



# Fenton Pre-treatment of a Birch Kraft Pulp for MFC preparation

Pia Hellström

Faculty of Health, Science and Technology

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Chemical Engineering

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VIPP VALUES CREATED IN  
FIBRE-BASED PROCESSES  
AND PRODUCTS



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## Abstract

The potential to use acidic hydrogen peroxide in the presence of ferrous ions (Fenton's reagent) as a pre-treatment when producing microfibrillar cellulose (MFC) from a fully bleached birch (*Betula verucosa*) kraft pulp was investigated and the properties of the produced MFC were compared to the properties of an MFC produced with enzymatic pre-treatment with a monocomponent endoglucanase (FiberCare®R). The mechanical treatment to MFC was performed in a laboratory colloid mill or in a pilot high-pressure homogeniser and the pre-treated pulps as well as the produced MFCs were chemically and morphologically characterised. Additionally, the MFCs produced in the colloid mill were evaluated as strength enhancers in test sheets representing the middle ply of paperboard.

From the chemical characterisation, it was concluded that the Fenton pre-treatment caused a decrease in the degree of polymerisation (DP) and an increase in both carboxyl- and carbonyl groups. The increase in carbonyl groups could not be explained by the formation of new reducing end groups due to depolymerisation and are instead assumed to be introduced along the cellulose chain. The enzymatic pre-treatment as performed in this study had less impact on the cellulosic material, i.e. resulting in a pulp with a higher DP and a much lower amount of carbonyl- and carboxylic groups compared with the Fenton pre-treated pulps. In the subsequent mechanical treatment in a colloid mill, the Fenton pre-treated pulps were easier to process mechanically i.e. they reached a higher specific surface area and a higher surface charge at a given mechanical treatment time compared to the enzymatic pre-treated pulps and the pulp not subjected to any pre-treatment. These findings were confirmed when MFCs were produced by homogenisation at high pressure in multiple passes; the birch kraft pulp was either pre-treated with Fenton's reagent or the combined mechanic and enzymatic pre-treatment methodology used at the Centre Technique du Papier (CTP, France). By size fractionation, rheology and scanning electron microscopy, it was revealed that Fenton pre-treatment resulted in an MFC suspension containing a significantly higher proportion of small sized fibrillar material ( $<0.2 \mu\text{m}$ ).

When the MFCs were evaluated as strength enhancers in test sheets produced from a furnish consisting of a spruce (*Picea abies*) chemithermomechanical pulp, MFC and a retention aid system containing cationic starch and an anionic silica sol, the Fenton pre-treated MFCs increased the strength properties more than the enzymatic pre-treated MFCs. The addition of 5 wt% Fenton pre-treated MFC resulted in an increase in z-directional strength of about 50%, an increase in tensile stiffness index of about 25% and an increase in tensile index of 35% compared to test sheets prepared without MFC addition.

**Keywords:** Microfibrillated cellulose, Fenton chemistry, enzymatic hydrolysis, carbonyl groups, tensile strength, z-directional strength, bending stiffness index, bending resistance index

## Sammanfattning

Möjligheten att använda sur väteperoxid i närvaro av järn (II)-joner (Fentons reagens) som förbehandling av en helblekt björksulfatmassa (*Betula verucosa*) vid framställning av mikrofibillärl cellulosa (MFC) undersöktes och egenskaperna hos producerad MFC jämfördes mot egenskaperna hos en MFC som framställdes med en enzymatisk förbehandling med ett monokomponent endoglukanas (FiberCare®R). Den mekaniska bearbetningen till MFC utfördes i laboratorieskala i en kolloidkvarn alternativt i pilotskala i en högtryckshomogenisator och de förbehandlade massorna liksom de framställda MFC-produkterna karakteriserades kemiskt och morfologiskt. De MFC-produkter som framställdes genom mekanisk bearbetning i kolloidkvarnen utvärderades dessutom som styrkegivare i laboratorieark representativa för mittskiktet i kartong.

Den kemiska karakteriseringen visade att en förbehandling med Fentons reagens minskade cellulosans polymerisationsgrad (DP) och ökade både karboxyl- och karbonylgrupperna i massan. Karbonylgruppsökningen kunde inte förklaras genom bildandet av nya reducerande ändgrupper som en konsekvens av den lägre polymerisationsgraden vilket indikerar att dessa istället introduceras längs cellulosedjan. Den enzymatiska förbehandlingen som den utfördes i denna studie påverkade cellulosamaterialet i mindre grad, d.v.s. resulterande i en massa med en högre DP och med ett väsentligt lägre innehåll av både karbonyl- och karboxylgrupper jämfört med Fenton-förbehandlade massor. I den efterföljande mekaniska behandlingen som utfördes i en kolloidkvarn var den Fenton-förbehandlade massan lättare att bearbeta mekanisk d.v.s. en högre specifik yta och högre ytladdning erhöles vid en given mekanisk bearbetningstid jämfört med de enzymförbehandlade massorna och den massa som inte förbehandlats. Detta bekräftades då MFC framställdes genom homogenisering vid högt tryck i flera passager; björksulfatmassan var antingen förbehandlad med Fentons reagens eller med den kombinerade mekaniska och enzymatiska förbehandling som utförs vid Centre Technique du Papier (CTP, Frankrike). Fenton-förbehandling gav MFC suspensioner som innehöll avsevärt mer fibrillärt finmaterial ( $<0.2 \mu\text{m}$ ) vilket baserades på storleksfraktionering, reologi och svepelektronmikroskopi.

När MFC utvärderades som styrkegivare i laboratorieark framställda av en mälld bestående av en kemitermomekaniskmassa av gran (*Picea abies*), MFC och ett retentionssystem bestående av katjonisk stärkelse och en anjonisk kiselnsyra sol, gav den Fenton-förbehandlade massan bättre styrkeegenskaper jämfört med den MFC som framställdes efter enzymatisk förbehandling. Tillsats av fem viktsprocent Fenton-förbehandlad MFC ökade z-styrkan med ca 50%, dragstyvhetsindex med ca 25% och dragindex med ca. 35% jämfört med styrkeegenskaperna hos laboratorieark utan MFC-tillsats.

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## List of papers

The following publications are included in the licentiate thesis:

- Paper 1**      The effect of Fenton chemistry on the properties of microfibrillated cellulose  
Hellström, P., Heijnesson-Hultén, A., Paulsson, M., Håkansson, H. and Germgård, U.  
*Cellulose*, 2014, 21(3), 1489-1503
- Paper 2**      Fenton pre-treated microfibrillated cellulose evaluated as a strength enhancer in the middle ply of paperboard  
Hellström, P., Heijnesson-Hultén, A., Paulsson, M., Håkansson, H. and Germgård, U.  
*Nordic Pulp and Paper Research Journal*, 2014, 29(4), 732-740
- Paper 3**      A comparative study of enzymatic- and Fenton pre-treatment applied to a birch kraft pulp used for MFC production in a pilot scale high-pressure homogeniser  
Hellström P., Heijnesson-Hultén, A., Paulsson, M., Håkansson, H. and Germgård U.  
*Manuscript*

## The author's contribution to the papers

The author's contributions to the papers in this thesis are as follows:

- Paper 1** Performing the experimental work and interpretation of results. The article was written in co-operation with co-authors.
- Paper 2** Performing the experimental work and interpretation of results. The article was written in co-operation with co-authors.
- Paper 3** Planning for and participating in the pilot trial. Fibre and fines content during pre-refining and homogenisation, examination in light microscope and high resolution scanning electron microscope (SEM) was performed by personnel at the Centre Technique du Papier (CTP, France). Surface charge measurement and size fractionation was performed by the author. The article was written in co-operation with co-authors.

## Related materials

Results related to this thesis have been presented at the following conferences:

The effect of Fenton chemistry on the properties of microfibrillated cellulose  
Hellström, P., Heijnesson-Hultén, A., Paulsson, M., Håkansson, H., Germgård, U.  
*3rd Avacell Conference, October 8-9, 2014, Gothenburg, Sweden, p. 59*

The effect of Fenton chemistry on the production of microfibrillated cellulose –  
Characterization and paper board application  
Hellström, P., Heijnesson-Hultén, A., Paulsson, M., Håkansson, H., Germgård U, March  
*5th Nordic Wood Biorefinery Conference, March 25-27, 2014, Stockholm, Sweden, pp. 269-270*

## 1. Introduction

In Europe and North America the forest based sector is struggling with high prices for raw materials and energy while the paper market is simultaneously declining. In order to address these trends, companies in the forestry industry are working to find new products and new application areas. One area of interest is the use of lignocellulosic materials for production of micro- and nanofibrillated cellulose (MFC and NFC). MFC was first produced by Turbak et al. (1983) in the early 1980s by intense mechanical treatment of wood fibres through a pressurised homogeniser. A variety of important industrial uses for MFC/NFC have been suggested, from additives to paper, cement and composites, to flexible electronics and in biomedical and pharmaceutical applications (Turbak et al. 1983; Zimmermann et al. 2004; Eriksen et al. 2008; Walker 2013; Chinga-Carrasco and Syverud 2014; Shatkin et al. 2014).

