lignin and cellulose, are tightly associated. Therefore, it has been proved to be difficult to separate hemicelluloses from cellulose and lignin without affecting the hemicelluloses. The sort as well as the amount of the hemicelluloses in a certain wood type varies widely depending on plant materials, type of tissues, method of extraction etc (Gellerstedt 2004).

The major hemicelluloses found in hardwoods are glucuronoxylan (15-30 % in wood) and glucomannan (2-5 % in wood). Glucuronoxylan consists of a xylan backbone of D-xylopyranose units linked β-(1→4) with acetyl groups at C-2 or C-3 of the xylose units. The xylan is substituted with rather short side chains of 4-O-methylglucuronic acid units linked to the xylan backbone α-(1→2). The other hemicelluloses, glucomannan, are composed of β-D-glucopyranose and β-Dmannopyranose units linked (1→4) (Rowell, et al. 2005).

### The fiber wall structure

The structure of the fiber wall is complex and consists of several different layers, which can be seen in figure 4.

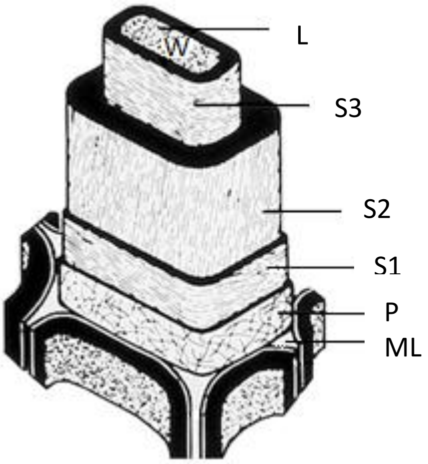


Figure 4 The different layers of the fiber wall (The University of Waikato 2009).

The wood cell consists of a number of cell wall layers which form the primary and secondary cell walls. The cell walls are in turn composed of microfibrils. The primary wall (P) is composed of only one layer, whereas the secondary walls (S1, S2 and sometimes S3) are composed of two or three cell wall layers. The intercellular region, called the middle lamella (ML), is a lignin rich zone gluing individual cells together. Despite the high lignin content in the middle lamella, approximately 25 % of the total lignin content is present in this region.

As depicted in figure 4, the primary wall forms the outer layer of the cell. This wall is comprised of randomly orientated cellulose microfibrils. The central layer of the secondary wall, S2, constitutes the major proportion of the cell wall in both softwoods and hardwoods. This thick layer has the greatest effect on how the cell behaves. The other two layers, S1 and S3, are comparatively thin. However, variations in the thickness of the cell wall layers arise, e.g. between early- and latewood cells and different cell types. In some cells, there is also a warty layer (W) present inside the S3-layer, adjacent to the cell lumen, L.

Noteworthy is that the fibril angle of cellulose chains differs for each sublayer. Thus, the individual layers of the primary and secondary cell wall can be distinguished from one another by the orientation of the cellulose microfibrils. The fibrils are wind around the cell axis in different directions; either to the right, named Z-helix, or to the left, named S-helix, within the layers. This alignment of the cellulose microfibrils could slightly be seen in figure 4. The S1-layer as well as the S3-layer contains fibrils which are almost horizontal orientated with regard to the fiber axis, while the fibrils are nearly vertical in the S2-layer. In what manner the cellulose microfibrils are orientated is of high importance for governing the physical properties of the wood cell and thereby the wood structure. The combination of the thickness and almost vertical orientation of the cellulose fibrils in the S2-layer makes this layer the most important giving wood cells strength and ultimately imparting the major physical and mechanical properties to wood products. The orientation of cellulose microfibrils is also referred to as the microfibril angle (MFA). Differences in the microfibril angle have a huge impact on properties of wood, in particular its stiffness. The orientation, i.e. the angle, of the microfibrils in the S2-layer is commonly used as a major feature for characterizing the strength properties of wood (Gellerstedt 2004) (Dietenberger, et al. 1999).

Naturally, the chemical composition of wood cell wall layers varies between cell types and also between hardwoods and softwoods. The middle lamella region has the highest lignin content, measured in g/g, of the different cell wall layers. This region also contains cellulose and pectin. The primary cell wall has high levels of both the hemicelluloses xyloglucan and pectin, and also the glycoprotein extensin, which is thought to hold the cellulose microfibrils in their zigzag network. The lignin content differs in the secondary cell wall layers with the highest concentration in the S1-layer. Cellulose and hemicelluloses are present to a larger extent in the S2-layer than in the S1- or S3-layers. Notice that these trends only can be seen as a general tendency, since it is very difficult to analyze the ultrastructure of the cell walls (Gellerstedt 2004).

## Kraft pulp

Pulp consists of fibers, and pulping is the process in which the fibers are liberated from the wood matrix. This can be done either mechanically or chemically. Mechanical pulping is a very energy demanding process but makes use of the whole wood material, hence have good yield. Mechanical pulps have high fines content. Fines are broken fibers and material from the surface of the fibers, contributing to its optical characteristics.

Chemical pulping, on the other hand, have low yield. Only half of the wood material is found in the final pulp. The process includes an efficient recovery system where spent cooking liquor and energy in the dissolved organic material is recovered; therefore no external energy is needed.

The chemical way to produce pulp is the removal of lignin, i.e. releasing the fibers. In this process, also called delignification, lignin molecules are degraded and charged groups are introduced keeping the fragments in solution.

Kraft cooking is the most common chemical pulping method around the globe. The cooking chemicals are sodium hydroxide, which keeps the lignin fragments in the solution, and sodium sulphide, which is the main delignifying agent. In the production of bleached pulp, an oxygen delignification stage is generally applied after cooking to reduce the lignin content before the pulp enters the final bleaching. Chemical pulp fibers are more flexible than mechanical pulp fibers. They also conform better to each other when forming the paper, and offer good strength properties (Gellerstedt 2004).

## Nanomaterials

The definition of nanomaterials reads as follows: nanomaterials can be defined as materials which have structured components with at least one dimension less than 100 nm. Materials which have one dimension in the nanoscale are layers, such as a thin films or surface coatings. Materials that are of nanoscale in two dimensions include nanowires and nanotubes. Materials which have all three dimensions in the nanoscale are particles, for instance precipitates, colloids and quantum dots. Also nanocrystalline materials, which are made up of nanometre-sized grains, fall into this third category (Quinzi and Di Francesco 2005)

At the nanoscale level, i.e. up to about 100 nm, unusual properties are often encountered (Wegner and Jones 2009). For instance, the chemical stability for certain nanomaterials may be improved and the mechanical properties will be better than those of the bulk material (Properties of nanomaterials 2010). The area of nanomaterial technology has been paid wide attention due to these super functionalities, which arises from their extremely large and active surface areas (Saito, Kimura, et al. 2007). Thus, nanomaterials deliver new, tremendous functionality and options of traditional materials.

Nanoscale particles exist in nature and are present in our daily lives, but the active manufacturing of nanomaterials has raised a huge debate regarding their overall environmental and health effects. Although nanotechnology is new, the field is expanding rapidly and research is needed to uncover its potential risks (Wegner and Jones 2009). Today, it is still unknown which properties of the nanoparticles that determine and/or influence whether it is toxic or not. Physical and chemical properties such as particle size, size distribution, surface area, surface chemistry, crystal structure, porosity, agglomeration state and method of synthesis need to be considered (Senjen 2009).

## Nanofibers

Nanofibers, as well as other nanomaterials, are expected to have unique properties. More exactly, nanofibers have large specific surface area, high porousness and small pore size, transparent appearance and excellent mechanical properties in relation to their weight.

Nanofibers are defined as nanoparticles with two dimensions at the nanoscale and an aspect ratio of greater than 3:1 (Wegner and Jones 2009). Aspect ratio is the proportional relationship between any two dimensions, in this case between the width and the length of the fiber. Since their diameter is smaller than the wave length of light, nanofibers are not visible in traditional microscopes. These extremely small fibers can only be studied by electron microscopes (Elmarco, Inc. 2009).

### *Preparation of nanofibers*

Process technologies to prepare nanofibers of natural and synthetic polymers include drawing, electrospinning, phase separation, template synthesis, sea-island composite spinning and modified melt-blowing. Though, in general it is hard to prepare highly crystalline nanofibers by these techniques, so called molecular-assembly processes. On the contrary, there are naturally occurring nanofibers with high crystallinities which are abundantly present in nature. These fibers are native celluloses, consisting of fibrils with a width of 2-20 nm and crystallinities ranging from 65 to 95 % depending on their origins (Saito, Kimura, et al. 2007).

In 2004, Isogai et al. patented their discovery of individualized cellulose nanofibrils followed by homogenization of oxidized cellulosic fibers. Cellulose fibers were oxidized by the TEMPO-mediated oxidation process. Noteworthy is that this oxidation procedure results in long, individualized nanofibrils with diverse surface functionalities, i.e. carboxyl, aldehyde- and hydroxyl groups in contrast to the conventional microfibrillation and acid hydrolysis processes which yield microfibril networks and short crystallite bundles. It is perceived that the unique chemical and physical properties of these fibrillated, oxidized celluloses could deliver significant potential in the areas of coatings, composites, packaging, reinforcement and drug delivery (Johnson 2009).

## TEMPO-mediated oxidation

During the last 15-20 years, nitroxyl catalysts, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), have confirmed applicability in catalytic carbohydrate oxidation. The class of compounds, to which TEMPO belongs are often referred to as nitroxyl or nitroxide radicals and are in fact secondary amine nitrogen oxides. The radicals are often extreme stabile towards dimerization or decomposition and inert to typical organic molecules.

In the reaction, polysaccharides are converted to the corresponding polyuronic acids. The method is suitable for selective oxidation of primary alcohol groups into aldehydes and/or carboxylic acid groups. The process is highly effective in the conversion of high molecular weight polysaccharides. Moreover, the reaction rate and the yield are high, the process is catalytic and highly selective and throughout the process the degradation of polysaccharides is just modest.

The regioselective TEMPO-mediated oxidation can be achieved with sodium hypochlorite and catalytic amounts of TEMPO and sodium bromide under aqueous conditions at pH 10 and room temperature (Isogai 2010). During the oxidation, the C-6 primary hydroxyl groups of cellulose are converted to carboxylate groups on the surface of the microfibrils, consuming only inexpensive sodium hypochlorite and sodium hydroxide (Saito and Isogai 2006). Throughout the reaction 1 mol of the C-6 primary hydroxyl groups are converted to 1 mol of C-6 carboxylate groups via a C-6 aldehyde structure by consuming 2 mol of sodium hypochlorite (Saito, Kimura, et al. 2007).

The introduction of carboxylate groups, that have anionic charges in water, results in formation of repulsive forces between cellulose microfibrils. Individualized nanofibers, 3-4 nm in width, can be obtained by simple mechanical disintegration of the oxidized celluloses in water (Iwamoto 2010).

However, the method has some shortcomings with respect to environmental impact and cost issues, which have to be overcome to meet the requirements of the chemical processes in the 21th century. Most seriously are the halide-based reagents, such as sodium hypochlorite and sodium bromide used as primary oxidant and co-catalyst, respectively. Until this day there is no commercial process in operation.

In order to function as an efficient oxidant of organic substrates the nitroxyl radical, TEMPO, (I), see figure 5, has to be converted into the more powerful nitrosonium salt (II). During the oxidation process, the nitrosonium ion is continuously regenerated in situ by oxidizing agents.

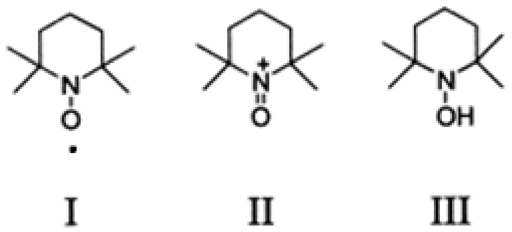


**Figure 5 I) TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), II) nitrosonium ion, III) hydroxylamine, reduced form of TEMPO (Bragd, Besemer and van Bekkum 2000).**

Under alkaline conditions, one equivalent of the nitrosonium ion reacts with one equivalent of substrate, oxidizing the substrate and generating hydroxylamine (III), see figure 6 (Bragd, van Bekkum and Besemer 2004).

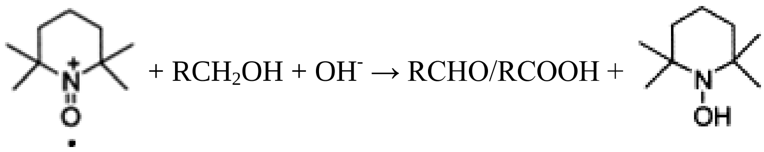


Figure 6 Oxidation of alcohols by the nitrosonium ion under alkaline conditions

The proposed mechanism between the nitrosonium ion and the substrate is shown in figure 7 and involves a sterically confined cyclic elimination that may preclude more hindered secondary alcohols as substrates. At alkaline pH, primary alcohols are generally oxidized much faster than the more hindered secondary alcohols, whereas at acidic pH the reaction rates are comparable. The amount of primary oxidant determines the yield of the oxidation reaction (Bragd, van Bekkum and Besemer 2004).

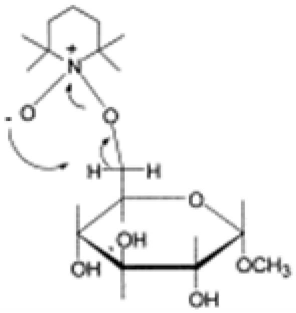


Figure 7 The proposed mechanism between the nitrosonium ion and the substrate (Bragd, Besemer and van Bekkum 2000).

The reaction scheme of the complete TEMPO-mediated oxidation is shown in figure 8. Sodium hypochlorite and sodium bromide are the regenerating oxidizing system of the nitrosonium ion. Hypobromide (NaBrO), which is the active oxidizing species, is formed in situ by oxidation of sodium bromide by sodium hypochlorite (Bragd, Besemer and van Bekkum 2000). The nitrosonium ion reacts with one molecule of the hydroxylamine to regenerate the TEMPO radical.  In most studies, the radical is added in catalytic amounts, i.e. approximately 1 % of the substrate (Bragd, van Bekkum and Besemer 2004).

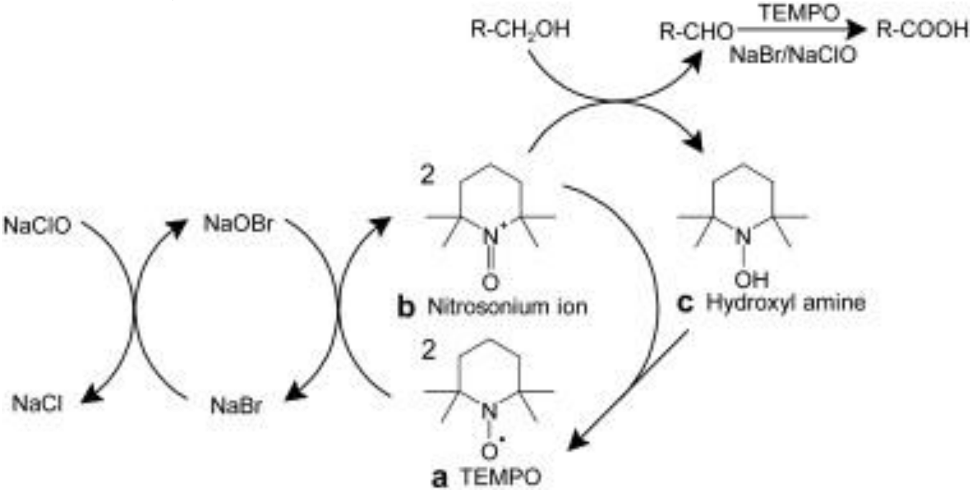


Figure 8 Reaction scheme of the TEMPO-mediated oxidation (Iwamoto, et al. 2010).

## Process parameters

In the following section, the most important process parameters in the TEMPO-mediated oxidation are shortly described.

### *Sodium hypochlorite*

The addition of sodium hypochlorite primarily affects the carboxylate content, which increases with increasing amounts of sodium hypochlorite added as the co-oxidant. The maximum attainable carboxylate- and aldehyde contents are approximately 1500 and 100-300 mmol/kg, respectively (Saito, Nishiyama, et al. 2006). The aldehyde groups are both C-6 aldehydes present as the intermediate structure and the reducing ends formed from the glycosidic bonds by β-elimination at pH 10.5 during the oxidation. However, sodium hypochlorite used in the oxidation is consumed not only for the formation of carboxyl and aldehyde groups in the water-insoluble fractions but also for the formation of water-soluble fractions, especially under harsh conditions such as extended oxidation time or excess sodium hypochlorite addition (Saito and Isogai 2004).