Several pre-treatment methods have been proposed in order to overcome problems involving clogging of the equipment and high energy consumption (12-65 MWh/t) (Klemm et al. 2011). For example: enzymatic (Henriksson et al. 2007; Pääköö et al. 2007) and chemical modification such as carboxymethylation (Bhandari et al. 2012) or TEMPO-mediated oxidation (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl) (Isogai and Atalla 1998; Isogai et al. 2011). Chemical modification is often linked with high chemical charges, up to several hundred kilogrammes per tonne of pulp, including non-environmentally friendly chemicals, and generates an MFC product with a high total charge. During the last five years, the interest in MFC/NFC has increased dramatically due to the fact that the protection determined under the earliest patent applications has expired (Charreau et al. 2013).

### 1.1 Objectives

The two objectives of this study were:

- To evaluate whether the MFC produced after pre-treating a fully bleached birch (*Betula verrucosa*) kraft pulp with hydrogen peroxide and ferrous ions at an acidic pH (Fenton's reagent) has the potential to become a commercially interesting product with respect to energy consumption and MFC properties.
- To evaluate whether the produced MFC could improve the strength of a paperboard product when added to a spruce (*Picea abies*) chemithermomechanical pulp furnish.



## 2. Background

This section presents background information of importance for understanding the results presented in this thesis. First is an overview of wood cell types, cell wall architecture and the main components of wood with a focus on cellulose and its structural organisation from elementary fibril to fibre. Next is a brief description of the kraft pulping processes; fibre separation and bleaching followed by more detailed information about the preparation of micro- and nanofibrillated cellulose (MFC/NFC). Enzymatic hydrolysis and Fenton chemistry, which are the pre-treatment methods used in this work, are discussed in greater detail. Finally, a brief introduction to paper strength properties and the use of MFC/NFC in paper applications is presented.

### 2.1 Wood cell types and cell wall architecture

Softwood is composed of two different cell types, longitudinal tracheids normally forming between 90-95% of the total cell volume and ray parenchyma cells which corresponds to 5-10 vol%. Longitudinal tracheids are long and slender cells which main functions are support (latewood) and conduction of fluids (earlywood). In the shorter ray parenchyma cells storage and radial transport of assimilates takes place. Hardwoods contain several cell types, specialised for different functions; vessels, fibres (libriform fibres, fibre tracheids) and parenchyma (longitudinal and ray cells). The main function for the vessel cells are conduction and the main function for the fibres and parenchyma are support and storage, respectively. Birch consists of 65-70% of libriform cells and fibre tracheids and about 25% vessel cells, calculated on wood volume. The term fibre is often used for the supporting tissue of any kind of wood cells i.e. include both libriform cells and tracheids. The typical length of a softwood fibre is 1-3 mm and with a width of roughly 10-50  $\mu\text{m}$ . The dimensions of a birch libriform fibre are 0.8-1.6 mm in length and 14-40  $\mu\text{m}$  in width (Fengel and Wegener 1989a; Sjöström 1993a).

A generalised model of the wood fibre can be seen in *Figure 1*, including the defined layer of the primary cell wall (P) and secondary cell wall layers S1, S2 and S3. The layers differ with respect to thickness, chemical composition and inclinations of the cellulose fibrils toward the cell axis. The middle lamella (ML), between adjoining tracheids or libriform fibers acts as a cementing agent and contains a high amount of lignin (Brändström 2001). The degree of polymerisation (DP) of the cellulose cell wall polymer differs between the layers. The primary cell wall cellulose has a DP of about 8 000 and the cellulose in the secondary walls has a DP up to 15 000 (Brown 2004). An increased microfibril angle decreases the cell wall stiffness but increases the strain to fracture. This interrelation enables plants to adjust both stiffness and toughness of their tissues by shifting the cellulose fibril orientation in the cell wall.

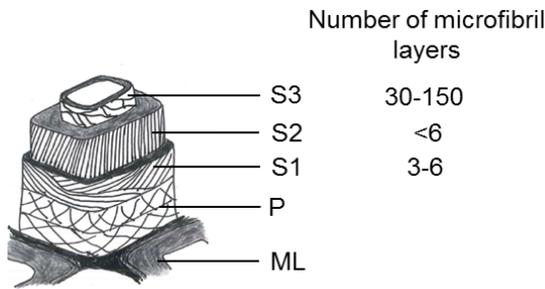


Figure 1. Schematic illustration of the structure of the wood cell wall of softwood tracheids and hardwood libriform fibres (Fengel and Wegener 1989) and the typical number of microfibril layers (da Silva Perez 2009).

## 2.2 Wood components

The main chemical components of wood are cellulose, lignin and hemicelluloses. A minor, but for pulping and papermaking processes important part consists of extractives and inorganic material.

### 2.2.1 Cellulose

Cellulose is synthesised by a great diversity of living organisms such as plants, bacteria, certain fungi, algae and even by some marine animals and is considered to be the most abundant organic compound on the planet (Lynd et al. 2002). The worldwide production is estimated to be between  $10^{10}$  and  $10^{11}$  tonnes each year (Samir et al. 2005).

In vascular plants, such as trees, cellulose is synthesised in enzyme complexes called rosettes located in the plasma membrane, (Figure 2). The rosette complex as a whole is able to synthesise one elementary fibril containing 36 cellulose chains (Brown and Saxena 2000; Ding and Himmel 2006; Festucci-Buselli et al. 2007; Taylor 2008; Brodin et al. 2014).

Depending on the biological origin (plant, wood, bacteria), the elementary fibrils have a diameter from 2 to 20 nm and a lengths that can reach several micrometres (Samir et al. 2004). The elementary fibrils are packed into larger units known as microfibrills and these in turn are assembled into cellulose fibres (Fengel and Wegener 1989b; Lynd et al. 2002). Regardless of source, cellulose consist of a linear homopolysaccharide composed of anhydro-D-glucose units which are linked together by  $\beta(1\rightarrow4)$ -glycosidic bonds (cf. Figure 3). The hydroxyl groups, positioned at C2 and C3 (secondary hydroxyl groups) and C6 (primary hydroxyl group) are capable of forming intra- and intermolecular hydrogen bonds that allow the formation of highly ordered three-dimensional structures.

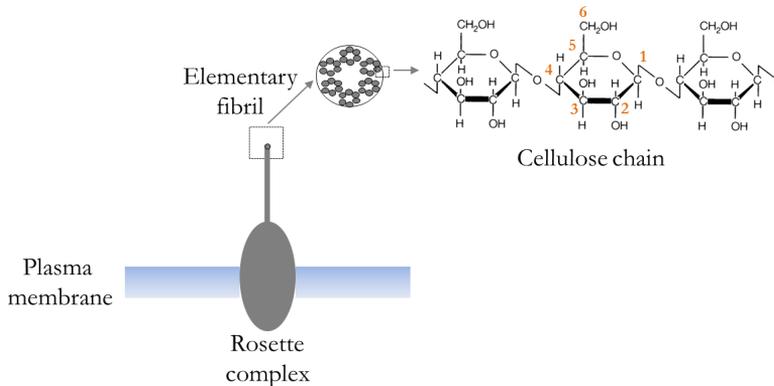


Figure 2. Hypothetical model of the cellulose synthases complex (rosettes). The denotation of the carbon atoms (C1-C6) is shown in one of the glucose units.

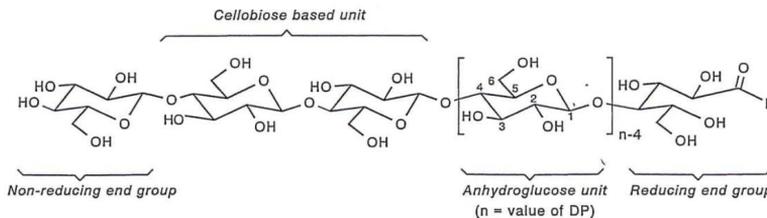


Figure 3. Molecular structure of cellulose. Adapted from Klemm et al. (1998).

Cellulose isolated from native sources is always polydisperse, i.e. consisting of a mixture of macromolecules with differing chain lengths and therefore not possessing a definite molecular weight. The molecular weight of cellulose and other polysaccharides is often given as the degree of polymerization (DP), i.e. how many anhydroglucose units on average that are found in one cellulose chain. According to Sjöström (1993b), native cellulose in wood has a DP of approximately 10 000 anhydroglucose units. Two different groups are found in the chain ends, a non-reducing group where a closed ring structure is found and a reducing end group with both an aliphatic structure and a carbonyl group, *Figure 3*.

Native cellulose exists in two crystalline forms, cellulose I which is the most common, and also in a more rare form, cellulose II, which is found in bacteria and algae. The two forms differ in the inter-chain hydrogen bonding pattern, resulting in a parallel arrangement of the cellulose chains in cellulose I and an anti-parallel arrangement for cellulose II (Koyama et al. 1997; Henriksson and Lennholm 2009).

An important feature of cellulosic material is their two-phase morphology, crystalline regions which is more ordered and amorphous regions where the cellulose lattice is slightly disturbed, *Figure 4*. The amorphous parts of the fibre are weak spots and considered to be more accessible and more reactive compared to the crystalline regions.

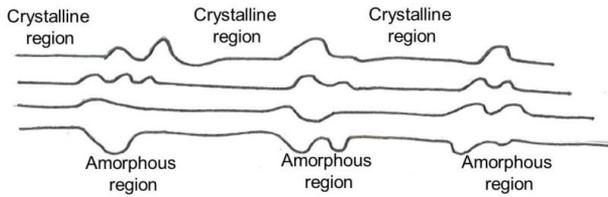


Figure 4. Schematic presentation of cellulose crystallites linked by amorphous areas.

### **2.2.2 Hemicelluloses**

Hemicelluloses are found in the matrix between the cellulose fibrils in the cell wall. Their complete roles are not fully understood but they are known to contribute to the mechanical properties of the cell wall, to serve as an energy source and are thought to take part in important biochemical functions (Teleman 2009). Unlike cellulose the hemicelluloses are often branched and of low molecular weight (DP up to 300) and will generally have a chemical and thermal stability lower than that of cellulose (John and Thomas 2008). The main hemicelluloses in softwood are galactoglucomannans (20%) and arabinoglucuronoxylan (5-10%) while hardwood mainly consists of glucuronoxylan (15-30%) and glucomannan (2-5%) (Sjöström 1993b).

### **2.2.3 Lignin**

Lignin is always closely associated with cellulose, hemicelluloses and pectin in plants and is therefore difficult to isolate without structural changes. The complete structure of lignin is therefore not fully elucidated. However, lignin is known to possess complex three dimensional structures composed of up to three different phenyl propane monomers, coumaryl-, coniferyl-, syringyl alcohol units. Coniferyl alcohol is the predominant lignin monomer found in softwoods and coniferyl and sinapyl alcohols are the building blocks of hardwood lignin while *p*-coumaryl alcohol is a minor component of grass and forage lignins (Fengel and Wegener 1989c). Beyond the structural function as a cementing and fixation polymer lignin also inhibits swelling by decreasing the water transported across the cell walls and serves as protection against insects and microbial growth.

### **2.2.4 Extractives**

The term wood extractives include a large number of compounds which can be extracted from wood by means of polar- and non- polar solvents. The main classes of extractives are: terpenoids, steroids, fats, waxes and phenolic substances such as stilbenes, lignans, flavonoids and tannins. The amount of extractives is typically only a few percent in the wood (Fengel and Wegener 1989d; Sjöström 1993c). Different types of extractives have different biological functions; fats and fatty acids are energy sources, steroids are part of

the enzymatic system and resins and phenolic extractives protects against insects and micro-organisms.

### 2.2.5 Inorganic materials

The inorganic constituents in wood, i.e. the ash content after burning, is low in woods that grow in temperate zones, 0.1-1% of the dry wood weight. The main metal components are calcium, potassium and magnesium. Manganese and iron can be present in amounts up to 100 mg/kg, whereas usually only trace amounts of other metals are present (Sjöström 1993c).

### 2.3 Kraft pulping

The aim of the pulping process is to liberate the fibres from the wood matrix and this can be achieved either mechanically or chemically. In chemical pulping the fibres are liberated in a process referred to as cooking or digestion. The cooking process is performed at elevated temperatures and with the addition of chemicals aimed at dissolving the lignin. In kraft cooking (also named sulphate cooking) which is the dominant chemical pulping method, the main active compounds are sodium hydroxide and sodium sulphide. At the end of the cook, the pressure in the digester is abruptly reduced as the content of the digester is discharged, resulting in a substantial individualisation of the fibres. Most of the lignin is solubilised; and roughly 2-3% of the lignin will be left in the final pulp at the end of the cook. Alkaline degradation of both cellulose and hemicelluloses appears during the cook. The hemicelluloses are degraded to a higher extent compared to cellulose due to their low degree of polymerisation (Sjöström 1993d). The changes in wood component yields as a result of kraft cooking of pine and birch wood are shown in *Table 1*.

Table 1. Typical values (% on wood) for individual wood components before and after kraft cooks of pine and birch wood (Gellerstedt 2009).

Wood component	Unit	Pine		Birch	
		In wood	In pulp	In wood	In pulp
Cellulose	%	39	35	40	34
Glucomannan	%	17	4	3	1
Xylan	%	18	5	13	16
Other carbohydrates	%	5	~0	4	~0
Lignin	%	27	3	20	2
Extractives	%	4	<0.2	3	0.5

### 2.4 Bleaching

Bleaching is necessary to restore or to increase the brightness for production of high-quality paper products. Oxygen delignification is often used as an initial bleaching stage of chemical pulps due to low costs compared with other bleaching chemicals and due to the fact that the bleach effluent can be included in the pulp mills recovery cycle. The use of

oxygen is limited to remove about half of the residual lignin since further use will cause considerable attack on the polysaccharides, resulting in poor strength properties and low yields. To establish a fully bleached pulp with a brightness >80% ISO, a multistep bleaching sequence is applied with various combinations of for example chlorine dioxide, sodium hydroxide (alkaline extraction), hydrogen peroxide and ozone (Sjöström 1993e). Bleaching based on chlorine dioxide and where no other chlorinebased chemical such as chlorine gas or hypochlorite is used is denoted as ECF (elementalchlorine free bleaching). If chlorine dioxide is not used (and no other chlorine containing bleaching chemicals) the bleaching is called TCF (totally chlorine free bleaching). In parallel with the bleaching reaction, there is also an attack on the carbohydrates which can be seen as a simultaneous decrease in the DP.

## **2.5 Nanocelluloses**

Cellulosic materials consisting of cellulose fibres or fibrils with at least one external dimension in the range of 1-100 nm are generally called nanocelluloses (Chinga-Carrasco 2011; Abdul Khalil et al. 2012). Fibrillated cellulose such as MFC/NFC can be considered as a class of nanocellulose, produced by mechanical treatment or with combinations of chemical or enzymatic treatments and mechanical processing. MFC products generally consist of a mixture of unaffected fibres, fibre fragments and small sized fibrils i.e. having a broad size distribution while NFC consist of smaller and more uniform microfibrils. However, there is no clear distinction when a material should be called micro- or nanofibrillated cellulose. Standardisation groups are working on international classifications (SIS-CEN ISO/TS 27687:2009 and Tappi standard WI 3021). Other classes of nanocelluloses are micro crystalline cellulose (MCC) and nanocrystals also called nanowhiskers which are produced by acid hydrolysis of cellulose containing material (Cranston and Gray 2006). In contrast to fibrillar celluloses, nanocrystals are stiff and rod like with typical dimensions ranging from 5 to 10 nm in diameter and from 100 to 500 nm in length (Siqueira et al. 2010a).

## **2.6 MFC/NFC preparation**

Cellulose fibres can be disintegrated to their structural nano-components by intensive mechanical processing. The first MFC was produced in the early nineteen eighties by Turbak et al. (1983) by several passes of a fibre suspension through a pressurized homogeniser. During the mechanical treatment, the fibres are downsized to fibril bundles of various diameters (macro- and microfibrils) and finally to the smallest building block, the elementary fibril. A drawback for industrial commercialisation was clogging of the equipment and high energy requirements. Energy consumption of up to 12-65 MWh/t has been reported (Klemm et al. 2011). By using pre-treatments such as enzymatic hydrolysis (Henriksson et al. 2007; Pääkkö et al. 2007) or chemical modifications such as TEMPO-mediated oxidation (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl) (Isogai and Atalla

1998; Iwamoto et al. 2010; Isogai et al. 2011) or carboxymethylation (Bhandari et al. 2012) the energy consumption may be reduced to 1-10 MWh/t. Enzymatic hydrolysis is discussed in more details in Section 2.6.1.