The oxidation time is also affected by the concentration of sodium hypochlorite. In 2007, Saito et al. reported that increasing the amount of sodium hypochlorite from 3.8-5.0 mmol/gram of cellulose only increased the carboxylate content 200-300 mmol/kg, while the oxidation time increased from 40-45 minutes to 115-130 minutes. It was also shown that the water retention value increased with increasing the carboxylate content, both never-dried and once-dried oxidized celluloses hade similar water retention values of more than 400 % when the carboxylate content reached approximately 1500 mmol/kg.

In 1999, Kitaoka et al. discussed the influence of sodium hypochlorite on the degree of polymerization of TEMPO-oxidized bleached hardwood kraft pulp. It was shown by viscosity measurements using cupriethylenediamine hydroxide that the degree of polymerization drastically dropped and leveled off at about 200 with increasing amounts of sodium hypochlorite.

Noteworthy, Bragd et al. reported in 2000 that in order to minimize unwanted side reactions, such as glycolic cleavage of the C-2 and C-3 vicinal diol moiety, sodium hypochlorite was added in portions of 2 ml throughout the oxidation.

### *TEMPO*

Earlier this year, it was reported in a study on kinetics and reuse of spent liquor in the TEMPO-mediated oxidation of mechanical pulp, that the concentrations of the catalysts TEMPO and sodium bromide significantly influence the reaction rate, which was shown to be first-order in each reactant. The concentrations of the catalysts however, seemed to have little effect on the maximum attainable carboxyl content on mechanical pulp. Additionally, it was shown that the spent liquor can be recycled with reinforced addition of sodium hypochlorite but without any additional TEMPO or sodium bromide, and it still remain effective in generating carboxylic acid groups on mechanical pulp (Mao, et al. 2010).

In 2004, it was found that addition of excess TEMPO and sodium bromide, together with high temperatures and longer oxidation time, brought about lower degree of polymerization values for the oxidized products (Isogai and Kato 1998).

### *Sodium bromide*

In 2000, Bragd el al. investigated the TEMPO-mediated oxidation of starch in absence of sodium bromide as a co-catalyst. To overcome the low reaction rate associated with this process it was performed at increased temperatures. It was reported that at temperatures and pH below 20 °C and 9, respectively, the oxidation proceeded at high selectivity and with minor depolymerization. Degradation of the starch skeleton and side-reactions of the nitrosonium ion was found to lower the yield of the oxidation at higher temperatures and more alkaline conditions, above 25 °C and pH 9. From an industrial point of view, a bromide-free process is desirable, since the presence of bromide in the waste stream is highly unwanted due to environmental and corrosion concerns.

### pH

The conversion of primary hydroxyl groups of polysaccharides into carboxylate groups in the TEMPO-mediated oxidation is pH-dependent. The pH influences the efficiency or the time required for oxidation. It has been reported that pH 10 is optimum for shortening the oxidation time. In this study, 5.0 mmol NaClO/gram of cellulose was applied to never-dried cellulose at pH 9.5, 10 and 10.5, respectively. The required oxidation times for these reactions were 285, 130 and 195 minutes (Saito, Kimura, et al. 2007).

The pH also influences the reaction rate. An increase of pH starting from mildly alkaline conditions is followed by an increase in reaction rate, but at high alkalinity the rate is again lowered. In an earlier research, reported by Bragd et al., the bromide-free TEMPO-mediated oxidation of starch was studied. It was shown that the pH optimum is somewhat lower in the absence of sodium bromide, approximately 9.3 compared to 10.5 for a sodium bromide-catalyzed oxidation. It was showed that high pH caused severe depolymerization. However, it is well known that C-6 oxidized glucopyranosides are susceptible to β-alkoxy elimination reactions under alkaline conditions (Bragd, Besemer and van Bekkum 2000).

### Temperature

Temperature is an important factor concerning the reaction rate. In 2000, Bragd et al. showed that the rate of a bromide-free oxidation at 15-20 °C was in the same range as for the corresponding sodium bromide-catalyzed oxidation at 2 °C.

Another investigation showed that pH 10 at 4 °C was optimum conditions for minimizing the depolymerization of amorphous cellulose. On the other hand, Isogai and Kato applied the oxidation system at room temperature in 1998 to increase the carboxylate group content of different cellulosic samples. It was found that the amount of TEMPO, reaction time and temperature were the key factors controlling the depolymerization of regenerated or mercerized cellulose (Tahiri and Vignon 2000).

### Oxidation time

It has been shown that the oxidation time is shortened at pH 10 and if the amount of sodium hypochlorite increases the oxidation time is prolonged (Saito, Kimura, et al. 2007).

Saito and Isogai showed in 2004 that the oxidation time affected the recovery ratio of the water-insoluble fraction. As the oxidation time increased the recovery ratio decreased, approximately 20 % of the original cotton linter was lost after oxidation for 24 hours by the washing process. The degree of polymerization of original cotton linter dropped from 480 to about 200 within 0.5 hours in the oxidation. Similar results were obtained in the TEMPO-mediated oxidation of bleached hardwood kraft pulp with different amounts of sodium hypochlorite (Saito and Isogai 2004).

### Example of process parameters

In 2007, Saito and Isogai performed the TEMPO-mediated oxidation on bleached hardwood kraft pulp. The amount of chemicals added and other process parameters can be seen in table 2.

Table 2 An example of process parameters and addition levels in the TEMPO-mediated oxidation

| Process parameter | Amount in the oxidation |
|---|---|
| **NaClO [mmol/g]** | 1.3-5.0 |
| **TEMPO [mg/g]** | 16 |
| **NaBr [mg/g]** | 100 |
| **pH** | 10 |
| **Temperature [°C]** | Room temperature |
| **Oxidation time [min]** | Until no consumption of NaOH was observed |
| **P.C. [1] [%]** | 1 |
| **Agitation [rpm]** | 500 |

## Properties of oxidized pulp fibers

To characterize the oxidized pulp fibers, properties such as total fiber charge, degree of swelling, degree of polymerization, fiber dimensions and morphology are of high importance. Additional features of interest regarding the oxidized pulp fibers and also the whole oxidation process are for instance crystallinity, transparency and yield.

The total carboxylate content, i.e. the total fiber charge, in cellulose fibers is usually determined by an electric conductivity titration method (Saito and Isogai 2006). It has been shown that the oxidation level is essential for the degree of microfibrillation. However, disintegration does not require complete oxidation of the surface (Saito, Nishiyama, et al. 2006).

Also, the degree of swelling is an important property. The ability of the fibers to swell and retain water, measured as their water retention value (WRV) after centrifugation, has been shown to increase markedly after the TEMPO-mediated oxidation (Saito and Isogai 2004). This high water retention value in combination with little morphological changes is typical for TEMPO-oxidized native cellulose (Saito, Kimura, et al. 2007).

Regarding the degree of polymerization, several studies have shown a decrease in intrinsic viscosity during the oxidation procedure. Depolymerization of cellulose chains having glucuronic acid residues at alkaline pH may occur to some extent by β-elimination during the oxidation (Kitaoka, Isogai and Onabe 1999).

However, Saito and Isogai, reported in 2004 that the degree of polymerization of original cotton linter dropped from 480 to 200 within 0.5 hours in the oxidation. It was argued that some depolymerization is inevitable in the TEMPO-mediated oxidation of regenerated cellulose but that some radical species formed in situ in the oxidation system are likely to participate in the depolymerization mechanism. Additionally, because of the alkalinity of the copper ethylenediamine used for the viscosity measurement, some depolymerization must have occurred on the water-insoluble fractions during the dissolution process by β-elimination of the glycosidic bonds (Saito and Isogai 2004).

The morphology of the fibers is also a property of interest which can be studied using transmission electron microscopy (TEM), scanning electron microscopy (SEM) as well as atomic force microscopy (AFM) (Saito, Shibata, et al. 2005). For instance, pictures from TEM-observations of highly oxidized celluloses have indicated individual cellulose fibrils, i.e. nanofibers, 3-4 nm in width and a few µm in length. It has also been shown that the fibers were mostly unchanged after the oxidation, even at high

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[1] P.C: pulp consistency

water retention values (Saito, Kimura, et al. 2007). Under harsh conditions, i.e. 5-6 mmol NaClO/g fiber, using native celluloses, TEM-pictures showed kinks suggesting serious damage of the nanofibers (Okita, Saito och Isogai 2009). Probably, the kinks could also be a result from the mechanical treatment (Saito, Nishiyama, et al. 2006).

### *Dry strength and wet strength*

In the paper industry, carbonyl and carboxyl functionalities are of great importance in the final paper properties. It has been shown that the tensile index of sheets made from partially oxidized fibers slightly increased with increasing carboxylate content. The introduction of carboxylate groups had a different effect on the wet tensile index. Sheets made without polyamideamine-epichlorohydrin (PAAE) showed a clear increase in wet tensile index up to a carboxyl content of 120 mmol/kg and then decreased at higher carboxylate content. The maximum wet tensile index was four times as high as for the original pulp. Furthermore, the introduction of carboxylate groups resulted in higher retention values of PAAE on the paper sheets. The improved properties were explained by the increased opportunity of electrostatic interactions between anionic pulp and cationic PAAE, which was added as a wet-strength agent in some experiments (Kitaoka, Isogai and Onabe 1999).

Some years ago it was reported that the dry- and wet strength indices increased 38 and 208 % respectively, of a hardwood bleached kraft pulp after TEMPO-mediated oxidation. It was suggested that the wet strength development was due to intermediate structures formed during the oxidation, probably surface aldehyde groups that form hemiacetal linkages with cellulose hydroxyl groups at the inter-fiber bonds (Saito and Isogai 2005). Furthermore, a 33 % increase in tensile properties and a 48 % increase in tear properties of a bleached hardwood kraft pulp as a result of TEMPO-mediated oxidation have been shown in earlier research (Duarte, et al. 2006).

## Environmental issues

Due to the fact that TEMPO, sodium bromide and sodium hypochlorite all have a negative impact on the environment, the extent of use of these chemicals has to be considered.

### TEMPO

TEMPO, which can be seen in figure 9, has the chemical formula $C_9H_{18}NO$ and is classified as a hazardous compound (Prevent 2010). It is a corrosive, stable radical which is suitable to act as a catalyst. The stability is caused by the four methyl groups adjacent to the nitrogen, which can be seen in figure 9. TEMPO has an unpleasant odor which makes it unacceptable in packaging aimed for food for instance. Moreover, it is an expensive chemical which is associated with health effects and environmental issues.

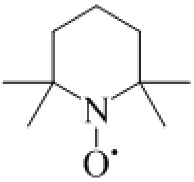

Figure 9 Structural formula of TEMPO (Taylor & Francis Group 2010).

### Sodium bromide

Bromine compounds in general are associated with especially severe environmental and health effects. These issues include the categories PBT and CMR, which are abbreviations of persistent, bioaccumulative and toxic, and carcinogenic, mutagenic and disturbance of the reproduction, respectively (Petersson 2006).

### Sodium hypochlorite

Sodium hypochlorite is a fairly strong oxidizing agent which is classified as harmful and corrosive. It has a strong, clorine-like odor and is a stable compound that reacts with organic compounds (Oxford University 2007).

Solutions of sodium hypochlorite decompose slowly and this decomposition is speeded up by heat, sunlight and some metals such as nickel, cobalt and cupper. In contact with acids, sodium hypochlorite emits the toxic chlorine gas (Swed Handling chemicals 2007)

# Experimental

This chapter contains a description of how the TEMPO-mediated oxidation was carried out. The experiments were divided into a short screening followed by a more expanded plan, defined as the main experiments, focused at suitable parameter levels. These parameter levels were chosen from literature. This part also presents the different characterization methods used. All of the experimental work as well as the analyses were carried out at Eka Chemicals in Bohus, Product Development.

The pulp used in all the experiments is a chemical bleached birch pulp called “silver anchor” from Iggesund. In table 3, some important properties of this pulp are listed. The brightness, Kappa number and intrinsic viscosity were determined in earlier research at Eka Chemicals by using ISO standard methods (ISO brightness: 2470, Kappa number: 302, viscosity: 5351), whereas the dry content was measured in connection with this master thesis.

**Table 3 Important properties of the birch pulp**

| | |
|---|---|
| **Brightness [% ISO]** | 88.6 |
| **Kappa number** | 0.62 |
| **Intrinsic viscosity [$dm^3$/kg]** | 997 |
| **Dry content [%]** | 42.54 |

## Oxidation procedure

The TEMPO-mediated oxidation was carried out according to figure 10.

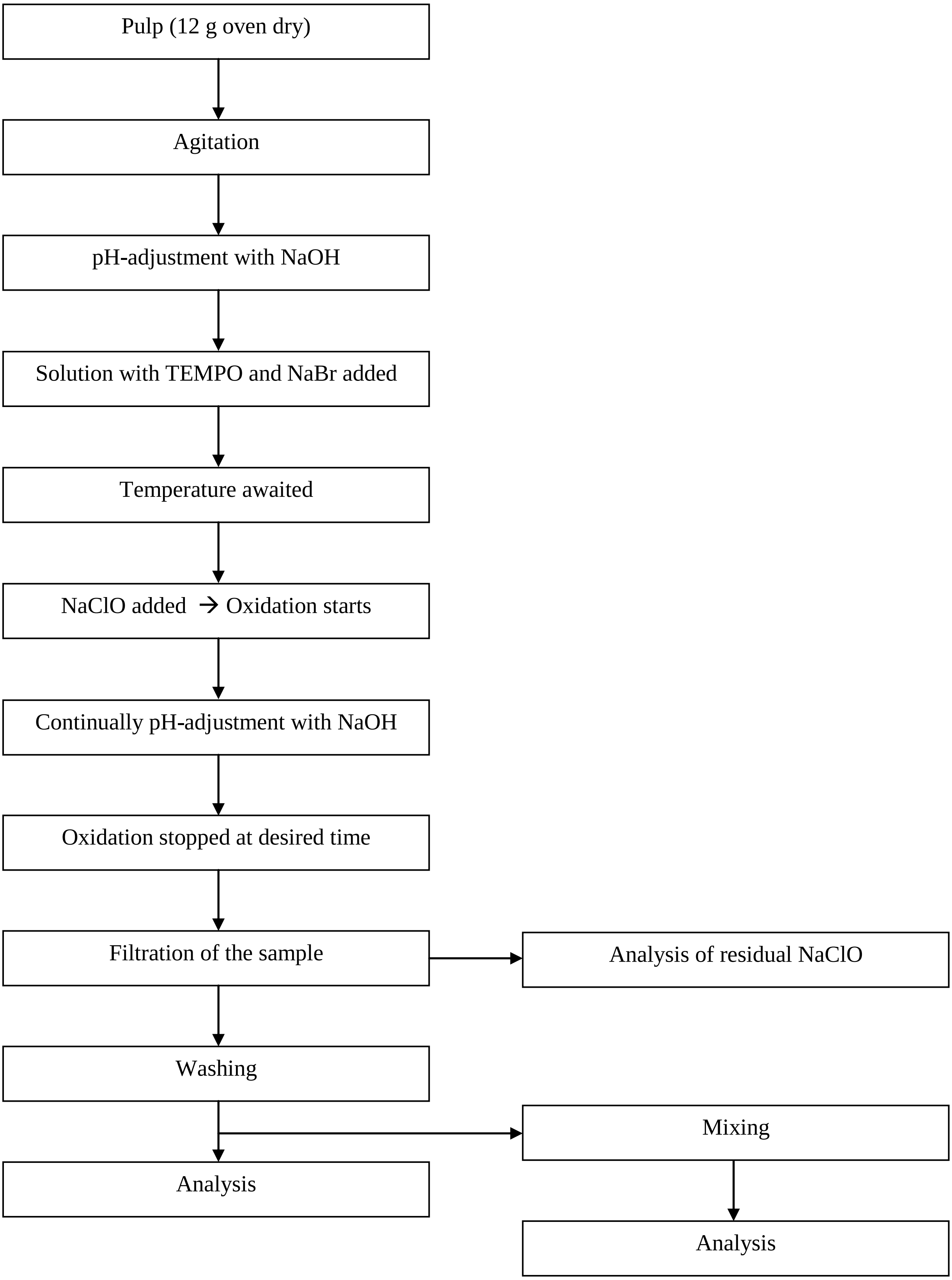

**Figure 10 General description of the oxidation procedure.**

The TEMPO treatment was performed at 1-3 % pulp consistency. The following oxidation procedure is described for 2 % pulp consistency, in total 600 ml liquid was added. Preparation of chemicals and TEMPO treatment were performed in a fume cupboard.

Cellulose (12 g oven dry pulp) was suspended in approximately 375 ml of deionized water in a 2000 ml glass beaker. The pulp suspension was put on agitation by using a propeller, and then placed in a water bath on a heating plate. A pH electrode and a thermometer were assembled.

A designed amount of the chemicals TEMPO, supplied by Acros Organics, and sodium bromide, supplied by Scharlau, corresponding to 4-16 mg/g cellulose and 25-100 mg/g cellulose, respectively, were diluted in approximately 200 ml of deionized water. A magnetic stirrer was used to secure a homogenous solution.