Almost any cellulosic material can be considered as a potential source for micro- and nano sized cellulosic structures. Commonly studied sources are not only wood, but also crop residues, sugar cane bagasse, bacterial cellulose and tunicate (Klemm et al. 2011; Lavoine et al. 2012; Henniges et al. 2014). The starting materials for nanocelluloses from wood based materials are often bleached chemical pulps to utilise a material with low amount of lignin and hemicelluloses (Dufresne 2012). Sulphite pulps (Ahola et al. 2008a; Zimmermann et al. 2010; Bilbao-Sainz et al. 2011; Wang et al. 2011a) are frequently used since they are thought to be easier to delaminate compared to kraft pulps. Kraft pulps from pine (Taipale et al. 2010; Syverud et al. 2011), eucalyptus (Syverud et al. 2011) and birch (Ferrer et al. 2012; Tapin-Lingua 2013) have also been used for MFC preparation. A few studies have been performed with mechanical pulps (Abe et al. 2009; Osong et al. 2013; Ramiro and Berglund 2013; Osong et al. 2014).

### **2.6.1 Enzymatic hydrolysis**

Enzymes are very efficient and catalyse a single reaction, which is determined by the substrate and the type of chemical bond cleaved or synthesised. Since wood is composed of many different chemical polymers with different chemical compositions, a multi-enzyme-system is required for a completed degradation. Cellulases, hemicellulases and lignocellulases refer to groups of enzymes that degrade cellulose, hemicellulose and lignin respectively. Cellulases are commonly divided in three main groups with different approaches to the substrate (Horn et al. 2012). Exoglucanases are able to attack the crystalline parts by acting on either end of the cellulose chain and progressively release soluble cellobiose units. In turn, endoglucanases generally require some disorder in the cellulose structure and randomly attack accessible intramolecular  $\beta$ -1,4-glucosidic bonds in the middle of the cellulose chains and consequently generates oligomers of different size and new reducing end groups. The third group,  $\beta$ -glucosidases do not act directly on the cellulose chain but prevent cellobiose inhibition by hydrolysing cellobiose to glucose (Horn et al. 2012). A schematic illustration of the cellulase enzyme system acting on the cellulose chain can be seen in *Figure 5*. The effect is impacted by substrate properties such as the degree of polymerisation, crystallinity, accessible area, presence of lignin, substrate concentration as well as the concentration of enzyme per mass unit of material (Cao and Tan 2002; Engström et al. 2006).

In pre-treatment for MFC/NFC production, endoglucanases are commonly used in combination with a pre-mechanical stage in order to increase the accessible surface area and thereby facilitate the enzymatic hydrolysis (Henriksson et al. 2005; Henriksson et al. 2007; Pääkkö et al. 2007). An additional mechanical step before the final processing in the homogeniser or fluidiser is often used to reduce the risk of clogging (Henriksson et al.

2007). For MFC/NFC production, a mild or moderate enzymatic hydrolysis is preferred in order to create highly networked fibrils that can be distinguished from the rod like shapes resulting from strong acid- or enzymatic hydrolysis (Siqueira et al. 2010b; Qing et al. 2013). Through the use of the enzymatic protocol, the energy requirement is reported to be 2-15 MWh/t (Ankerfors 2012). Enzymatic pre-treatment of cellulosic materials has also been used to increase the reactivity of dissolving pulps (Henriksson et al. 2005; Engström et al. 2006).

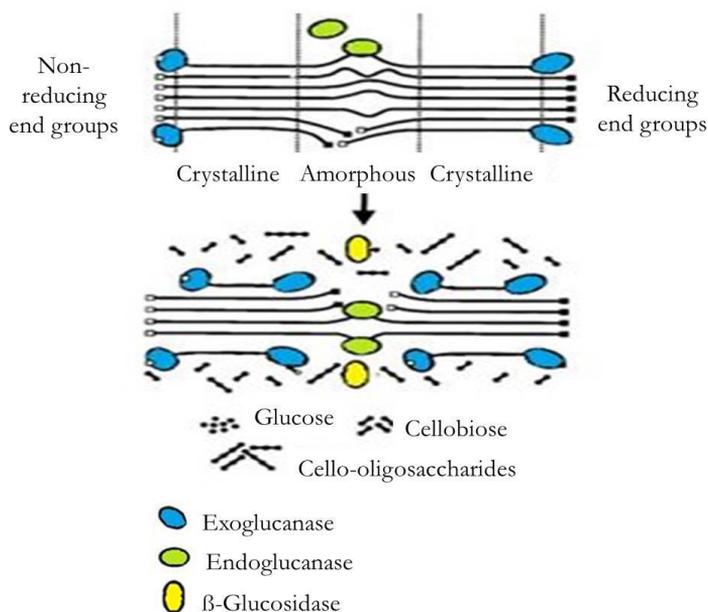


Figure 5. A schematic illustration of the cellulose enzyme system acting on the cellulose chain. Adapted from Lynd et al. (2002).

### 2.6.2 Fenton chemistry

The application of Fenton chemistry to lignocellulosic materials has been described in various scientific studies for example to enhance the fermentability of prehydrolysates obtained from steam explosion pre-treatment of biomass (Oliva et al. 2005), to decrease the energy demand in mechanical pulping (Walter et al. 2009) and to enhance the enzymatic hydrolysis response for cotton substrates (Jain and Vigneshwaran 2012) as well as in pre-treatment for MFC production (Heijnesson-Hultén 2007). In the Fenton reaction, active oxygen species, such as hydroxyl radicals ( $\text{OH}\cdot$ ) are formed through the one-electron reduction of hydrogen peroxide, catalysed by transition metals ions such as soluble ferrous ions ( $\text{Fe}^{2+}$ ) (Fenton 1894; Haber and Weiss 1934), see *Reaction 1*. Different reaction

mechanisms have been proposed, the so called classical Fenton mechanism by Haber and Weiss in 1934 and further development of the radical intermediate concept was made by Barb et al. (1951).



The produced ferric ions are slowly regenerated to ferrous ions by reaction with hydrogen peroxide under formation of hydroperoxyl radicals ( $\text{HOO}\cdot$ ), i.e. the iron will react as a catalyst in the oxidation system. The formed hydroxyl radical may also oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  or decompose  $\text{H}_2\text{O}_2$  to water and  $\text{HOO}\cdot$ . The pH range for the Fenton reaction utilizing free iron is restricted to about pH 3-4 due to the precipitation of ferric iron at a higher pH. Besides the described theory including free radicals some researchers claim the participation of the ferryl ion ( $\text{FeO}^{2+}$ ) as an active intermediate (Sychev and Isak 1995). The attendance of hydroxyl radicals in the reaction between acidic hydrogen peroxide and ferrous ions in a cellulosic substrate has been demonstrated by Walter et al. (2013).

Organic compounds such as lignocellulosic materials, oxidized in radical chain reactions, encompass a series of complex reactions including numerous radical intermediates and consecutive reactions. The reaction mechanisms are not fully elucidated, but are suggested to involve the formation of various radicals such as alkyl and carbon radicals produced by hydrogen abstraction. The hydroxyl groups at C2, C3 and C6 in cellulose and hemicelluloses are susceptible to direct oxidation and the resulting aldehyde or keto groups may initiate further degradation reactions such as dehydration and cleavage of the glycosidic linkages (Lai 2001; Wang et al. 2011b; Henniges et al. 2012; Jeong et al. 2014). *Figure 6* shows the positions in the cellulose chain that may be subjected to oxidation.

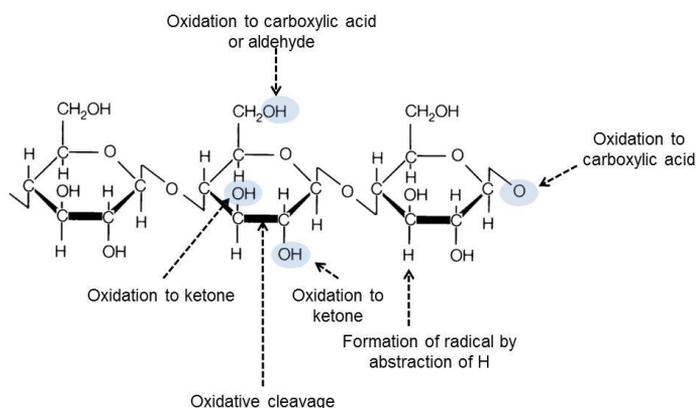


Figure 6. Positions in the cellulose chain possible to participate in oxidation reactions, partly adapted from Norimoto (2001).

### **2.6.3 Mechanical treatment**

Three main families of devices are used for the mechanical defibrillation: high-pressure homogeniser, micro-fluidiser and grinder. In the homogeniser, the fibre suspension enters the valve area at high pressure and low velocity and a corresponding drop in pressure occurs (Missoum et al. 2013). This combination of forces promotes a high degree of fibrillation of the cellulose fibres.

An alternative to the homogenizer is the micro-fluidizer in which the fibre suspension is forced to pass through an intensifier pump that increases the pressure followed by an interaction chamber. High shear forces and impacts against the channel walls and colliding streams cause defibrillation of the fibres. The interaction chamber can be designed with different geometrics to produce different sized materials (Abdul Khalil et al. 2014).

In the grinder device the cell wall structure breaks down thanks to shearing forces generated by two grinding discs with counter wise rotation or one disc in rotation and the other acting as a stator. The surfaces of the discs consist of bars and groves against which the fibres are subjected to repeated cyclic stresses (Dufresne 2012).

## **2.7 Characterisation**

Organisations for the development of international standards have ongoing activities to set appropriate standardised measurements and characterisation methods for the most essential parameters describing the properties of the nanocelluloses i.e. particle size, size distribution, shape, specific surface area, surface charge and fibrillation degree etc. At present, numerous different characterisation techniques are used that are more or less laboratory and research group specific and this makes a comparison between various MFC/NFC complicated (Kangas et al. 2014). The most commonly used direct analysis methods is based on visualisation and image analysis using electron and atomic force microscope, direct single particle measurements using light or radiation scattering and diffraction methods (Abe et al. 2007; Ahola et al. 2008a; Johansson et al. 2011). All of these methods are time consuming and based on subjective assessments of small areas in the larger sample and prevent an accurate statistical analysis. A further complication is that the morphology of the samples is dependent of sample preparation such as handling and drying conditions (Peng et al. 2013; Kaushik et al. 2014). Indirect methods such as viscosity, settling rate or water retention capacity may also be used.

## **2.8 Paper strength properties**

Paper can be describes as a layered structure of a fibrous material mainly composed of cellulose fibres and also, in some cases, chemical additives and fillers. The paper is formed through filtration of a diluted fibre suspension on a wire. The formed fibre mat is thereafter pressed and dried. The mechanical properties of a paper product are related to the individual fibre strength, the bonding strength per unit area and the bonded area of the fibres (Page 1969; Torgnysdotter et al. 2007). One of the most commonly used methods to

increase the connectivity of cellulose fibres within a paper network is by beating. During beating, the fibres are made more flexible so that they can conform more easily to each other's surfaces. The strength of paper can also be improved by increasing the number of bonds between the fibres by adding dry strength additives such as starch or carboxymethylcellulose, often together with a drainage improving additive such as cationic polyacrylamide. In research work, the mechanical properties of paper products are known to be improved through the addition of fines (Aaltio 1962; Retulainen et al. 1993; Bäckström et al. 2008).

### ***2.8.1 MFC/NFC as strength enhancers in paper applications***

The benefits of using MFC/NFC as strength enhancers in paper applications have been explored by several researchers in recent years and comprehensively described in reviews made by Kajanto et al (2012) and Brodin et al (2014). Introduction of MFC/NFC in paper and paperboard products is one of the more promising application areas and are predicted to be in commercial scale in the nearest future (Brodin et al. 2014).

da Silva Perez et al. (2010) demonstrated a clear relationship between the MFC/NFC quality and the reinforcement effect in paper sheets prepared from both softwood and hardwood pulps. The MFC with the smallest particles and the most homogenous particle size distribution had the greatest improvement in tensile and tear properties. At an addition level of 5% of MFC/NFC, the improvement was 20-25% in both tensile- and tear index compared with sheets prepared without the addition of MFC/NFC. These results are consistent with an earlier study made by Eriksen et al. (2008) who evaluated the addition of MFCs with different average fibril sizes to hand sheets prepared from thermomechanical pulp. Addition of 4% MFC with an average particle size of 40  $\mu\text{m}$  revealed an increase in tensile index of about 20% compared to handsheets prepared without addition of MFC. Osong et al. (2014) produced NFC from bleached kraft pulp fines and chemithermomechanical pulp (CTMP) fines by mechanical treatment in a homogeniser. The produced NFC's were blended with bleached kraft pulp and CTMP pulp and the strength properties were evaluated on hand sheets. At an addition level of 5% NFC, the strength improvement were moderate; 5-10% in z-strength and not significant for tensile index and bending stiffness when compared with sheets without the addition of NFC. Deviations in sheet preparation, furnish composition and MFC quality makes it difficult to compare published results.



### 3. Materials and methods

Throughout this study, the source for the microfibrillated cellulose was an elemental chlorine free bleached birch (*Betula verucosa*) kraft pulp. Birch fibres were chosen since they are proven to give MFC with good quality and, with its relatively short fibre length, the risk for clogging of the homogeniser is reduced (Tapin-Lingua et al. 2013). An experimental overview of the thesis work together with the experimental methods that have been developed or modified are described in detail in this section. For other materials or methods see the appended Papers 1-3.

#### 3.1 Overview of the thesis work

The work is divided into three parts, Papers 1-3. The experimental outline can be seen in *Figure 7*.

	Cellulose source	Pre-mechanical treatment	Pre-treatment	Pre-mechanical treatment	Mechanical treatment	Product	Evaluation
Paper 1	Birch kraft pulp		Fenton		Colloid mill	MFC	Characterization
			Enzyme		Colloid mill	MFC	Characterization
Paper 2	Birch kraft pulp		Fenton		Colloid mill	MFC	Paper board application
			Enzyme		Colloid mill	MFC	Paper board application
Paper 3	Birch kraft pulp		Fenton	Refining	Homogeniser	MFC	Characterization
		Pre-refining	Enzyme	Refining	Homogeniser	MFC	Characterization

Figure 7. The experimental outline of Papers 1-3.

Paper 1 comprises an evaluation of the pulp characteristics obtained after pre-treatment with enzymatic hydrolysis (monocomponent endoglucanase, FiberCare®R, Novozymes AS, Denmark) and with Fenton’s reagent (acidic hydrogen peroxide in the presence of ferrous ions) as well as a characterisation of the MFC products obtained after mechanical treatment in a colloid mill for 0, 10, 30 and 53 minutes. In Paper 2, the MFC products characterised in Paper 1 were evaluated as strength enhancers in a paperboard application.

The work continued in Paper 3 with a comparative study between Fenton pre-treatment and the combined mechanical and enzymatic pre-treatment used at Centre Technique du Papier (CTP, France). In Paper 3, the final mechanical processing was performed in a pilot high-pressure homogeniser.

### 3.2 Fractionation of the MFC products

The fractionation was performed in a stirred ultrafiltration cell (Model 8400) from Amicon, *Figure 8*. Five hundred mg calculated as dry material was diluted with 3000 mL de-ionized water and transferred to container A, which was stirred using a magnetic agitator. When a pressure of 0.5 bar was applied by compressed air, the diluted fibre suspension flowed to the ultrafiltration unit to a level of about 300 mL. The fractionation proceeded until the total amount of fibre suspension had been filtered through the mounted membrane and collected in container B. After thorough cleaning with de-ionized water (~25 mL), the wash water was evaporated together with the screen and dried overnight at 105°C. After cooling in a desiccator, the screen with the fibre material was weighted and the amount of the fraction was calculated. The fractionation procedure was repeated allowing the collected filtrate to pass through the next screen. Altogether, three screens with various pore sizes were used: a 112 µm nylon net from Derma AB, 20 µm nylon net (NY20) and a 0.1 µm Durapore® membrane filter (VVPP) both from Millipore. Three screening stages give four fractions: >112 µm, 20-112 µm, 0.1-20 µm and <0.1 µm. The final permeate is too diluted for appropriate measurement of the solid content and is therefore calculated as the residual not found in the other screening stages.



Figure 8. Picture of the experimental set-up used for size fractionations.