The pH of the pulp suspension was adjusted with sodium hydroxide to about 9 before the TEMPO/sodium bromide solution was added to the pulp suspension. The temperature was awaited to reach a designed value, corresponding to 25-30 °C and thereafter approximately 25 ml (4 mmol/g cellulose) of sodium hypochlorite, supplied by Akzo Nobel Base Chemicals, was quickly dosed to the pulp suspension. The pH was maintained at the desired level, 9-11, by manually adding sodium hydroxide. The oxidation was stopped after the decided oxidation time.

After the oxidation, the pulp was transferred to a Büchner funnel and filtered. The filtrate was analyzed for residual sodium hypochlorite. To avoid losses of fines the filtrate was recirculated once. The pulp sample was washed directly after the treatment with deionized water at approximately 1 % pulp consistency and stirred for 40 minutes. The pulp was dewatered and the filtrate was recirculated once. The washing procedure was further repeated two times, if possible. The oxidized fibers were transferred to a glass can, and then stored at 6 °C before further analysis

As can be seen in figure 10, some part of the samples was mixed in order to convert the oxidized fibers into nanofibers before further analyses.

## Methods

The following analyses were done in order to characterize the oxidized pulp fibers.

### Residual sodium hypochlorite

The residual sodium hypochlorite in the filtrate was analyzed by the Eka standard ANA 014.

### Mixing

To get a quick, visual view of the oxidized pulp sample, more exactly to know if the cellulose fibers can be converted into individualized nanofibers, the sample was mixed in a household mixer for a given time.

1 g oven dry oxidized pulp was transferred to a household mixer and 100 ml of deionized water was added. The sample was mixed for 2 minutes before another 100 ml deionized water was added. The sample was further mixed for 3 minutes, transferred to a plastic can and then stored at 6 °C prior to further analyses.

### Total fiber charge

The total fiber charge was determined by an electric conductivity titration method according to literature (Katz, Beatson and Scallan 1984). The titration procedure was performed using a titration unit, 712 Conductometer and a program from Metrohm.

### Fiber dimensions

Fiber dimensions such as mean length, mean width, mean shape, coarseness, kink angle, number of kinks per mm and number of kinks per fiber were analyzed by using Lorentzen & Wettre Fiber Tester, program default.

### Water retention value

The water retention value is an empirical measurement of the fiber's ability to retain water when subjected to centrifugation under standard conditions. It can be specified as grams of remaining water in the fiber per gram of oven dry pulp or in percentage. The WRV-measurements were performed using Eka Chemicals standard method: Massa 002 based on SCAN-C 62:00.

### Intrinsic viscosity

The intrinsic viscosity was determined by using the ISO standard method 5351. The limiting viscosity number in cupriethylenediamine (CED) solution was calculated, which gives an indication of the average degree of polymerization of the cellulose.

## Evaluation of nanofibers as a binder in paper sheets

To be able to set the strength properties of the nanofibers in relation to dry- and wet strength applications, paper sheets were formed and then analyzed with respect to tensile strength, Z-strength, bending resistance, burst strength and wet strength.

### Sheet formation

Paper sheets with the grammage of 100 g/m$^2$ were prepared from a high temperature chemithermomechanical pulp (HT-CTMP) fiber suspension (conductivity: 1 200 µS/cm, pH: 7) using a dynamic sheet former, DSF. The paper sheets were pressed in a plane press at 10 bars pressure and thereafter dried in a plane dryer for 10 minutes at 85 °C. The paper sheets were then conditioned in climate room at 23 °C and 50 % relative humidity for 24 hours before further analyses.

The amounts of chemicals added to the suspension, based on the dry weight of pulp, and addition time prior to pumping are listed in table 4. In the tables throughout the report, units considering the addition levels of chemicals are based on dry weight of pulp and presented in for example kg/t or mg/g.

Table 4 The amounts of chemicals added and the addition times

| Time (s) | Amount (kg/t) | Product | Chemical | Explanation |
|---|---|---|---|---|
| 0 | 0, 10, 20, 50 | NF, nanofibers | | |
| 10 | 1 | Eka ATC-8210 | PAC, polyaluminium chloride [2] | Anionic trash catcher |
| 15 | 1.3 | Eka WS X0 | PAAE, polyamideamine-epichlorohydrin | Cationic wet strength agent |
| 30 | 2 | Eka DR28 | AKD, alkyl ketene dimer | Cationic sizing agent |
| 45 | 10 | PB970 | Potato starch | Cationic dry strength agent |
| 60 | 0.3 | PL1510 | PAM, polyacrylamide | Cationic retention aid |
| 75 | 0.5 | NP442 | Nanoparticles | Anionic retention aid |
| 90 | Sheet formation | | | |

Two sheet formations were done, with the only difference that polyaluminium chloride was added to one of those.

### Sheet characterization

The paper sheets prepared were analyzed for tensile strength, Z-strength, bending resistance, burst strength and wet strength according to the standard methods in table 5.

Table 5 Standard methods used in the sheet characterization

| Property | Standard method | Instrument |
|---|---|---|
| Grammage | ISO 536 | |
| Thickness | ISO 534 | |
| Tensile strength (X-Y direction) | ISO 1924 | Alwetron TH1 |
| Z-strength | SCAN-P 80 | Lorentzen & Wettre ZD Tensile Tester |
| Bending resistance (50 mm, angle: 15°) | ISO 2493 | Lorentzen & Wettre |
| Burst strength | ISO 2758 | Lorentzen & Wettre |
| Wet strength | ISO 3781 | Alwetron TH1 |

## Experimental design

The experimental design was prepared and evaluated by using partial least squares projections to latent structures (PLS) in MODDE 8.0 software. It was done in order to find relationships in multivariate datasets with minimal number of trials. PLS has been extensively described in literature and is a multivariable regression method, which is considered to be robust. This method deals with many responses simultaneously, taking their covariance's into account. It provides an overview of the relationship between the results and how all the variables affect all the results (Eriksson, et al. 2000).

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[2] Only added in the second sheet formation

The purpose of the experimental design was to find out in what intervals the process parameters should be varied, thus finding the optimal conditions for the oxidation process.

### Screening experiments

The screening was used in order to find out which factors that influence the process, and to what extent. For each experiment, 12 g oven dry pulp was used and the addition level of sodium hypochlorite was set to 4 mmol/g. In Appendix A, the complete experimental plan for the screening is shown.

In table 6, the parameters that were varied in the screening can be seen.

Table 6 Parameters that were varied in the screening experiments

| Parameter | Low level | Centre point | High level |
|---|---|---|---|
| **TEMPO [mg/g]** | 8 | 12 | 16 |
| **NaBr [mg/g]** | 50 | 75 | 100 |
| **pH** | 9 | 9.5 | 10 |
| **Temperature [°C]** | 25 | 27.5 | 30 |
| **P.C. [%]** | 1 | 2 | 3 |
| **Agitation** | 1 | 3 | 5 |

### Main experiments

In the following experiments some changes compared to the screening were done in order to optimize the process conditions. As in the screening, 12 g oven dry pulp was used for each experiment. In table 7, the fixed parameters can be seen. In Appendix B, the complete experimental plan for these experiments is shown.

Table 7 Parameters that were fixed in the main experiments

| Parameter | Level |
|---|---|
| **NaClO [mmol/g]** | 4 |
| **Temperature [°C]** | 30 |
| **P.C. [%]** | 2 |
| **Agitation [rpm]** | 570 (“good”) |

The parameters that were varied in the main experiments are presented in table 8.

Table 8 Parameters that were varied in the main experiments

| Parameter | Low level | Centre point | High level |
|---|---|---|---|
| **TEMPO [mg/g]** | 4 | 6 | 8 |
| **NaBr [mg/g]** | 25 | 37.5 | 50 |
| **pH** | 9 | 10 | 11 |
| **Oxidation time** | 120 | 160 | 180 |

# Results and discussion

The results of this study are divided into two parts. The first part deals with the relationship between the process conditions in the TEMPO-mediated oxidation and the second part evaluates the nanofibers as a binder in paper sheets.

## TEMPO-mediated oxidation

The TEMPO-mediated oxidation was carried out in two steps. First, a screening was made in order to find the most important process parameters. Using the gained experience and results from these experiments another set of experiments was carried out, which are referred to as the main experiments.

### Screening experiments

The results from these experiments are presented in table 9. These results were then evaluated and used for planning of further experiments, trying to find the optimum process conditions for manufacturing of nanofibers.

Table 9 Properties of the oxidized fibers in the screening experiments

| Exp. No. | TEMPO [mg/g] | NaBr [mg/g] | pH | T [C°] | P.C. [%] | Ag.[3] [rpm] | Oxidation time [min] | Residual NaClO [kg/t] | Length [mm] | Width [µm] | Charge [mmol/kg] | Viscosity [dm$^3$/kg] | WRV [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Ref.** | | | | | | | | | 0.85 | 21.3 | 45 | 997 | |
| **2** | 8 | 50 | 9 | 30 | 1 | 5 | 260 | 11.6 | 0.93 | 21.8 | 1189 | 153 | 380 |
| **3** | 8 | 100 | 10 | 30 | 1 | 1 | 210 | 2.1 | 0.92 | 22.0 | 980 | 134 | 440 |
| **4** | 16 | 100 | 9 | 25 | 1 | 5 | 210 | 11.5 | 0.94 | 21.5 | 1080 | 157 | 460 |
| **5** | 16 | 50 | 10 | 25 | 1 | 1 | 200 | 3.9 | 0.92 | 22.0 | 1007 | 133 | 480 |
| **6** | 12 | 75 | 9.5 | 27.5 | 2 | 3 | 134 | 1.7 | 0.92 | 21.7 | 1033 | 143 | 430 |
| **7** | 12 | 75 | 9.5 | 27.5 | 2 | 3 | 171 | 1.4 | 0.93 | 21.6 | 1050 | 136 | 440 |
| **8** | 12 | 75 | 9.5 | 27.5 | 2 | 3 | 135 | 1.2 | 0.92 | 21.4 | 1109 | 144 | 380 |
| **9** | 8 | 50 | 10 | 25 | 3 | 5 | 156 | 1.5 | 0.90 | 22.2 | 1032 | 136 | 820 |
| **10**[4] | 16 | 100 | 10 | 30 | 3 | 5 | 92 | 1.5 | 0.55 | 24.9 | 1004 | 118 | 790 |
| **11** | 16 | 50 | 9 | 30 | 3 | 1 | 120 | 1.5 | 0.65 | 24.9 | 786 | 110 | 930 |
| **12** | 8 | 100 | 9 | 25 | 3 | 1 | 115 | 3.3 | 0.90 | 23.4 | 963 | 133 | 780 |
| **8B**[5] | 12 | 75 | 9.5 | 27.5 | 2 | 3 | 130 | 0.9 | 0.92 | 21.7 | 1071 | | |
| **10B** | 16 | 100 | 10 | 30 | 3 | 5 | | 0.9 | 0.91 | 21.7 | 910 | 133 | |

The difference between the oxidized fibers and the reference pulp can be seen by comparing the total fiber charge, the water retention value and the intrinsic viscosity. The total fiber charge and the water retention value are much higher for the oxidized fibers. The total fiber charge is greatly increased by the oxidation. The reference pulp has a total fiber charge of approximately 45 mmol/kg, which can be compared to the oxidized fibers that range from 1000 to 1200 mmol/kg in total fiber charge. It can be seen in table 9 that the oxidation increases the water retention value of the fiber. Contrariwise, the viscosity of the oxidized fibers is immensely lower compared to the reference pulp. More exactly, a tenfold decrease in viscosity, from 997 to about 140 dm$^3$/kg, can be seen. These results are in accordance with earlier published research. Concerning fiber swelling, measured as the water retention value, the bulk charges are of high importance, since a large number of bulk charges contribute to the swelling behavior and flexibilization of the fiber (Horvath 2006). This swelling behavior of the fiber is

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[3] Ag.: Agitation, 1: low, 3: medium, 5: high
[4] Sample 10 and 11 were excluded
[5] One of the center points was done twice at lower oxidation time

encountered whenever any substance is added or removed from the wood cell wall, e.g. in chemical modifications (Mantanis, Young and Rowell 1994).

In table 9, it can be seen that the oxidized fibers with a pulp consistency of 1-2 % showed quite uniform fiber dimensions. The length is approximately 0.92 mm and the width ranging from 21.5 to 22 µm, which is consistent with the unoxidized fiber dimensions used as a reference in this table. However, when the pulp consistency was changed to 3 % the character of the oxidized fibers altered compared to 1-2 % pulp consistency. The fiber dimensions differed significantly, the length decreased and the width increased. The increased width indicated a swelling of the fibers. Furthermore, a drop in both total fiber charge and viscosity, and an increase in water retention value were also observed for these samples.

Two of the samples, number 10 and 11, differed radically from the other samples without any obvious reason. Therefore, one of these samples, number 10, was repeated in order to control if these odd results were correct or not. This time the amount of sample was tripled, i.e. increased from 12 to 36 g, in order to get a better agitation. The most unaccountable result from the first experiment was the fiber length which was considerably shorter than all the other samples. The underlying cause of the shorter fibers in the first experiment can be associated with the locally unstable pH, probably due to bad agitation in combination with high pulp consistency. This may have caused scissoring of the fibers. Therefore, these two samples were excluded from the experimental plan.

The purpose of the screening was to evaluate what process parameters that influence the oxidation and to what extent. In figure 11, an example of an effect plot can be seen. This plot shows the difference between the highest and the lowest level in the experimental plan, i.e. it describes at which level the experiments have been carried out. As can be seen in figure 11, the total fiber charge decreases with increasing pH. The remaining effect plots can be seen in Appendix C.

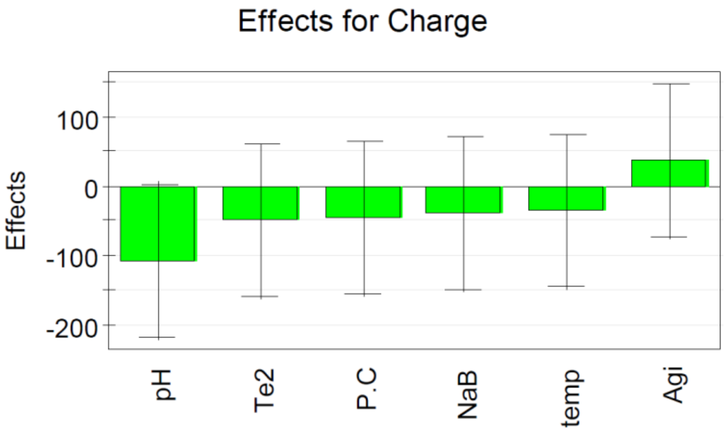

**Figure 11 The effect plot for the total fiber charge in the screening experiments. Te2: TEMPO, P.C: pulp consistency, NaB: sodium bromide, temp: temperature, Agi: agitation.**

From the screening experiments and as have been discussed above the pulp consistency as well as pH appeared to be very important parameters in the TEMPO-mediated oxidation. In Appendix C, the effect plots reveal that pH is a significant variable for nearly all results. According to the literature, the optimum pH-value for hardwood celluloses with regard to oxidation time is pH 10 (Saito, Kimura, et al. 2007). Due to that, in combination with the fact that pH appeared to play a significant role in the performed experiments, pH will be varied in further experiments, but between 9 and 11 instead of 9 and 10.

Regarding the pulp consistency, it was decided to keep it on a constant level in further experiments, more exactly at 2 %. This was done in order to overcome the agitation problems.

From the effect plots, see Appendix C, the effects of the TEMPO and the sodium bromide addition levels were minor and not significant. These addition levels were probably not low enough to be able to see any effects, i.e. the amounts were not limiting. It is desirable to reduce the addition levels both from an economical and an environmental point of view. Therefore, these amounts were reduced in the plan for further experiments. More exactly, the lowest amounts of both TEMPO and sodium bromide from the screening corresponds to the highest amounts in further experiments.

Furthermore, it appeared to be very hard to model the amount of residual sodium hypochlorite without having a given oxidation time. Therefore, the oxidation time was set to a given time and varied, in three different levels, in further experiments. The addition level of sodium hypochlorite was remained at the same level as in the screening experiments, i.e. 4 mmol/gram.

In all, or at least in nearly all, of the screening experiments the temperature was higher than what it should be. This is because the reaction is exothermic. Therefore, it was decided to set the temperature to one given value. The best choice seemed to be the highest temperature, 30 °C, since the reaction rate is higher the higher the temperature. The agitation during the oxidation process is quite important. The low, medium and high agitations from the screening are thereby replaced by just one degree of agitation, i.e. good agitation.

### *Summary of the screening experiments*

Based on the results from the screening study it was decided that the main experiments ought to be carried out at a temperature of 30 °C. The addition levels of TEMPO and sodium bromide were to be further reduced and the amount of sodium hypochlorite was kept at 4 mmol/g. Furthermore, the pulp consistency was set to 2 % and all main experiments were carried out with good agitation. It was decided to control the oxidation time and vary it between 120-180 minutes. The pH range was expanded to include pH 11.

## Main experiments

In the following pages the results from the main experiments will be presented and discussed. These results are separated into groups depending on pH. First, the experiments carried out at pH 9 are discussed, followed by pH 10, pH 11 and pH 10.5.

### *pH 9*

During these experiments no specific observations were made, except for that after approximately 30 minutes the slurry turned splashy. A different sound could be heard and the agitation was therefore decreased from 570 $\text{min}^{-1}$ to approximately 500 $\text{min}^{-1}$. This transition was also observed in the other experiments but after different oxidation times, indicating different reaction rates. The analytical methods following the oxidation were carried out according to the standard procedures and no difficulties were encountered.

**Table 10 Properties of the oxidized fibers in the main experiments carried out at pH 9**

| Exp. No. | TEMPO [mg/g] | NaBr [mg/g] | pH | Oxidation Time [min] | Residual NaClO [kg/t] | Length [mm] | Width [µm] | Charge [mmol/kg] | Viscosity [$dm^3$/kg] | WRV [%] |
|---|---|---|---|---|---|---|---|---|---|---|
| **13** | 4 | 25 | 9 | 120 | 51.4 | 0.91 | 21.4 | 885 | 155 | 390 |
| **14** | 8 | 25 | 9 | 120 | 16.5 | 0.91 | 22.5 | 1070 | 137 | 580 |
| **15** | 8 | 50 | 9 | 120 | 11.9 | 0.92 | 22.0 | 1006 | 143 | 410 |
| **16** | 4 | 25 | 9 | 180 | 17.1 | 0.92 | 22.4 | 1016 | 144 | 500 |
| **17** | 8 | 25 | 9 | 180 | 5.8 | 0.89 | 22.5 | 1041 | 141 | 520 |
| **18** | 8 | 50 | 9 | 180 | 11.3 | 0.92 | 22.1 | 1017 | 135 | 460 |
| **19** | 4 | 50 | 9 | 160 | 22.2 | 0.91 | 21.8 | 996 | 148 | 400 |
| **20** | 4 | 41.7 | 9 | 120 | 44.0 | 0.92 | 21.5 | 1075 | 150 | 340 |
| **21** | 6 | 37.5 | 9 | 150 | 6.8 | 0.93 | 22.2 | 1082 | 141 | 430 |

The oxidized fibers at pH 9 are similar in character, which can be seen in table 10. A higher viscosity, approximately 20 units higher, was observed at pH 9 compared to the oxidized pulps at pH 10. The fiber dimensions were uniform, the fiber length was approximately 0.91 mm and the width was about 22 µm. The water retention value varied from 340 to 580 % and the total fiber charge ranges from 885 to 1082 mmol/kg. In general, the combination low total fiber charge, low water retention value and high viscosity can be seen. But this is not always true, for example number 20 has high total fiber charge but low water retention value and high viscosity.

In the experiment number 13 which was carried out with minimum dosages, i.e. 25 mg NaBr/g and 4 mg TEMPO/g, and oxidation time 120 minutes, a large amount of residual sodium hypochlorite was found in the filtrate after the oxidation. However, the total fiber charge is somewhat lower, 885 mmol/kg compared to 1000-1100 mmol/kg. This difference is probably due to higher reaction rate when the amount of catalysts is increased. If the amount of TEMPO was doubled to 8 mg/g, less sodium hypochlorite was left in the filtrate, probably due to a higher reaction rate. The fact that low addition levels of TEMPO and sodium bromide bring about lower reaction rate is in accordance with earlier published research.

### *pH 10*

In the experiments at pH 10 the splashy character of the slurry was observed earlier than at pH 9, approximately after 15-20 minutes. Some problems were also encountered during the second washing step, it took long time to finish and the filtrate had to be recirculated two or three times in order to recover fines material. The results from these experiments are listed in table 11.

**Table 11 Properties of the oxidized fibers in the main experiments carried out at pH 10**

| Exp. No. | TEMPO [mg/g] | NaBr [mg/g] | pH | Oxidation Time [min] | NaClO [kg/t] | Length [mm] | Width [µm] | Charge [mmol/kg] | Viscosity [$dm^3$/kg] | WRV [%] |
|---|---|---|---|---|---|---|---|---|---|---|
| **22** | 6.7 | 25 | 10 | 120 | 2.5 | 0.90 | 24.1 | 961 | 121 | 790 |
| **23** | 5.3 | 50 | 10 | 120 | 1.6 | 0.89 | 23.8 | 1058 | 117 | 750 |
| **24** | 4 | 33.3 | 10 | 180 | 1.4 | 0.77 | 25.0 | 918 | 124 | 880 |
| **25** | 8 | 37.5 | 10 | 150 | 1.4 | 0.84 | 24.5 | 1003 | 115 | |

When the pH was increased to 10 the fiber dimensions were altered, i.e. the oxidized fibers became a bit shorter and the wider, see table 11. The intrinsic viscosity was also lower, which can be related to the decrease in fiber length. Swelling can be related to the increased water retention value, which also was observed. By comparing the water retention values from pH 9 and pH 10, a rather big difference can be seen. It is known that a more pronounced fiber swelling occurs at higher pH and this observation can to some extent be explained by this fact. Though, the water retention values at pH 10 are nearly twice as high as those at pH 9. Therefore, in this case it may have to do with a combination of high pH and something else. The total fiber charge is an important factor regarding the fiber swelling, but the total fiber charges of the different pH-values are nearly the same. So, these results are rather tricky to explain.

Regarding the total fiber charge, which also affects the water retention value, no significant difference in comparison to the results using pH 9 was observed. However, there was considerably less hypochlorite left in the filtrate after the oxidation, indicating a higher reaction rate.

### *pH 11*

During the experiments carried out at pH 11, major problems were encountered. These are of high importance from a process technical point of view. It was found that the pH was almost impossible to keep at a constant level, which affects the whole oxidation process to a large extent.

In the experiments performed at pH 9 and 10, a kind of a transition in viscosity of the fiber suspension was clearly observed. After a while, the slurry became splashier. This behavior was seen after approximately 60 minutes when the pH was set to 11.

A decrease in the viscosity of the pulp suspension was observed. It seemed as if the pulp consistency had decreased and the suspension appeared milk-white. The filter cake after oxidation seemed much thinner with no gel character; it seemed dry and very dense. Lots of fines could be seen in the filtrate after the washing procedure. Only one or two washing steps were done due to the difficulties in the washing. These observations indicate yield loss and scissoring of the fibers. The significantly different result in the TEMPO-mediated oxidation at high pH might therefore be explained by fiber scissoring. Due to the low total fiber charge, it seems that the desired reaction on the C-6 position on the cellulose does not occur to the same extent as at lower pH. Instead the chemicals might attack the fiber elsewhere; an undesired side-reaction could be a ring opening at the C-2 – C-3 position.

In earlier research it was believed that side-reactions of the nitrosonium ion account for the rate decrease at high pH (Bragd, Besemer and van Bekkum 2000). Furthermore, it has been reported that the nitrosonium ion reacts with hydroxyl ions at pH-levels above 9 and reverts to the TEMPO radical, while forming hydrogen peroxide (Endo, et al. 1984).

In 2007, Dang et al. discussed depolymerization of polysaccharides during TEMPO-mediated oxidation. Several explanations from earlier research was mentioned, such as the effect of sodium hypochlorite in the oxidation, which may cause scissioring at C-2 – C-3 of the glucose unit, resulting in the formation of dialdehyde and dicarboxylic structures. It was also mentioned that the presence of carbonyl groups at C-2 and C-3 in glucose units can cause depolymerization of celluloses via β-alkoxy fragmentation at alkaline conditions. Furthermore, β-elimination was also mentioned as a probable cause of depolymerization (Dang, Zhang and Ragauskas 2007).

In addition, it was not possible, or very difficult, to perform the pretreatments of either total fiber charge– or water retention value measurements. The filter cakes became very hard and were easily broken, even a bit brittle and the filtration took very long time. However, two total fiber charge measurements were done but not according to the standard procedures, the starting conductivity might have been too high.

**Table 12 Properties of the oxidized fibers in the main experiments carried out at pH 11**

| Exp. No. | TEMPO [mg/g] | NaBr [mg/g] | pH | Oxidation Time [min] | Residual NaClO [kg/t] | Length [mm] | Width [µm] | Charge [mmol/kg] | Viscosity [$dm^3$/kg] |
|---|---|---|---|---|---|---|---|---|---|
| **26** | 8 | 25 | 11 | 120 | 47.5 | 0.55 | 26.0 | 472 | |
| **28** | 4 | 50 | 11 | 180 | 1.4 | 0.33 | 33.6 | | |
| **29** | 8 | 25 | 11 | 180 | 15.7 | | | | |
| **31** | 4 | 25 | 11 | 160 | 63.3 | 0.61 | 24.2 | 556 | 137 |
| **32** | 4 | 50 | 11 | 140 | 8.2 | | | | |

Due to the above mentioned difficulties, these samples have not been characterized fully. However, it can be said that these fibers were short, very much swelled and had low total fiber charge compared to the other samples at pH 9 and 10, see table 12.

Because of technical problems and results that differed markedly from the other experiments, it was decided that the remaining experiments aimed to be carried out at pH 11, were carried out at pH 10.5 instead.

### *pH 10.5*

The results of the oxidation at pH 10.5 were similar as for pH 11.These experiments behaved in similar manner as previously. Therefore, it was decided that the oxidation time should be halved. This was done in order to study if the theory of the chain scissoring could be a possible reason.

Still, it was difficult to keep the pH at a constant level. Furthermore, the slurry went straight through the 112 µ nylon sieve, when it was filtrated. Turning to 5µ, the filter cake showed the same characteristics as earlier, i.e. dry and dense. Likewise, the washing steps were still problematic and time-consuming to perform. A lot of fines could be seen in the filtrate although the filtrate was recirculated two or three times.

**Table 13 Properties of the oxidized fibers in the main experiments carried out at pH 10.5**

| Exp. No. | TEMPO [mg/g] | NaBr [mg/g] | pH | Oxidation Time [min] | Residual NaClO [kg/t] | Length [mm] | Width [µm] | Charge [mmol/kg] | Viscosity [$dm^3$/kg] |
|---|---|---|---|---|---|---|---|---|---|
| **27** | 8 | 50 | 10.5 | 120 | 1.7 | 0.37 | 29.0 | 836 | 104 |
| **27B** | 8 | 50 | 10.5 | 60 | 17.4 | 0.79 | 24.6 | 779 | 114 |
| **30** | 8 | 50 | 11 | 180 | | | | | |
| **31B** | 4 | 25 | 10.5 | 80 | 76.5 | 0.56 | 24.0 | 759 | 121 |
| **33** | 4 | 33.3 | 11 | 120 | | | | | |
| **34** | 6 | 37.5 | 10.5 | 180 | 1.3 | 0.34 | 30.1 | | |
| **35B** | 6 | 37.5 | 10.5 | 75 | 55.5 | 0.46 | 26.5 | 650 | 108 |
| **36** | 6 | 37.5 | 11 | 150 | | | | | |
| **37B** | 6 | 37.5 | 10.5 | 75 | 52.8 | 0.48 | 26.3 | | |

At first, the decreased oxidation time seemed to be better. Two experiments, number 27B and 31B, were somewhat easier to control. When comparing the results from number 31, pH 11 and 160 minutes, and number 31B, pH 10.5 and 80 minutes, some interesting differences could be seen. The fiber length is slightly decreased but the total charge of the fibers increased from 556 to 759 mmol/kg, as can be seen in table 13. As have been discussed earlier, the pH affects the reaction rate but the total charge of the fiber was also increased, indicating that the reaction is directed towards the cellulose C-6 position. Additionally, when the time is halved, comparing the results from number 27 and 27B, the fiber length was almost doubled and less swelling was seen. On the other hand, the fiber was less charged, decreased from 836 to 779 mmol/kg. Apparently, the oxidation reaction happens first and then the scissoring takes over.

The two last experiments, number 35B and 37B, were also difficult to perform. Yield losses were observed during the first washing-step, and were further increased during the second step. Thus, no filter cake was obtained. Probably, stirring caused fiber swelling and decomposition.

As expected, it was troublesome to prepare the total fiber charge- and water retention value measurements according to the standard procedures, due to aforementioned problems during the washing and filtration.

In the main experiments, the number of parameters has been reduced compared to the screening. As in the screening, the pH was found to be a significant parameter which affects all of the results, to varying extents. This effect can be seen in figure 12, where the effect plot for the total fiber charge is shown as an example. Furthermore, there were more significant parameters compared to the screening.

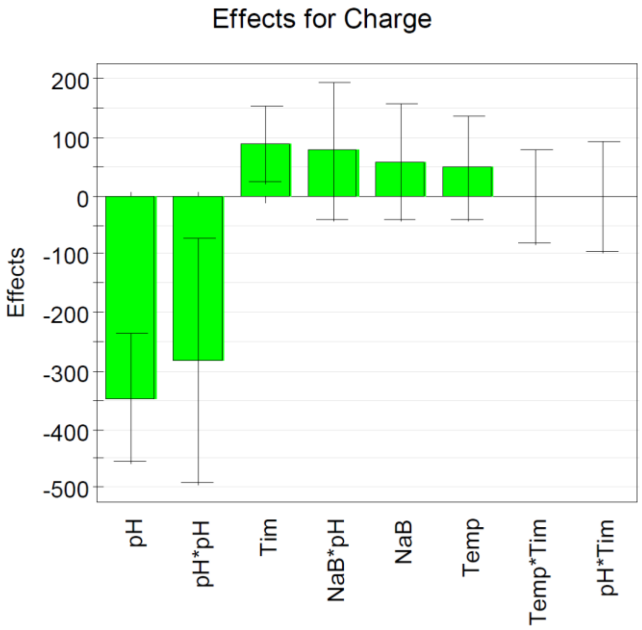

**Figure 12 The effect plot for the total fiber charge in the main experiments. pH*pH: combination effect of pH, Tim: time, NaB*pH: combination effect of sodium bromide and pH, NaB: sodium bromide, Temp: Tempo, Temp*Tim: combination effect of Tempo and time, pH*Tim: combination effect of pH and time.**

The predicted model showed no extreme errors. In the figures in Appendix E, the standard deviations can be seen in the normal distribution plots. Because the standard deviations showed a linear relationship, the error in the model can be regarded as standardized.

Regarding the prediction plots, optimum conditions can for instance be seen for the residual hypochlorite, the intrinsic viscosity and the water retention value.

The model predicted that the total fiber charge will decrease as pH is increased. The total fiber charge predicted for pH is shown in figure 13. The black line is the mean expectation value and the blue and the green line represent the upper and the lower confidence interval, respectively. The remaining prediction plots for pH can be seen in Appendix F.

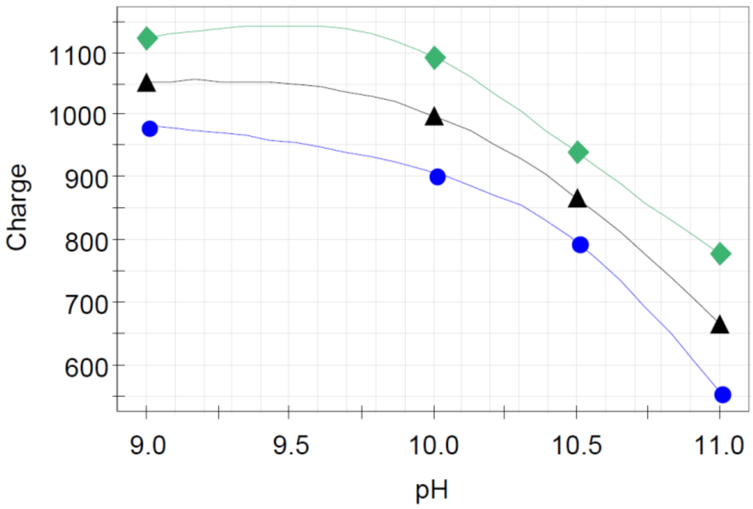

Figure 13 The total fiber charge predicted for pH.

## Mixing of the oxidized fibers

Some of the oxidized fibers were converted into nanofibers by using a mixing procedure. In table 14 it can be seen that the fiber dimensions are affected by the mixing, i.e. the length of the remaining fibers was much shorter than before. However, because there were remaining fibers left after mixing this procedure has to be further developed in order to achieve complete conversion to nanofibers. When the mixed oxidized fibers were centrifuged almost no separation could be seen. This result indicated that the remaining fibers were well embedded in the nanofiber gel.