### 3.3 Surface charge determination

The method used is a development of the method described by (Bhardwaj et al. 2004) with the modification that the variations in pH and ionic strength were accounted for. The surface charge was determined on pulp suspensions by polyelectrolyte titration with a streaming current detector. The analysis was performed without an acidic wash and without transferring the pulps to its sodium form. The procedure was as follows: 0.5 g calculated as dry material was diluted with de-ionised water to 0.5% w/w where-after the pH was adjusted to pH 6.5-7.0 with 0.05 M NaOH, the pH was stable for at least one hour before the electrolyte concentration was adjusted to 110-140  $\mu\text{S}/\text{cm}$  with NaCl, corresponding to 0.4-0.7 mM NaCl. A polydiallyldimethylammonium chloride (PolyDADMAC) solution with a molecular weight of 200 000-350 000 g/mole (50 mL, 2000  $\mu\text{eq}/\text{L}$ ) was added to the fibre suspensions and the samples were stirred using a magnetic stirrer for 120 minutes. Five mL of the sample, fibres included, was diluted with 5 mL de-ionized water and thereafter titrated with polyethene sodium sulfonate (Na-PES) (1000  $\mu\text{eq}/\text{L}$ ) using a PCD-03 from MÜTEK. The surface charge was calculated using Equation 1 below:

$$q = \frac{V_{\text{PolyD}} \cdot C_{\text{PolyD}} \cdot m_2 - V_{\text{NaPES}} \cdot C_{\text{NaPES}} \cdot \left( m_1 \cdot \frac{100-PC}{100} + V_{\text{PolyD}} + V_{\text{H}_2\text{O}} + V_{\text{NaOH}} + V_{\text{NaCl}} \right)}{m_1 \cdot m_2 \cdot PC \cdot 10} \quad [1]$$

where  $q$  is the surface charge ( $\mu\text{eq}/\text{g}$ ),  $V_{\text{PolyD}}$  is volume of PolyDADMAC (mL),  $C_{\text{PolyD}}$  is the concentration of the PolyDADMAC solution ( $\mu\text{eq}/\text{L}$ ),  $V_{\text{NaPES}}$  is the volume of Na-PES used in the polyelectrolyte titration (mL),  $C_{\text{NaPES}}$  is the concentration of titrant ( $\mu\text{eq}/\text{L}$ ),  $V_{\text{H}_2\text{O}}$  is the volume of water (mL),  $V_{\text{NaOH}}$  is the volume of sodium hydroxide used for pH adjustment (mL),  $V_{\text{NaCl}}$  is the volume of sodium chloride used for conductivity adjustments (mL),  $PC$  is the pulp consistency of the fibre suspension to be analysed (w/w%),  $m_1$  is the weight of the fibre suspension to be analysed (g) and  $m_2$  is the amount of the sample used in the polyelectrolyte titration (g). The 95% confidence interval was determined to  $\pm 2.3 \mu\text{eq}/\text{g}$  by calculation of the pooled standard deviation for five sets of samples performed in triplets.



## 4. Result and discussion

This section summarises the most important findings in this thesis and will include chemical and morphological characterisation after enzymatic- and Fenton pre-treatments and after the subsequent mechanical treatment in a laboratory colloid mill or in a pilot high-pressure homogeniser as well as an evaluation of MFCs produced in the colloid mill as strength enhancer in a paperboard application. More details and results are presented in the appended Papers 1-3.

### 4.1 Effect of chemical and enzymatic pre-treatments

The conditions employed for the chemical and enzymatic pre-treatments of the fully bleached birch (*Betula verrucosa*) kraft pulp as well as sample denotations can be seen in Table 2. Three levels of Fenton's reagent were studied. In *Acid Peroxide*, 10 kg/t hydrogen peroxide was charged at an acidic pH without the addition of ferrous ions i.e. using the metals present in the pulp for catalysis (Cu 0.6 mg/kg, Fe 1.9 mg/kg, Mn 0.3 mg/kg). In *Fenton Low* and *Fenton High*/*Fenton CTP* the addition of hydrogen peroxide was 10 and 50 kg/t and the charge of ferrous ions 0.04 and 0.2 kg/t. The enzymatic treatment (*Enzyme High*) was performed as described by Pääkkö et al. (2007) besides the choice of raw material, a birch kraft pulp was used instead of a sulphite pulp (40% pine and 60% spruce) and the exclusion of pre-milling before the enzymatic treatment. *Enzyme CTP* was prepared using the combined mechanic and enzymatic pre-treatment method used at the Centre Technique du Papier (CTP, France).

Table 2. The conditions employed for the chemical and enzymatic pre-treatments together with sample denotations.

Conditions	Acid Peroxide	Fenton Low	Fenton High	Enzyme High	Fenton CTP	Enzyme CTP
H <sub>2</sub> O <sub>2</sub> , kg/t	10	10	50		50	
Fe <sup>2+</sup> , kg/t		0.04	0.2		0.2	
H <sub>2</sub> SO <sub>4</sub> , kg/t	0.6	0.5	0.3		0.3	
pH <sub>start</sub>	3.5	3.5	3.5	7	3.5	5
FiberCare <sup>®</sup> R, ECU/g				2		4.5
Consistency, %	10	10	10	4	10	4.5
Time, min.	150	150	150	120	150	60
Temperature, °C	90	90	90	50	90	50
Mechanical treatment	-----Laboratory colloid mill-----				Pilot homogeniser	

Both the enzymatic pre-treatment with endoglucanase and the acidic hydrogen peroxide pre-treatment in the presence of ferrous ions caused cleavages in the cellulose chains, i.e. decreased the degree of polymerisation (DP), (*Table 3 in Paper 1*). The chain cleavage after

Fenton pre-treatment is not caused by alkaline degradation of the cellulose through  $\beta$ -elimination by the alkalinity of the cupriethylenediamine solvent used when measuring the intrinsic viscosity since neither oxidation with sodium chlorite nor reduction with sodium borohydride before measurement affected the intrinsic viscosity, *Figure 9*.

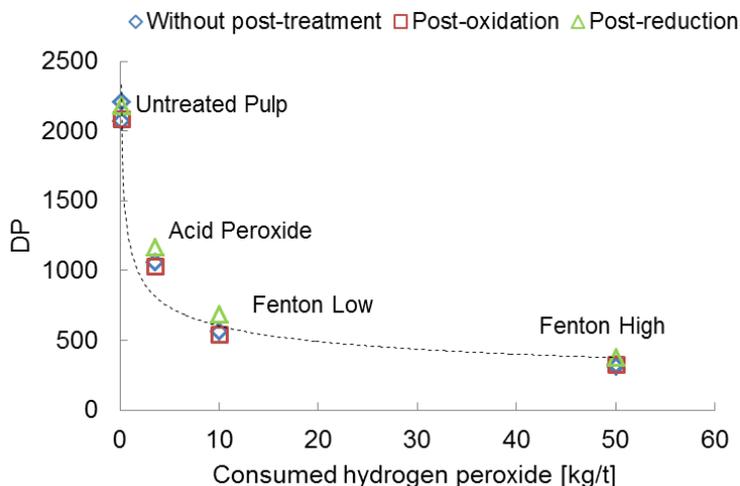


Figure 9. The degree of depolymerisation (DP) as a function of consumed hydrogen peroxide. For explanation of sample denotations, see *Table 2*.

Carbonyl groups are formed as new reducing end groups are introduced when the DP is decreased and by oxidation reactions forming carbonyl groups along the cellulose chains (Pouyet et al. 2014). The degree of polymerisation was calculated from the intrinsic viscosity data ( $\eta$ ) using *Equations 2* and *3* below (Marx-Figini 1978).

$$\text{DP} (<950) \quad \eta = 0.42 \cdot \text{DP} \quad [2]$$

$$\text{DP} (>950) \quad \eta = 2.28 \cdot \text{DP}^{0.76} \quad [3]$$

For the enzymatically pre-treated pulps (*Enzyme High*, *Enzyme CTP*) and the pulp pre-treated with acidic hydrogen peroxide (*Acid Peroxide*), the amount of carbonyl groups is in the same range as the calculated amount of carbonyls in the reducing end groups, *Figure 10*. For *Fenton Low*, *Fenton High* and *Fenton CTP*, the pre-treatment resulted in an additional formation of carbonyl groups along the cellulose chains. The dotted line in *Figure 10* indicates the sum of the calculated amount of carbonyl groups in the reducing end groups and the amount of carbonyl groups situated along the cellulose chain in the pulp without pre-treatment. Similar effects, i.e. a decrease in molar mass and an increase in carbonyl group content have been reported when hydroxyl radicals were introduced by  $\gamma$ -radiation

to cotton linter, bleached beech sulphite pulp, bleached eucalyptus kraft pulp and softwood kraft pulp (Henniges et al. 2012).

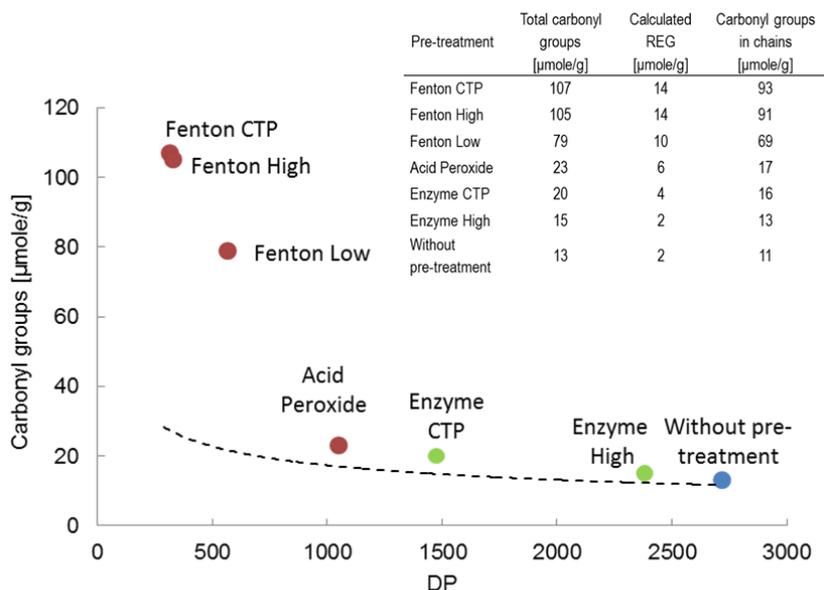


Figure 10. The graph presents the total carbonyl group content as a function of the degree of polymerisation (DP). The dotted line represents the sum of the carbonyl groups in the reducing end groups (REG) calculated from the intrinsic viscosity according to Marx-Figini (1978) and the carbonyl groups situated along the cellulose chain in the pulp without pre-treatment. The table inserted in the graph presents the measured total amount of carbonyl groups and the calculated amount of carbonyls in REGs and cellulose chains. For an explanation of sample denotations, see *Table 2*.