Table 14 Fiber dimensions before and after mixing

| Exp. No. | Length before mixing [mm] | Width before mixing [μm] | Length after mixing [mm] | Width after mixing [μm] |
|---|---|---|---|---|
| **Ref.** | 0.85 | 21.3 | | |
| **2** | 0.93 | 21.8 | 0.67 | 23.6 |
| **3** | 0.92 | 22.0 | 0.40 | 24.0 |
| **4** | 0.94 | 21.5 | 0.90 | 22.0 |
| **5** | 0.92 | 22.0 | 0.57 | 24.1 |
| **6** | 0.92 | 21.7 | 0.60 | 23.9 |
| **7** | 0.93 | 21.6 | 0.54 | 24.1 |
| **8** | 0.92 | 21.4 | 0.62 | 23.9 |
| **9** | 0.90 | 22.2 | 0.40 | 25.6 |
| **10** | 0.55 | 24.9 | 0.58 | 23.7 |
| **11** | 0.65 | 24.9 | 0.63 | 22.6 |
| **12** | 0.90 | 23.4 | 0.62 | 23.4 |
| **8B** | 0.92 | 21.7 | 0.61 | 24.2 |
| **10B** | 0.91 | 21.7 | 0.33 | 25.3 |

During the screening experiments it was shown that the mixing process after the oxidation has a large impact on the conversion to nanofibers, a larger impact than previously thought. In the beginning of this master thesis an old mixer was used, that worked well for certain mixing times and volumes. The mixing resulted in very nice gels. However, when a new mixer was used the gels appeared to have a lower rheology and the fiber length was somewhat longer, see table 15, indicating a lower degree of fiber delamination. The viscosity of the gels is associated with the amount of nanofibers. The old mixer was probably better in converting the oxidized pulp fibers into nanofibers.

Table 15 Fiber dimensions after mixing in two different household mixers

| Exp. No. | Length before mixing [mm] | Length after mixing, old mixer [mm] | Length after mixing, new mixer [mm] |
|---|---|---|---|
| **Ref.** | 0.85 | | |
| **2** | 0.93 | 0.56 | 0.67 |
| **3** | 0.92 | 0.36 | 0.40 |
| **4** | 0.94 | 0.74 | 0.90 |

### *Summary of the main experiments*

Based on the results of the main experiments it has been shown that pH is of high importance during the oxidation. It affected the oxidation procedure as well as the oxidized fiber properties to a large extent. If the pH was raised above 10, the oxidation procedure became difficult to control and the analyses were complicated to perform. Above this pH-level the product properties deteriorated, yield losses and degradation were observed. Furthermore, the difficulties during the washing procedure were more pronounced with increasing pH.

The samples oxidized at pH 9 resulted in unchanged fiber dimensions and the highest total fiber charge. However, the total fiber charge of the oxidized fibers at pH 10 is comparable to the samples at pH 9. Regarding the water retention value, the samples from pH 10 resulted in higher values than those from pH 9. The reaction rate was also higher for the samples performed at pH 10, indicated by a lower amount of residual sodium hypochlorite in the filtrate.

Low addition levels of TEMPO and sodium bromide indicated a lower reaction rate, which in turn resulted in rather high amounts of residual sodium hypochlorite in the filtrate and lower total fiber charge at a given time.

## Evaluation of nanofibers as a binder in paper sheets

Three nanofiber products were used to evaluate their impact on the strength properties of paper sheets. In table 16, the total fiber charge of these nanofiber products can be seen.

For each product, three different addition levels of nanofibers were investigated; 10, 20 and 50 kg/t.

The purpose of adding polyaluminium chloride in one of the two sheet formations, was to improve the adhesion of nanofibers to the pulp fibers.

Table 16 The products evaluated as a binder in paper sheets

| Nanofiber product | Exp. No. | Charge [mmol/kg] | pH |
|---|---|---|---|
| **High charge** | 14 | 1070 | 9 |
| **Medium charge** | 22 | 961 | 10 |
| **Low charge** | 27 | 836 | 10.5 |

### Sheet formation number 1

In this sheet formation, no polyaluminium chloride was added. In table 17, properties of the paper sheets prepared in this sheet formation can be seen.

Table 17 Properties of the paper sheets in the first sheet formation

| Nanofiber product (Addition level) [kg/t] | Sample | Density [kg/m$^3$] | Tensile index [kNm/kg] | Tension index [%] | Work index [J/kg] | Stiffness index [MNm/kg] | Z-strength [kPa] | Bending resistance index [Nm$^6$/kg$^3$] | Burst strength [kPam$^2$/g] | Wet strength index [kNm/kg] |
|---|---|---|---|---|---|---|---|---|---|---|
| **0** | 1 | 223 | 11 | 0.79 | 47 | 2.3 | 63 | 40 | 0.34 | 0 |
| **0** | 2 | 288 | 29 | 1.29 | 238 | 4.0 | 180 | 37 | 1.41 | 5.3 |
| **High (10)** | 3 | 293 | 34 | 1.43 | 319 | 4.3 | [6] | 37 | 1.67 | 4.7 |
| **High (20)** | 4 | 317 | 39 | 1.55 | 396 | 4.8 | 216 | 34 | 1.88 | 5.9 |
| **High (50)** | 5 | 386 | 49 | 1.83 | 600 | 5.5 | 422 | 25 | 2.62 | 6.8 |
| **Medium (10)** | 6 | 309 | 34 | 1.68 | 368 | 4.1 | 204 | 33 | 1.84 | 5.5 |
| **Medium (20)** | 7 | 315 | 38 | 1.57 | 388 | 4.6 | 227 | 34 | 1.91 | 4.9 |
| **Medium (50)** | 8 | 357 | 44 | 1.74 | 512 | 5.1 | 348 | 30 | 2.50 | 5.8 |
| **Low (10)** | 9 | 309 | 34 | 1.46 | 318 | 4.3 | 236 | 33 | 1.87 | 5.3 |
| **Low (20)** | 10 | 320 | 35 | 1.55 | 357 | 4.4 | 251 | 33 | 2.08 | 4.9 |
| **Low (50)** | 11 | 355 | 38 | 1.5 | 379 | 4.9 | 338 | 28 | 2.44 | 5.0 |

In figure 14, it is clearly shown that the higher the addition levels of nanofibers the higher tensile strength. It can also be seen that a higher total fiber charge results in a higher tensile strength, i.e. the sample with high total fiber charge showed the best results regarding the tensile strength. Furthermore, the higher the addition levels of nanofibers the bigger difference between the three nanofiber products. The tensile strength is nearly 30 % higher for the product with high total fiber charge compared to the low fiber charge product when adding 50 kg/t.

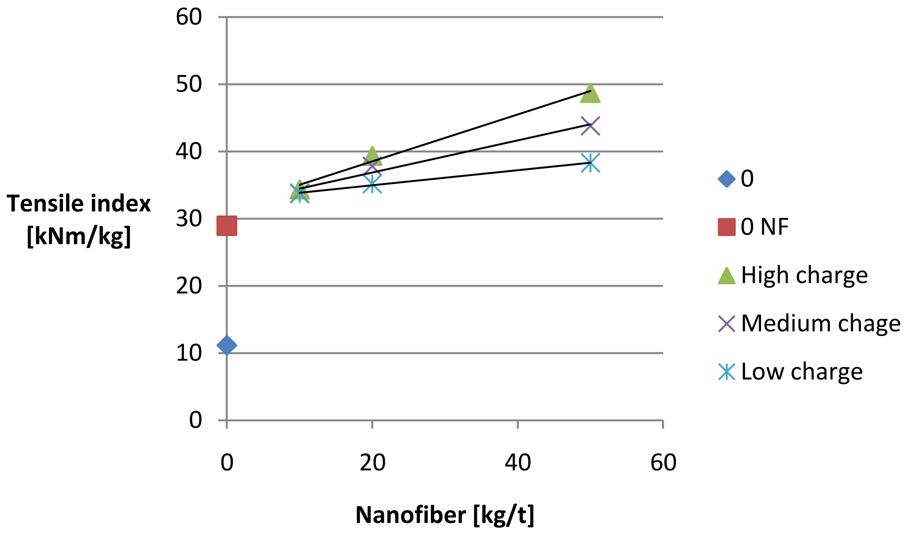

Figure 14 Tensile strength of the paper sheets in the first sheet formation.

The importance of having a good product with high total fiber charge should be highlighted. For instance, the addition level of the product with high total fiber charge can be reduced from 50 to 20

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[6] This measurement failed

kg/t and still retain the same tensile strength as if 50 kg/t of the product with low total fiber charge was added.

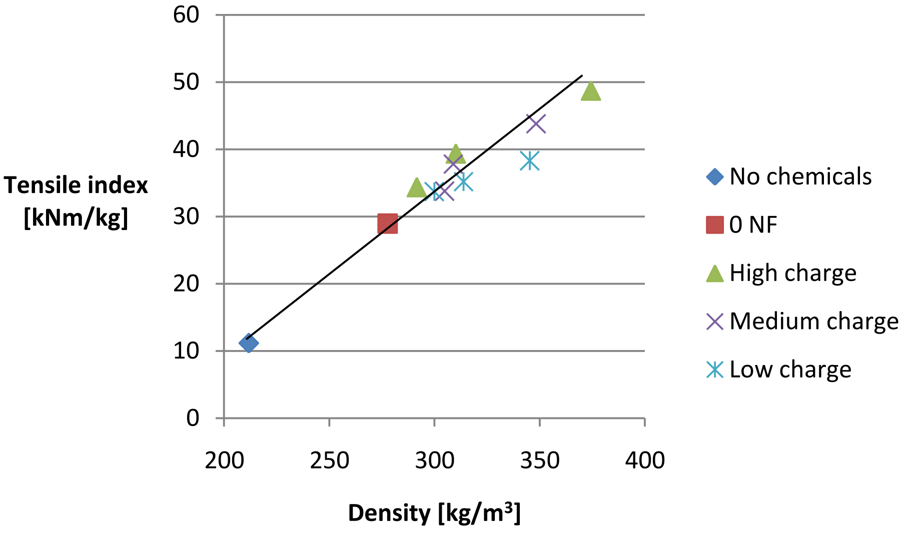

Figure 15 Relationship between tensile strength and density in the first sheet formation.

As expected, the relationship between the tensile strength and the density was linear, which is depicted in figure 15. It is well-known that strength properties correlate well with density.

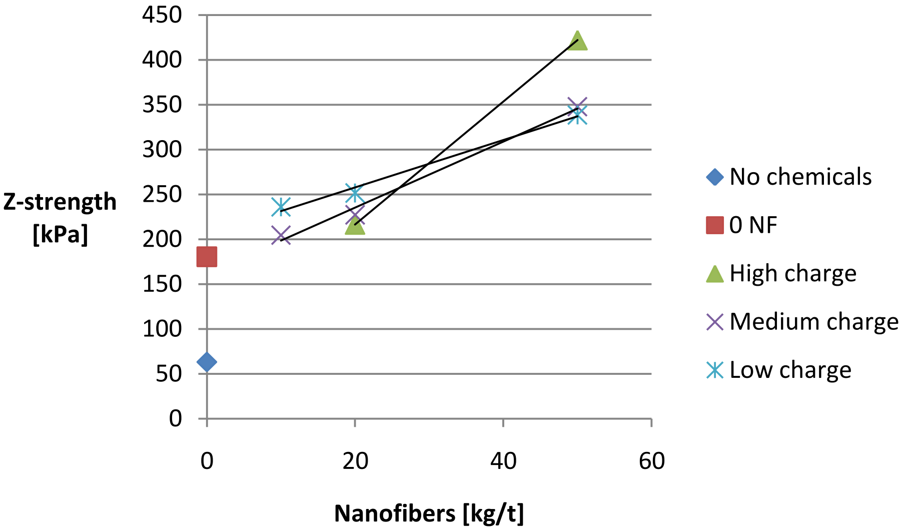

Figure 16 Z-strength of the paper sheets in the first sheet formation.

Regarding the Z-strength, the same trend as for the tensile strength can be seen, i.e. the higher the addition levels of nanofibers the higher Z-strength. This trend can be seen in figure 16. In addition, the sample with high total fiber charge resulted in the best Z-strength.

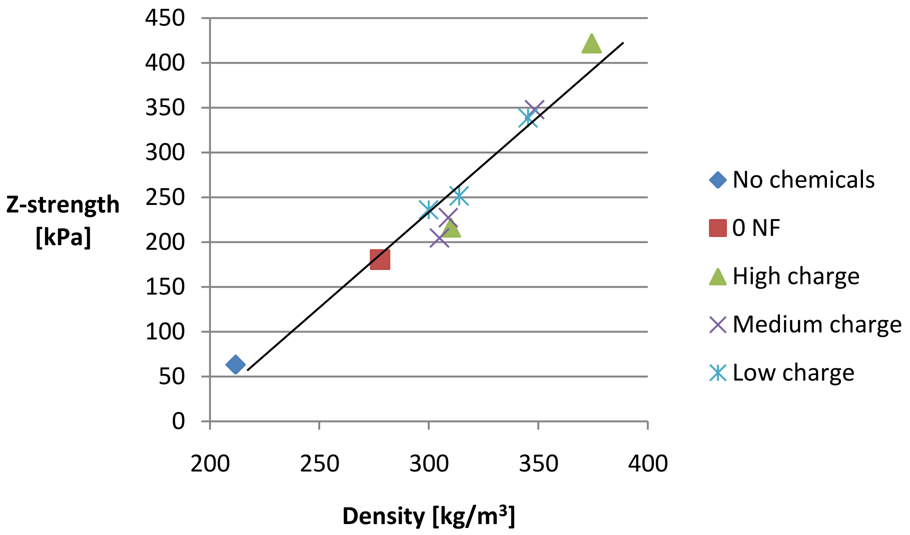

Figure 17 Relationship between Z-strength and density in the first sheet formation.

Also in this case, the density followed a linear relationship, which is shown in figure 17.

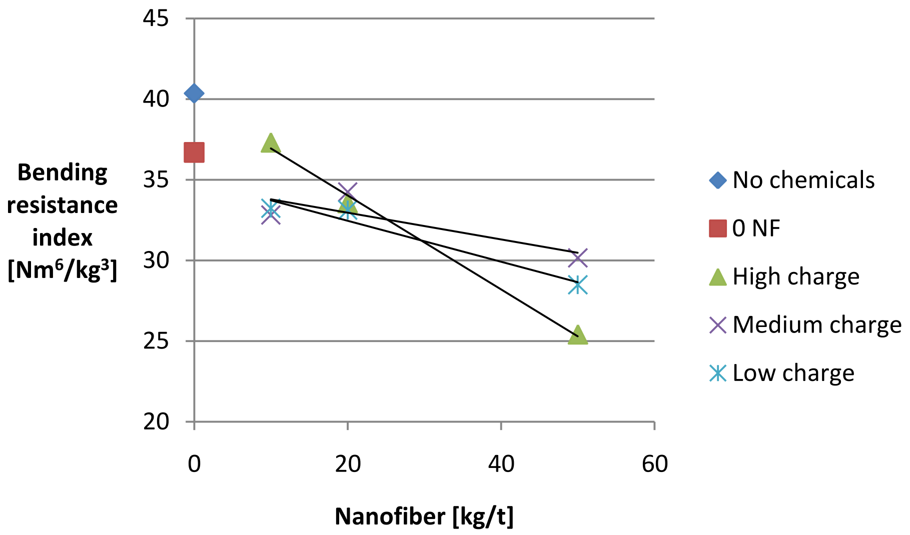

Figure 18 Bending resistance of the paper sheets in the first sheet formation.

In figure 18, it can be seen that higher addition levels of nanofibers resulted in a lower bending resistance. This is true for all the addition levels. Unlike both tensile strength and Z-strength, the reference samples gave better results concerning the bending resistance than the samples where nanofibers were added.

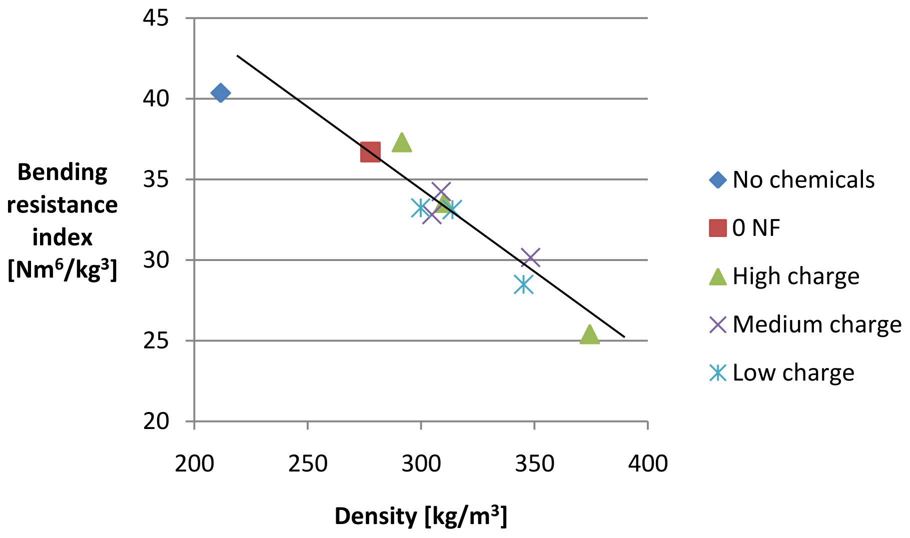

Figure 19 Relationship between bending resistance and density in the first sheet formation.

In figure 19, it can be seen that a high density resulted in a lower bending resistance.

The burst strength showed similar trends as for the aforementioned strength properties, i.e. the higher the addition levels of nanofibers the higher burst strength. In addition, the burst strength showed a linear dependence with the density, see table 16.

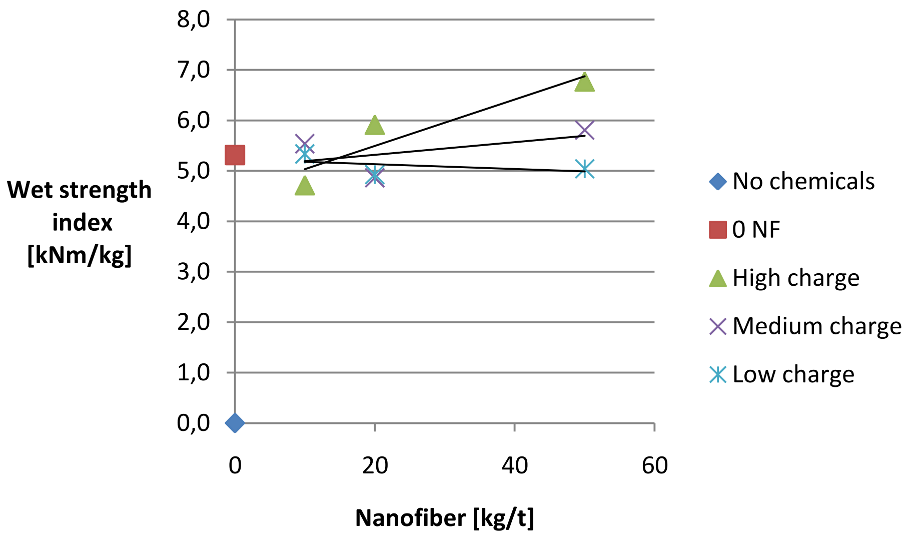

Figure 20 Wet strength of the paper sheets in the first sheet formation.

In figure 20, it can be seen that the wet strength is slightly improved by the addition of nanofibers. These results are in accordance with earlier published research. Probably, this improvement is due to the introduction of surface aldehyde groups contributing to hemiacetal linkages formed between the surface aldehyde groups and the hydroxyl groups of the cellulose at the inter-fiber bonds (Saito and Isogai 2006).

As for the dry strength properties, addition of highly charged nanofibers resulted in better wet strength properties. As earlier mentioned, adding 20 kg/t high charged nanofibers gave similar results as adding

50 kg/t low charged nanofibers. In this context, the amount of added nanofibers can be lowered. Additionally, if very good strength properties are requested, both the total fiber charge and the amount of nanofibers are important factors.

### Sheet formation number 2

In this sheet formation, polyaluminium chloride was added. The results from the measurements can be seen in table 18.

Table 18 Properties of the paper sheets in the second sheet formation

| Nanofiber product (Addition level) [kg/t] | Sample | Density [kg/m$^3$] | Tensile index [kNm/kg] | Tension Index [%] | Work index [J/kg] | Stifffness index [MNm/kg] | Z-strength [kPa] | Bending resistance index [Nm$^6$/kg$^3$] | Burst strength [kPam$^2$/g] | Wet strength index [kNm/kg] |
|---|---|---|---|---|---|---|---|---|---|---|
| **0** | 1 | 242 | 10 | 0.96 | 54 | 1.78 | 65 | 32 | 0.31 | 0 |
| **0** | 2 | 279 | 26 | 1.23 | 203 | 3.61 | 139 | 39 | 1.26 | 5.3 |
| **High (10)** | 3 | 292 | 31 | 1.36 | 266 | 4.01 | 163 | 37 | 1.61 | 5.9 |
| **High (20)** | 4 | 310 | 36 | 1.55 | 368 | 4.51 | 179 | 35 | 1.77 | 6.1 |
| **High (50)** | 5 | 360 | 45 | 1.65 | 485 | 5.12 | 332 | 29 | 2.71 | 7.5 |
| **Medium (10)** | 6 | 291 | 28 | 1.39 | 250 | 3.68 | 144 | 32 | 1.47 | 4.1 |
| **Medium (20)** | 7 | 303 | 33 | 1.42 | 303 | 4.25 | 170 | 37 | 1.69 | 5.7 |
| **Medium (50)** | 8 | 351 | 42 | 1.67 | 469 | 4.97 | 266 | 28 | 2.24 | 6.1 |
| **Low (10)** | 9 | 292 | 29 | 1.33 | 248 | 3.96 | 166 | 37 | 1.61 | 5.7 |
| **Low (20)** | 10 | 316 | 31 | 1.40 | 281 | 4.18 | 219 | 33 | 1.82 | 5.6 |
| **Low (50)** | 11 | 343 | 39 | 1.60 | 408 | 4.70 | 295 | 31 | 2.30 | 7.1 |

This sheet formation resulted in comparable results as the first sheet formation, i.e. the addition of nanofibers enhanced the strength properties of the paper sheets. However, the addition of polyaluminium chloride resulted in somewhat lower tensile strength, Z-strength, bending resistance and burst strength compared to the first sheet formation. However, polyaluminium chloride seemed to improve the wet strength to a small extent.

Polyaluminium chloride is highly charged and the purpose of adding this paper chemical was to try to enhance the adhesion of the nanofibers to the pulp fibers. Unfortunately, this did not work out as well as expected. This might be explained by the formation of precipitates.

By comparing the two sheet formations, it can be seen that the tensile strength in the first formation was better than in the second one, see figure 21. In other words, the addition of polyaluminium chloride caused a slightly lower tensile strength of the paper sheets.

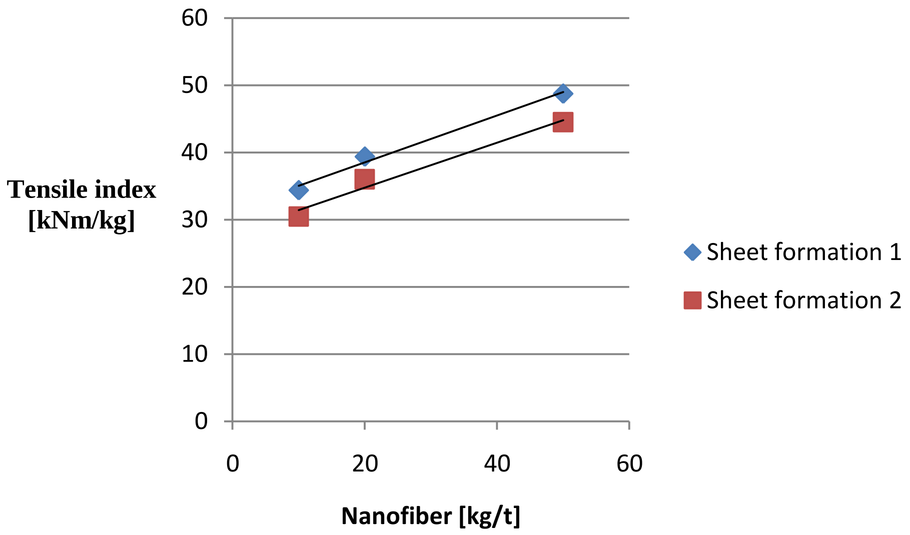

**Figure 21 Tensile index of paper sheets with high charged nanofibers in first and second sheet formation.**

Overall, no noteworthy positive effect by the addition of polyaluminium chloride could be seen.

### *Summary of the evaluation of nanofibers as a binder in paper sheets*

From the evaluation of nanofibers as a binder in paper sheets, it was concluded that nanofibers improve the strength properties of the paper sheets. It was shown that the higher the addition levels of nanofibers the higher strength properties of the paper sheets, both in the X-Y direction and in the Z-direction. The samples with a high total fiber charge resulted in overall better strength properties. Hence, the addition level can be reduced if the total fiber charge is increased. Furthermore, the bending resistance was found to decrease as the addition level of nanofibers increased. Notably, the addition of polyaluminium chloride resulted in an overall slightly lower tensile index compared to the tensile index found without polyaluminium chloride. It was also showed that the wet strength is slightly improved by adding nanofibers. The combination, nanofibers and polyaluminium chloride, additionally increased the wet strength of the paper sheets.

# Conclusions

The conclusions are divided into two parts; TEMPO-mediated oxidation and evaluation of nanofibers as a binder in paper sheets.

## TEMPO-mediated oxidation

- Nanofibers can be prepared at reduced amounts of TEMPO and sodium bromide
- pH is of high importance. It affects the oxidation procedure as well as the properties of the oxidized pulp fibers to a large extent.
- Above pH 10 the oxidation process was difficult to control and the analyses became complicated to perform. The product properties deteriorated, yield losses were evident and degradation significant.
- The difficulties during the washing procedure were more pronounced with increasing pH.
- The total fiber charge of the oxidized fibers was highest in the pH range 9-10.
- The pulp consistency affects the oxidation process; it should not exceed 2 % to assure good agitation.
- If the total fiber charge and the length of the fibers are considered to be the most important properties, the samples from pH 9 showed the best results.
- The reaction rate was also higher for the samples performed at pH 10, indicated by a lower amount of residual hypochlorite in the filtrate.
- Low amounts of TEMPO and sodium bromide indicated a lower reaction rate, which in turn resulted in rather high amounts of residual hypochlorite in the filtrate.
- The mixing process after the oxidation had a large impact on the nanofiber conversion, a much larger impact than previously thought.

## Evaluation of nanofibers as a binder in paper sheets

- In general, the higher the addition levels of nanofibers the better strength properties of the paper sheets.
- The products with high total fiber charge resulted in higher tensile index than the samples with low total fiber charge.
- Reversed, the addition levels of nanofibers can be reduced if the total fiber charge is increased.
- The higher the nanofiber content the lower bending resistance.
- The wet strength was somewhat improved by adding nanofibers.

# Future work

There are several opportunities for further development of the TEMPO-mediated oxidation process to make it more effective. It is of interest to continue to investigate the possibility of lowering the addition levels of both TEMPO and sodium bromide. Especially, the amounts of sodium bromide are important to keep as low as possible concerning its environmental issues. An alternative is a bromide-free process, which is mentioned in the literature.

Another way to trying to minimize the use of these two chemicals, is to evaluate the possibility of recirculating the spent liquor. If it is possible to do this several times, the amounts of TEMPO and sodium bromide used would be clearly reduced.

Concerning the problems with degradation and yield losses during the oxidations performed at high pH, one way to overcome these issues may probably be to keep the pH level at 9, or even lower.

The mechanical treatment after the oxidation, i.e. the conversion of nanofibers, also has to be further examined in order to achieve complete conversion. In this master thesis, two different household mixers have been used, which resulted in rather different appearances of the nanofiber gels. Thus, depending on the actual process conditions and the whole system, the mechanical treatment has to be designed in different ways to reach high conversion levels.

In summary, there are number of factors regarding the TEMPO-mediated oxidation which remain to be explained in order to improve the efficiency of the process.

# Acknowledgements

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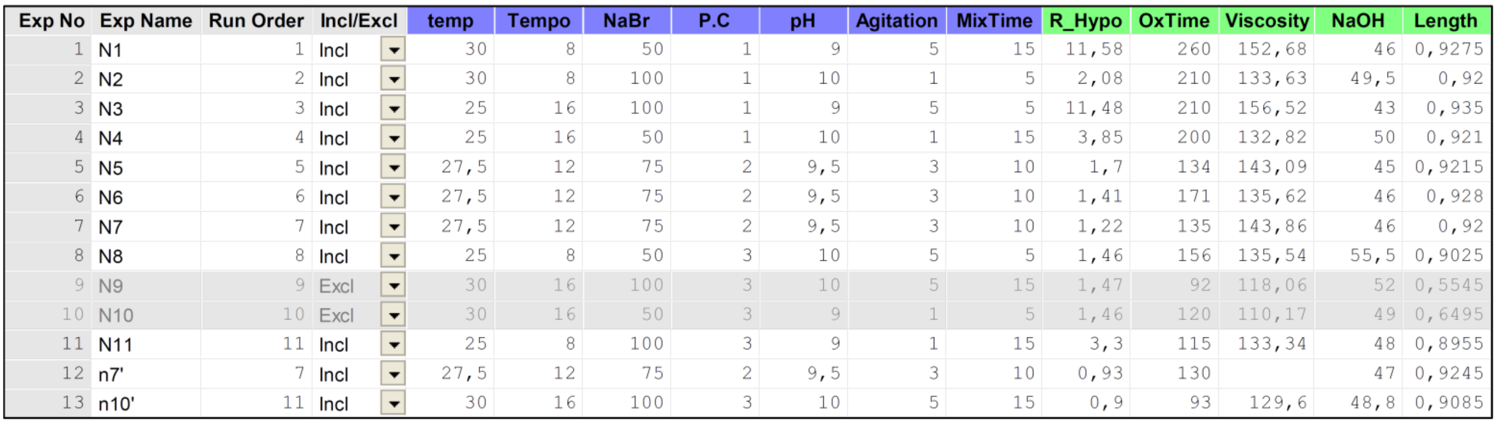
# Appendix A

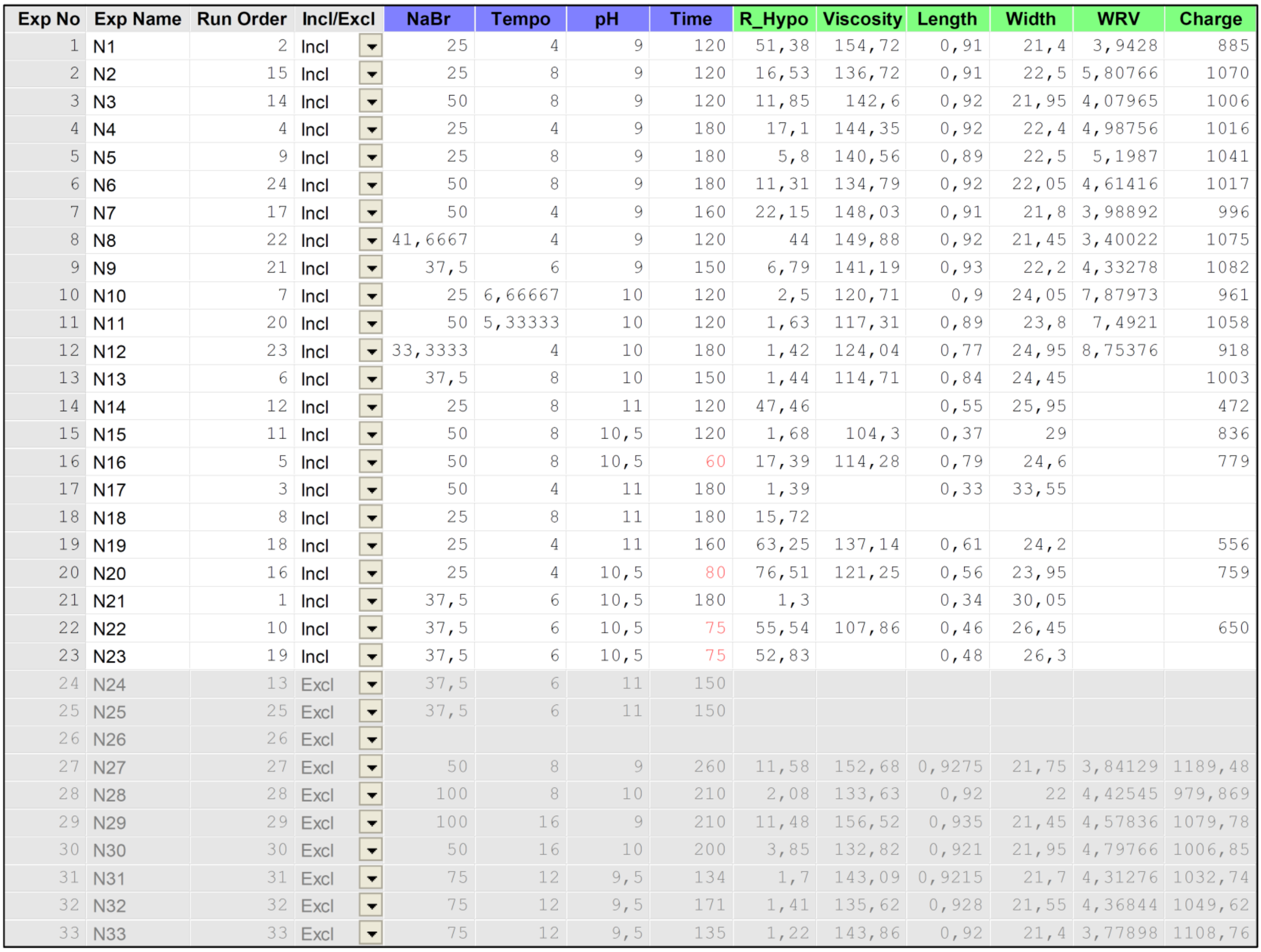
## The experimental plan for the screening