The pre-treatment with endoglucanase as performed in this study resulted in a moderate decrease in intrinsic viscosity, 85 dm<sup>3</sup>/kg for *Enzyme High* and 310 dm<sup>3</sup>/kg for *Enzyme CTP*, and a slight increase of the carbonyl groups. This indicates a mild enzymatic hydrolysis and less impact on the cellulosic material compared to the Fenton pre-treatment. Unlike enzymatic hydrolysis, the Fenton pre-treatment is capable of oxidising the cellulose which can be seen as an introduction of carbonyl groups along the cellulose backbone and an increase in the total charge (18 μeq/g for *Fenton High*, see *Table 3 in Paper 1*). The change in total charge for the other pre-treatments were low or within experimental error. No significant change in surface charge could be seen for any of the pre-treated pulps (*Table 3 in Paper 1*). Fenton pre-treatment with the addition of 10 or 50 kg/t hydrogen peroxide resulted in a yield loss of 2 and 4%, respectively. The calculation is based on a measurement of chemical oxygen demand (COD) and the theoretical amount of oxygen required to oxidize pure cellulose (Süss and Kronis 1998). The enzymatic pre-treatments did not increase the COD, whereas a minor increase was obtained for the *Acid Peroxide*

sample. Despite the variation in the amount of dissolved organic material, no significant difference in the carbohydrate composition for the untreated birch kraft pulp could be seen compared to pulps treated with Fenton chemistry or with enzymatic treatment; all variations were within the experimental error (*Table 2 in Paper 1*).

#### 4.2 Mechanical treatment in the colloid mill

During the mechanical treatment of the untreated, enzymatically or Fenton pre-treated birch kraft pulp in the laboratory colloid mill, the fibre suspension (1% consistency) is forced to pass a small gap (0.159 mm) between the stator and the rotor (see *Figure 11*). The mechanical treatment time was 10, 30 and 53 minutes, corresponding to an energy consumption of about 11 000, 33 000 and 58 000 kWh/t.



Figure 11. Picture of the colloid mill (IKA Magic Lab) and the MK module

With increasing mechanical processing time the fibres will be more and more fibrillated and the specific surface area will increase (*Table 4 in Paper 1*). As can be seen in *Figure 12*, the Fenton pre-treated pulps (*Acid Peroxide* and *Fenton High*) were easier to process mechanically i.e. reached a higher specific surface area measured as Brunauer-Emmett-Teller (BET) area at a given mechanical treatment time compared to the enzymatic pre-treated pulp (*Enzyme High*) and the pulp without pre-treatment, *Figure 13*.

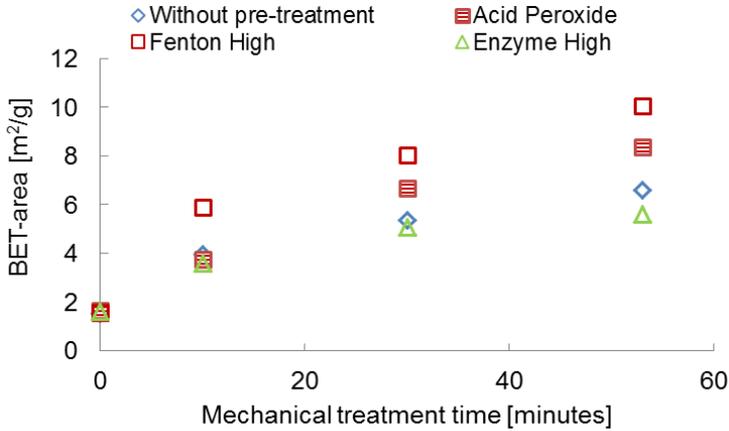


Figure 12. The specific surface area (BET) as a function of mechanical treatment time in the colloid mill. For explanation of sample denotations, see *Table 2*.

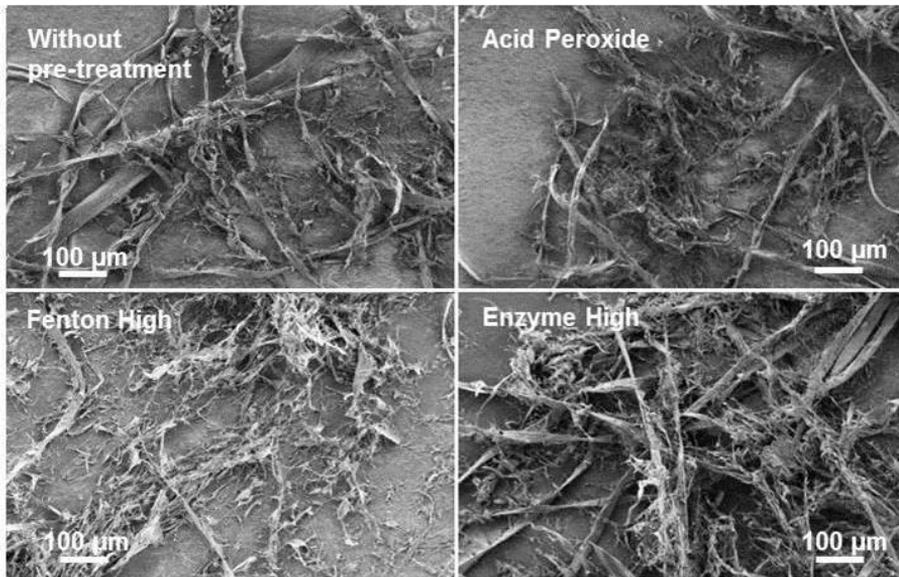


Figure 13. Scanning electron microscopy images of untreated and pre-treated birch kraft pulps after 30 minutes of mechanical treatment in the colloid mill. For explanation of sample denotations, see *Table 2*.

The BET-area is time consuming to determine and the results are dependent on the conditions during sample preparation. Small variations in the conditions during freeze drying may cause agglomeration of the fibrils and a change in the measured surface area (Peng et al. 2012; Peng et al. 2013). The surface charge increase after mechanical treatment

in the colloid mill were linearly proportional to the BET-area for untreated and pre-treated pulps in this thesis work (Figure 14). The determination of the surface charge is easier to perform and can be used for estimations of the surface area since new fibril surfaces are uncovered and surface charges are exposed during prolonged mechanical treatment (cf. Lindström and Winter 1988).

The size distribution of the cellulose fragments in the MFC suspension is important for quality assessment and for comparison between various MFC products. So far, no standardised methods are available. Several attempts have been made to use various techniques to estimate size distribution or fibrillation degree; Laitinen et al. (2011) used a tube flow fractionator for the classification of pulp and paper particles and Tanaka et al. (2012) characterised nanocelluloses with mechanical fractionation through screens and membranes. In this work, the MFCs were successively fractionated using filters/membranes with finer and finer aperture (see section 3.3). The studied pre-treatments generated a large variation in size profiles of the pulps after mechanical processing, Figure 15. After a mechanical treatment time of 30 minutes, the fraction of large fibres, i.e. fibres that do not pass a 112 µm nylon net, range from 79% for the MFC products *Without Pre-treatment*, 71% for *Acid Peroxide*, 68% for *Enzyme High*, 48% for *Fenton Low* down to 37% for *Fenton High*. The reduced amount of fibres and the increased amount of elements in the fractions 0.1-20 µm and <0.1 µm support the view that the Fenton pre-treatment resulted in a pulp that was easier to process mechanically. This is also supported by the SEM visualization of the MFC products, Figure 13.