| Exp No | Exp Name | Run Order | Incl/Excl | temp | Tempo | NaBr | P.C | pH | Agitation | MixTime | R_Hypo | OxTime | Viscosity | NaOH | Length |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | N1 | 1 | Incl | 30 | 8 | 50 | 1 | 9 | 5 | 15 | 11,58 | 260 | 152,68 | 46 | 0,9275 |
| 2 | N2 | 2 | Incl | 30 | 8 | 100 | 1 | 10 | 1 | 5 | 2,08 | 210 | 133,63 | 49,5 | 0,92 |
| 3 | N3 | 3 | Incl | 25 | 16 | 100 | 1 | 9 | 5 | 5 | 11,48 | 210 | 156,52 | 43 | 0,935 |
| 4 | N4 | 4 | Incl | 25 | 16 | 50 | 1 | 10 | 1 | 15 | 3,85 | 200 | 132,82 | 50 | 0,921 |
| 5 | N5 | 5 | Incl | 27,5 | 12 | 75 | 2 | 9,5 | 3 | 10 | 1,7 | 134 | 143,09 | 45 | 0,9215 |
| 6 | N6 | 6 | Incl | 27,5 | 12 | 75 | 2 | 9,5 | 3 | 10 | 1,41 | 171 | 135,62 | 46 | 0,928 |
| 7 | N7 | 7 | Incl | 27,5 | 12 | 75 | 2 | 9,5 | 3 | 10 | 1,22 | 135 | 143,86 | 46 | 0,92 |
| 8 | N8 | 8 | Incl | 25 | 8 | 50 | 3 | 10 | 5 | 5 | 1,46 | 156 | 135,54 | 55,5 | 0,9025 |
| 9 | N9 | 9 | Excl | 30 | 16 | 100 | 3 | 10 | 5 | 15 | 1,47 | 92 | 118,06 | 52 | 0,5545 |
| 10 | N10 | 10 | Excl | 30 | 16 | 50 | 3 | 9 | 1 | 5 | 1,46 | 120 | 110,17 | 49 | 0,6495 |
| 11 | N11 | 11 | Incl | 25 | 8 | 100 | 3 | 9 | 1 | 15 | 3,3 | 115 | 133,34 | 48 | 0,8955 |
| 12 | n7' | 7 | Incl | 27,5 | 12 | 75 | 2 | 9,5 | 3 | 10 | 0,93 | 130 |  | 47 | 0,9245 |
| 13 | n10' | 11 | Incl | 30 | 16 | 100 | 3 | 10 | 5 | 15 | 0,9 | 93 | 129,6 | 48,8 | 0,9085 |

# Appendix B

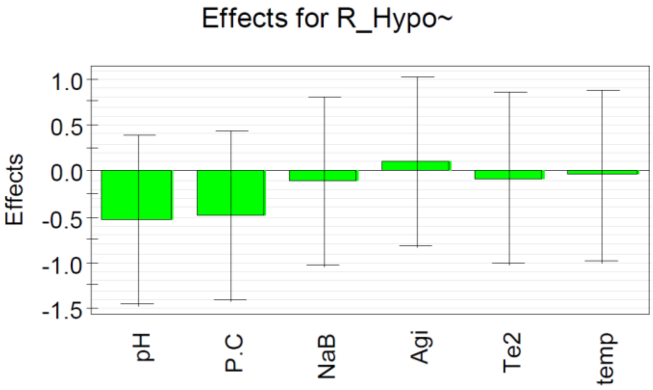
## The experimental plan for the main experiments

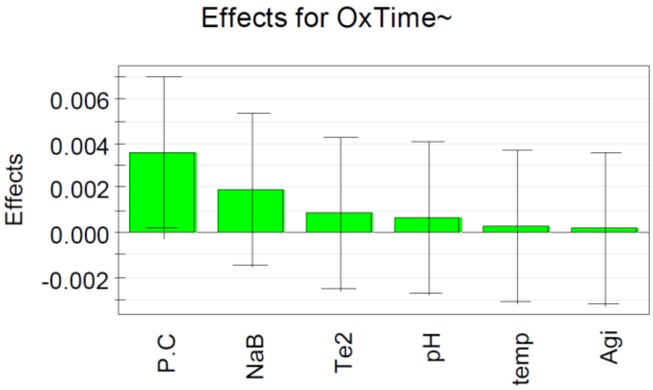


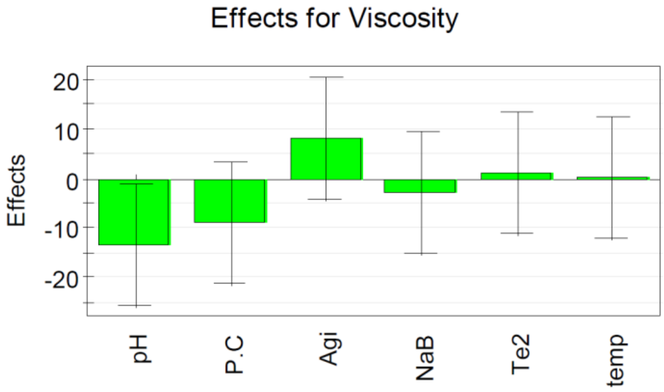
| Exp No | Exp Name | Run Order | Incl/Excl | NaBr | Tempo | pH | Time | R_Hypo | Viscosity | Length | Width | WRV | Charge |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | N1 | 2 | Incl | 25 | 4 | 9 | 120 | 51,38 | 154,72 | 0,91 | 21,4 | 3,9428 | 885 |
| 2 | N2 | 15 | Incl | 25 | 8 | 9 | 120 | 16,53 | 136,72 | 0,91 | 22,5 | 5,80766 | 1070 |
| 3 | N3 | 14 | Incl | 50 | 8 | 9 | 120 | 11,85 | 142,6 | 0,92 | 21,95 | 4,07965 | 1006 |
| 4 | N4 | 4 | Incl | 25 | 4 | 9 | 180 | 17,1 | 144,35 | 0,92 | 22,4 | 4,98756 | 1016 |
| 5 | N5 | 9 | Incl | 25 | 8 | 9 | 180 | 5,8 | 140,56 | 0,89 | 22,5 | 5,1987 | 1041 |
| 6 | N6 | 24 | Incl | 50 | 8 | 9 | 180 | 11,31 | 134,79 | 0,92 | 22,05 | 4,61416 | 1017 |
| 7 | N7 | 17 | Incl | 50 | 4 | 9 | 160 | 22,15 | 148,03 | 0,91 | 21,8 | 3,98892 | 996 |
| 8 | N8 | 22 | Incl | 41,6667 | 4 | 9 | 120 | 44 | 149,88 | 0,92 | 21,45 | 3,40022 | 1075 |
| 9 | N9 | 21 | Incl | 37,5 | 6 | 9 | 150 | 6,79 | 141,19 | 0,93 | 22,2 | 4,33278 | 1082 |
| 10 | N10 | 7 | Incl | 25 | 6,66667 | 10 | 120 | 2,5 | 120,71 | 0,9 | 24,05 | 7,87973 | 961 |
| 11 | N11 | 20 | Incl | 50 | 5,33333 | 10 | 120 | 1,63 | 117,31 | 0,89 | 23,8 | 7,4921 | 1058 |
| 12 | N12 | 23 | Incl | 33,3333 | 4 | 10 | 180 | 1,42 | 124,04 | 0,77 | 24,95 | 8,75376 | 918 |
| 13 | N13 | 6 | Incl | 37,5 | 8 | 10 | 150 | 1,44 | 114,71 | 0,84 | 24,45 |  | 1003 |
| 14 | N14 | 12 | Incl | 25 | 8 | 11 | 120 | 47,46 |  | 0,55 | 25,95 |  | 472 |
| 15 | N15 | 11 | Incl | 50 | 8 | 10,5 | 120 | 1,68 | 104,3 | 0,37 | 29 |  | 836 |
| 16 | N16 | 5 | Incl | 50 | 8 | 10,5 | 60 | 17,39 | 114,28 | 0,79 | 24,6 |  | 779 |
| 17 | N17 | 3 | Incl | 50 | 4 | 11 | 180 | 1,39 |  | 0,33 | 33,55 |  |  |
| 18 | N18 | 8 | Incl | 25 | 8 | 11 | 180 | 15,72 |  |  |  |  |  |
| 19 | N19 | 18 | Incl | 25 | 4 | 11 | 160 | 63,25 | 137,14 | 0,61 | 24,2 |  | 556 |
| 20 | N20 | 16 | Incl | 25 | 4 | 10,5 | 80 | 76,51 | 121,25 | 0,56 | 23,95 |  | 759 |
| 21 | N21 | 1 | Incl | 37,5 | 6 | 10,5 | 180 | 1,3 |  | 0,34 | 30,05 |  |  |
| 22 | N22 | 10 | Incl | 37,5 | 6 | 10,5 | 75 | 55,54 | 107,86 | 0,46 | 26,45 |  | 650 |
| 23 | N23 | 19 | Incl | 37,5 | 6 | 10,5 | 75 | 52,83 |  | 0,48 | 26,3 |  |  |
| 24 | N24 | 13 | Excl | 37,5 | 6 | 11 | 150 |  |  |  |  |  |  |
| 25 | N25 | 25 | Excl | 37,5 | 6 | 11 | 150 |  |  |  |  |  |  |
| 26 | N26 | 26 | Excl |  |  |  |  |  |  |  |  |  |  |
| 27 | N27 | 27 | Excl | 50 | 8 | 9 | 260 | 11,58 | 152,68 | 0,9275 | 21,75 | 3,84129 | 1189,48 |
| 28 | N28 | 28 | Excl | 100 | 8 | 10 | 210 | 2,08 | 133,63 | 0,92 | 22 | 4,42545 | 979,869 |
| 29 | N29 | 29 | Excl | 100 | 16 | 9 | 210 | 11,48 | 156,52 | 0,935 | 21,45 | 4,57836 | 1079,78 |
| 30 | N30 | 30 | Excl | 50 | 16 | 10 | 200 | 3,85 | 132,82 | 0,921 | 21,95 | 4,79766 | 1006,85 |
| 31 | N31 | 31 | Excl | 75 | 12 | 9,5 | 134 | 1,7 | 143,09 | 0,9215 | 21,7 | 4,31276 | 1032,74 |
| 32 | N32 | 32 | Excl | 75 | 12 | 9,5 | 171 | 1,41 | 135,62 | 0,928 | 21,55 | 4,36844 | 1049,62 |
| 33 | N33 | 33 | Excl | 75 | 12 | 9,5 | 135 | 1,22 | 143,86 | 0,92 | 21,4 | 3,77898 | 1108,76 |

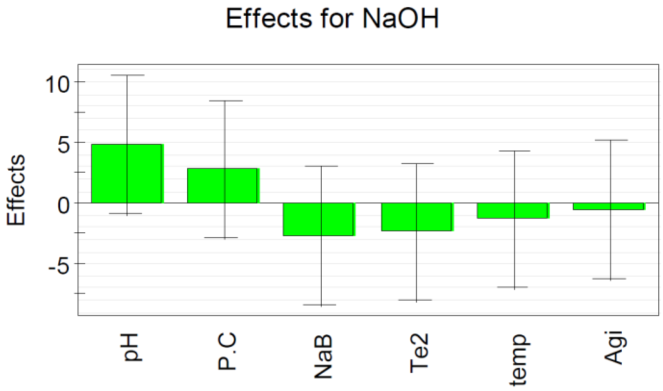
# Appendix C

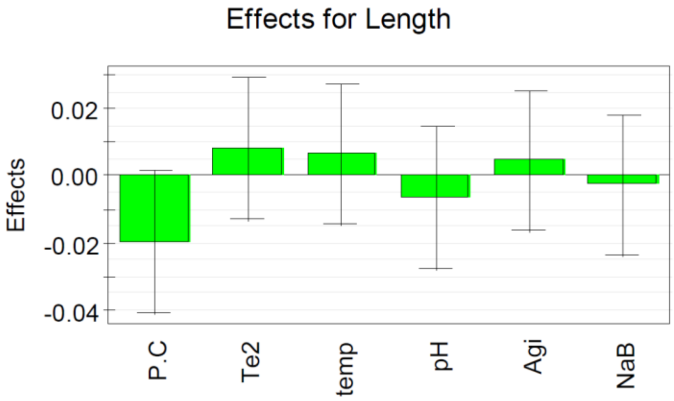
## The effect plots from the screening

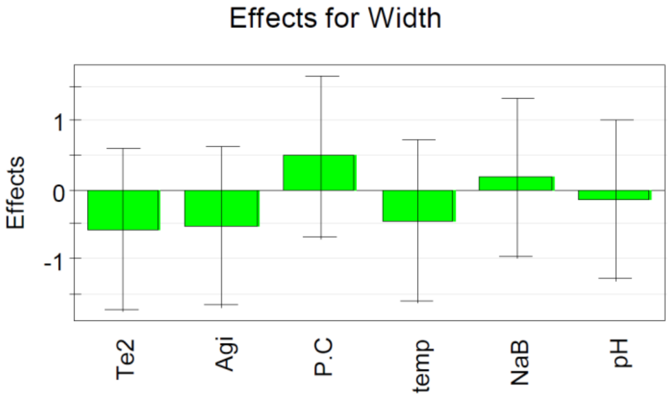


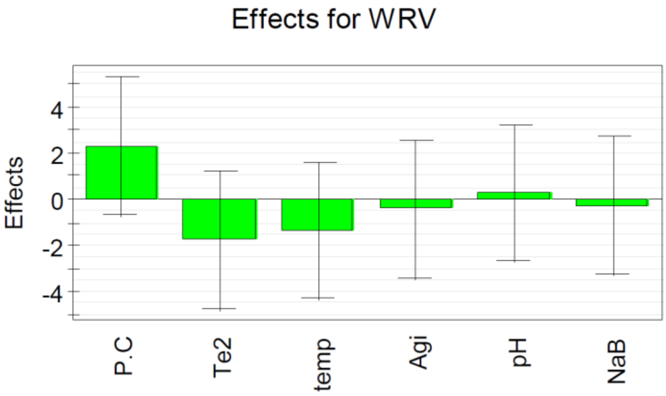


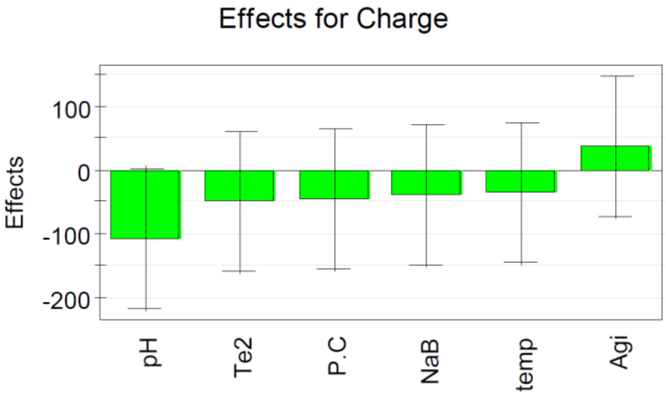






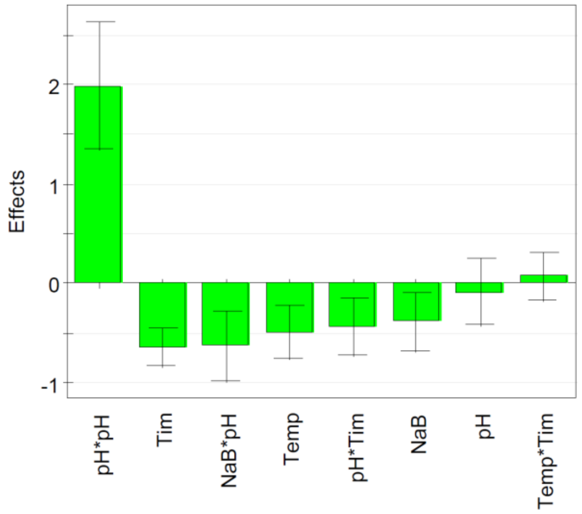


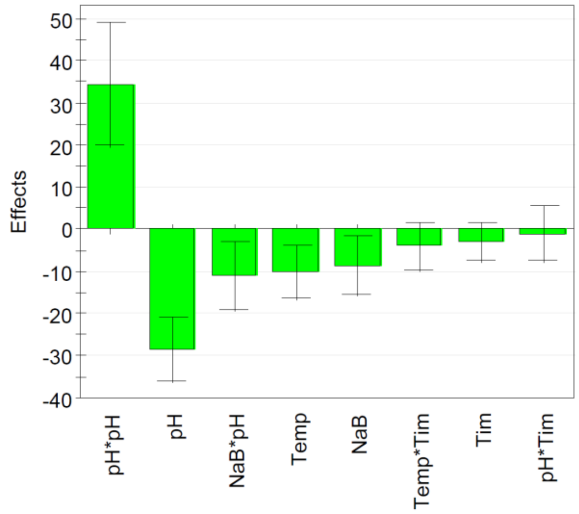


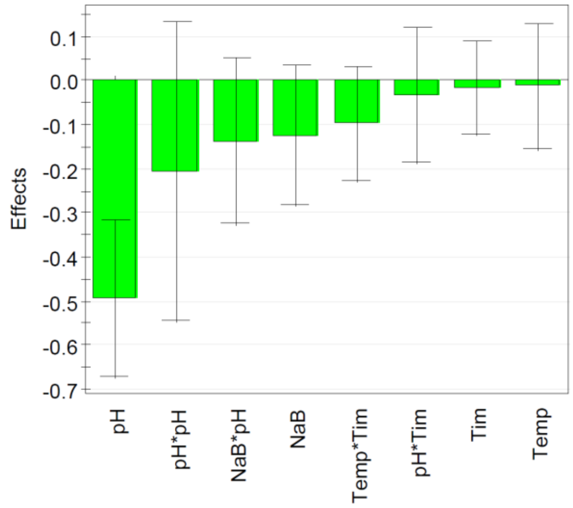


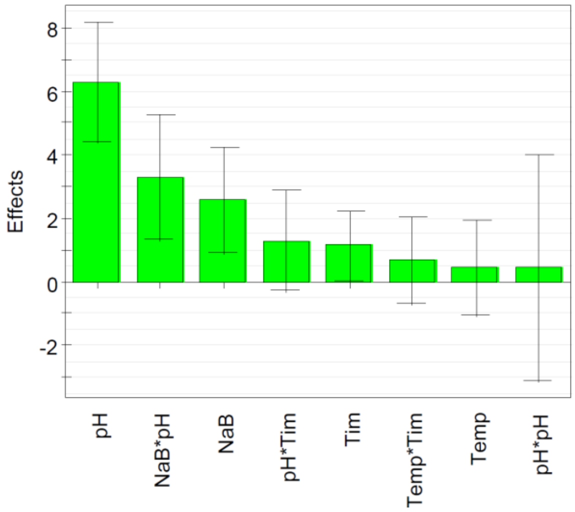
# Appendix D

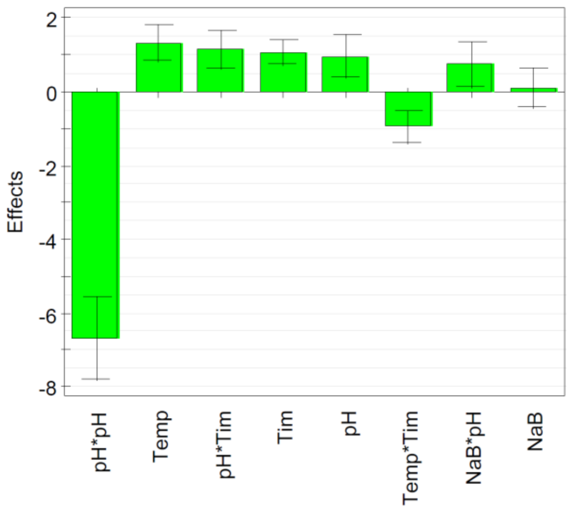
## The effect plots from the main experiments

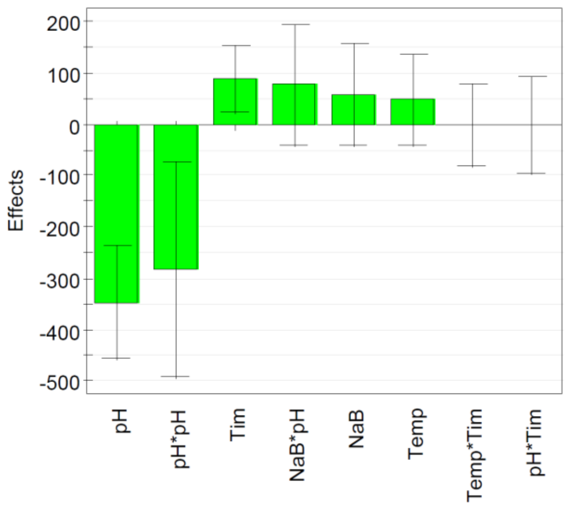

Effects for R_Hypo~


Effects for Viscosity


Effects for Length

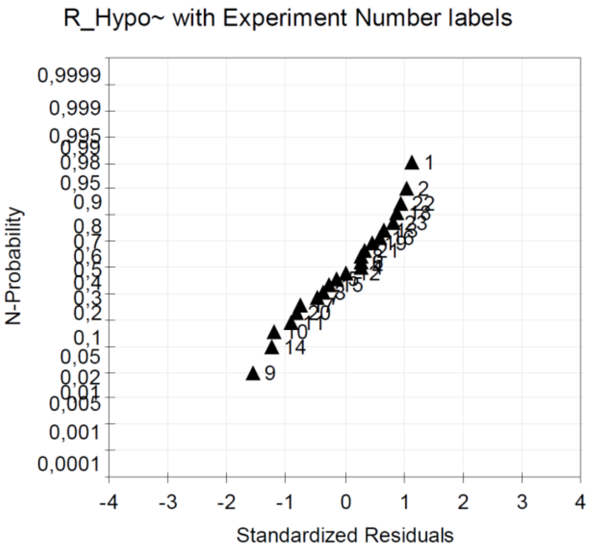

Effects for Width

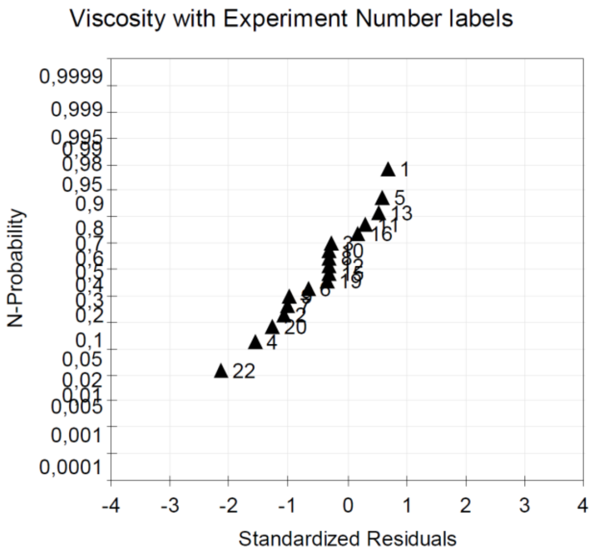

Effects for WRV

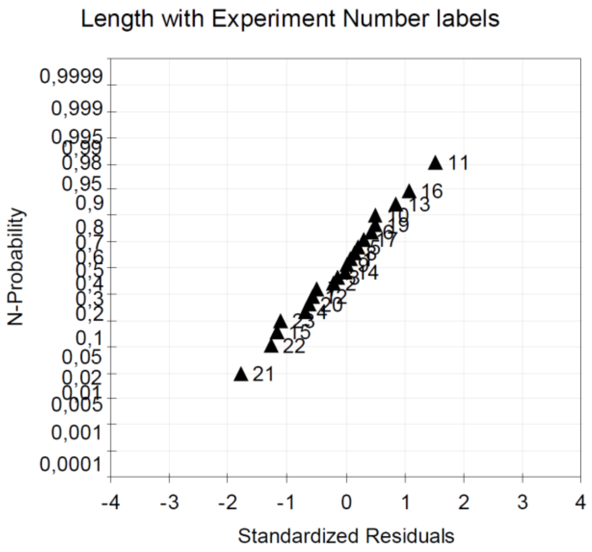

Effects for Charge

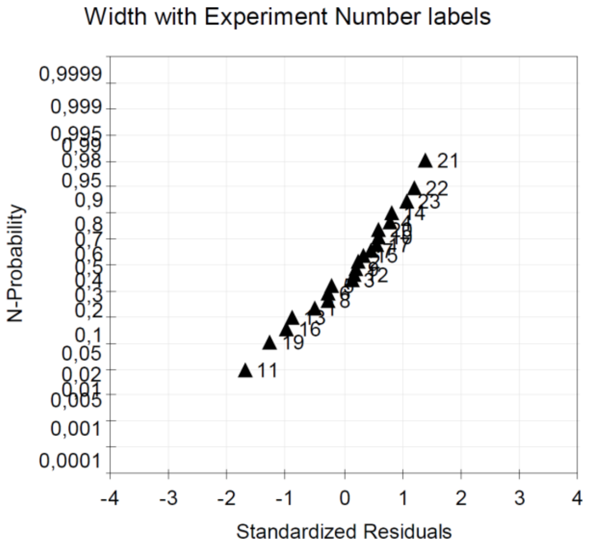
# Appendix E

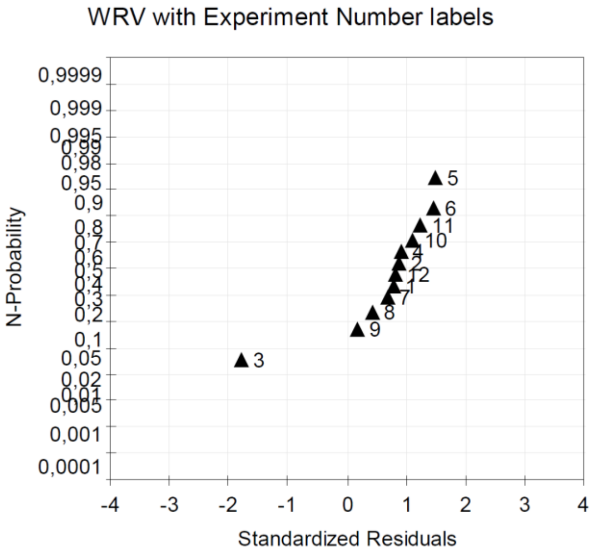
## The normal distribution plots from the main experiments

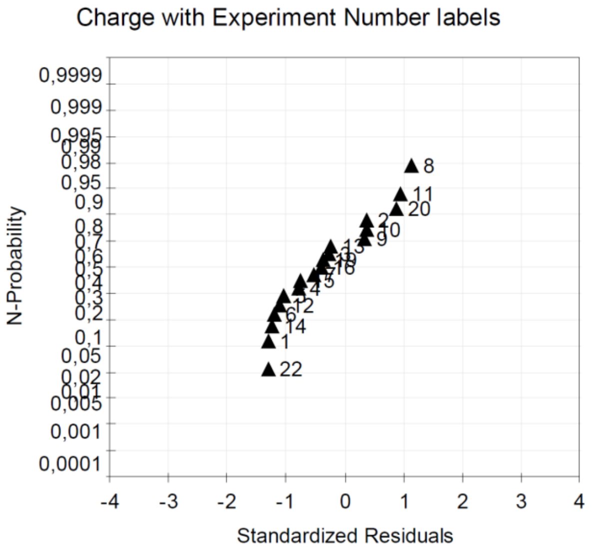

R_Hypo~ with Experiment Number labels


Viscosity with Experiment Number labels


Length with Experiment Number labels


Width with Experiment Number labels

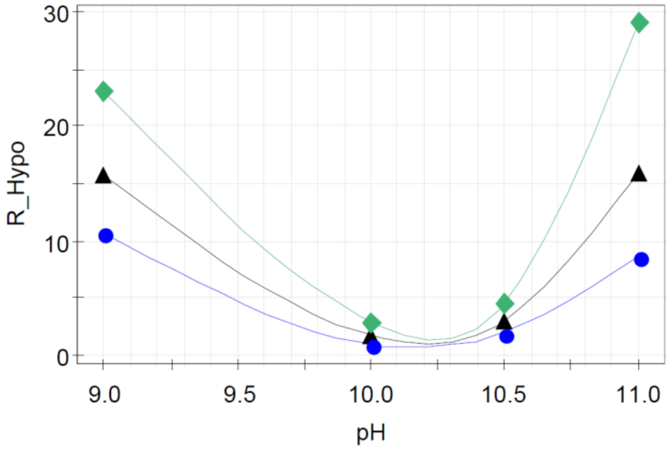

WRV with Experiment Number labels


Charge with Experiment Number labels

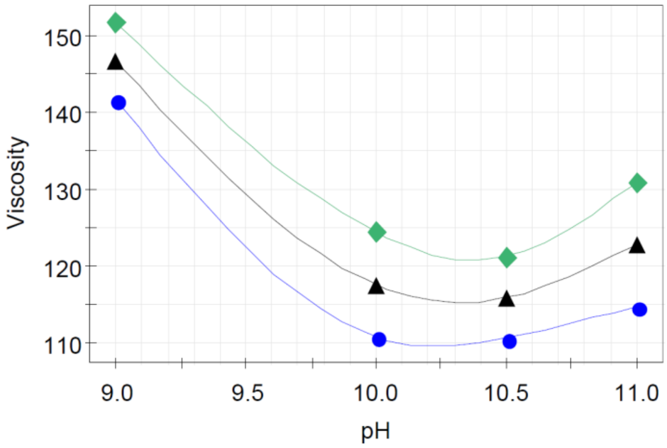
# Appendix F

## The prediction plots for pH from the main experiments

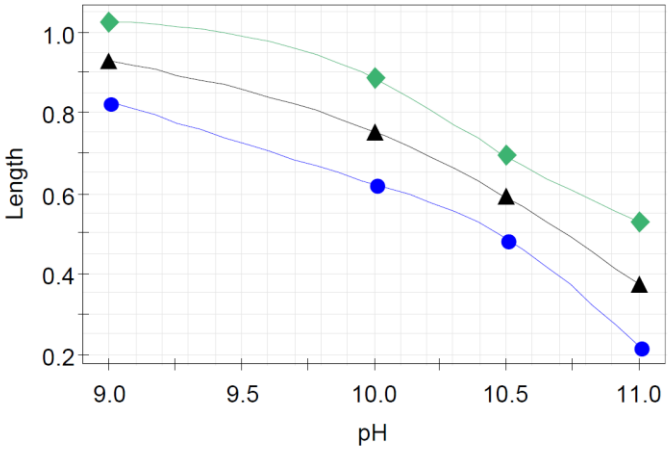
R_Hypo predicted for pH



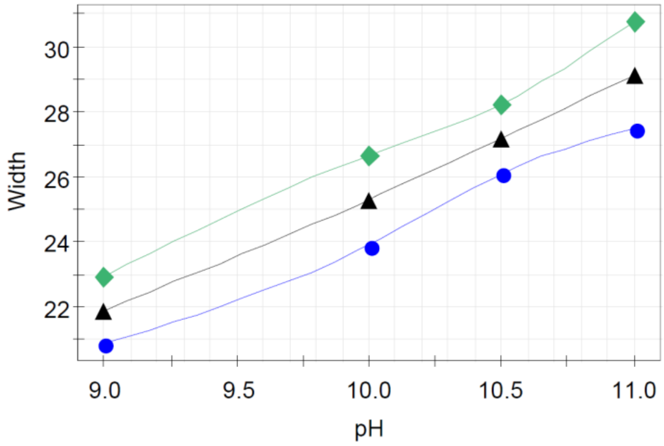
Viscosity predicted for pH



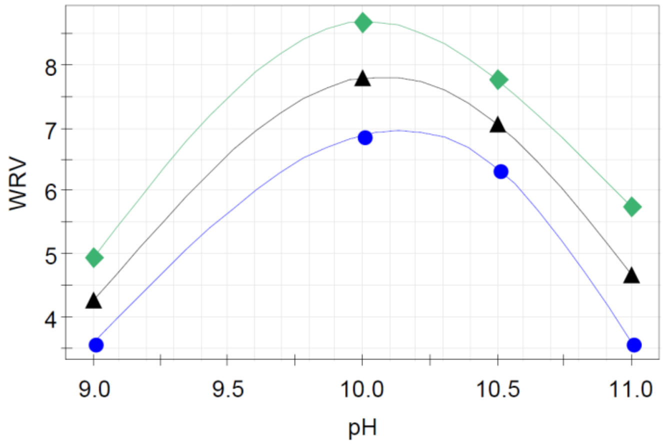
Length predicted for pH



Width predicted for pH



WRV predicted for pH



Charge predicted for pH