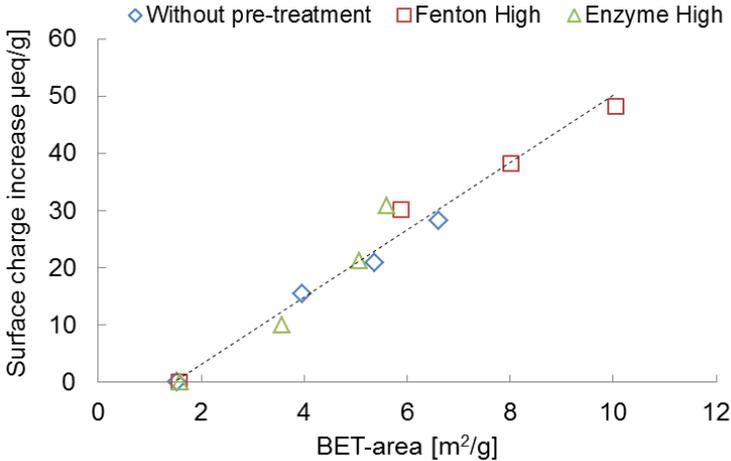


Figure 14. The surface charge increase after mechanical treatment in the colloid mill as a function of the specific surface area (BET). For an explanation of sample denotations, see Table 2.

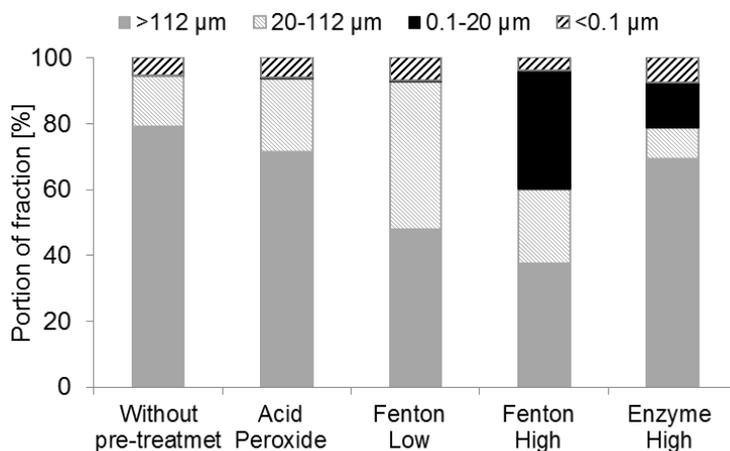


Figure 15. The weight in percent of untreated and pre-treated birch kraft pulps after successive fractionation with finer and finer filters/membranes resulting in fractions  $>112 \mu\text{m}$ ,  $20\text{-}112 \mu\text{m}$ ,  $0.1\text{-}20 \mu\text{m}$  and  $<0.1 \mu\text{m}$ . The fractionation was performed after 30 minutes of mechanical treatment in a colloid mill. For an explanation of sample denotations, see *Table 2*.

#### 4.3 Mechanical treatment in the high-pressure homogeniser

To compare with a recognised well-functioning production method, MFCs from a birch kraft pulp were produced in pilot homogenisation trials, where the pulp was pre-treated with either Fenton's reagent or with a combined mechanic and enzymatic pre-treatment method used at the Centre Technique du Papier (CTP, France). The pulp destined for enzymatic pre-treatment was pre-refined to a targeted drainage index of  $25^\circ\text{SR}$  before the enzymatic pre-treatment (see *Figure 7*). The purpose of the pre-refining was to open the fibre structure and facilitate the penetration of the enzyme and thus improve the efficiency of the enzymatic treatment. The Fenton pre-treatment was performed without this refining stage. To reduce the risk of clogging in the homogeniser, both the enzymatic and Fenton pre-treated pulps were refined until a mean fibre length of  $300 \mu\text{m}$  was achieved before entering the pilot high-pressure homogeniser. The procedure is described in detail in Paper 3. During the mechanical treatment in the high-pressure homogeniser, fibres are subjected to a large pressure drop and high shearing forces when the fibre suspension under high pressure ( $1\ 000\text{-}1\ 500 \text{ bar}$ ) is passed through a minute gap of the homogenizing valve (*Figure 16*). As a result, the fibers will be disintegrated into fibre fragments, fines and smaller fibrils (Missoum et al. 2013; Abdul Khalil et al. 2014).

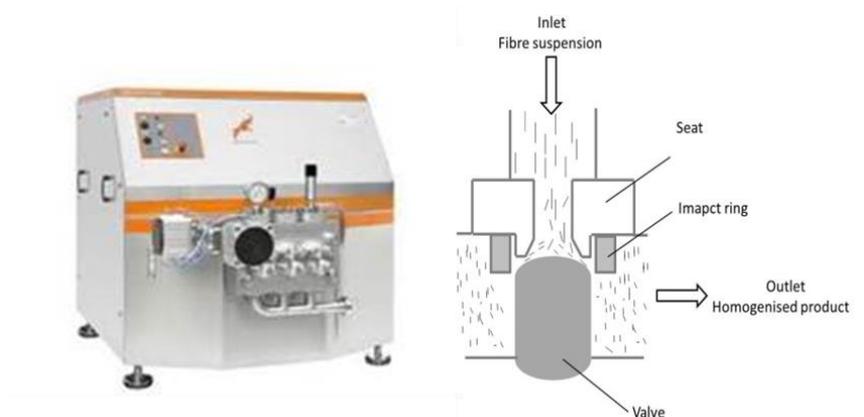


Figure 16. Picture of the high-pressure homogeniser (model NS3045 supplied by GEA Niro Soavi) and a schematic illustration of the homogeniser.

As the mechanical treatment in the homogeniser proceeds, coarser fibre fragments are transformed into smaller sized elements which can be followed as a decrease of the amount in fraction  $>112\ \mu\text{m}$  and an increase in fractions  $20\text{-}112\ \mu\text{m}$ ,  $0.1\text{-}20\ \mu\text{m}$  and  $<0.1\ \mu\text{m}$ . Already after the refining stage (P0), the Fenton pre-treatment resulted in a higher amount of material in fractions  $0.1\text{-}20\ \mu\text{m}$  and  $<0.1\ \mu\text{m}$  (Figure 17). A significantly higher amount of materials in fractions  $0.1\text{-}20\ \mu\text{m}$  and  $<0.1\ \mu\text{m}$  could be seen after each pass (P1, P3-P5) in the homogeniser for the Fenton pre-treated pulp compared to the enzymatic pre-treated pulp. The increased formation of small sized elements in *Fenton CTP* indicate a possibility to prepare an MFC product with a higher degree of fibrillation at the same number of passes or to produce an similar MFC quality after a fewer number of passes through the homogeniser. Examination with SEM (Figure 18) and rheological measurements (Figure 4 in Paper 3) confirmed a higher degree of fibrillation in *Fenton CTP*. The MFC prepared from the Fenton pre-treated pulp needs to be further evaluated and compared with MFC prepared after enzymatic pre-treatment in an application intended for MFC products before a proper evaluation of the possible energy reduction can be made. It is obvious however that the number of passes has a strong influence on the energy consumption since each pass through the homogeniser represents approximately 2 500 kWh/t.

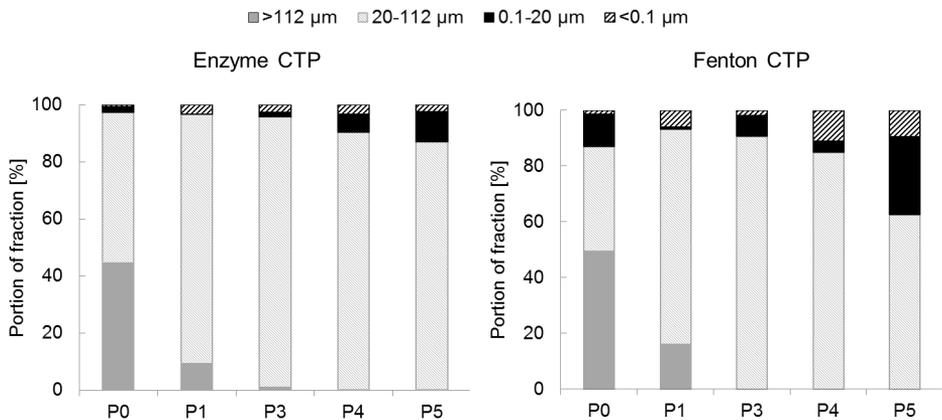


Figure 17. The weight in percent of enzymatic and Fenton pre-treated birch kraft pulps after successive fractionation with finer and finer filters/membranes resulting in fractions  $>112 \mu\text{m}$ ,  $20\text{-}112 \mu\text{m}$ ,  $0.1\text{-}20 \mu\text{m}$  and  $<0.1 \mu\text{m}$ . The fractionation was performed after refining (P0) and after one (P1), three (P3), four (P4) and five (P5) passes through a high-pressure homogeniser. For an explanation of sample denotations, see *Table 2*.

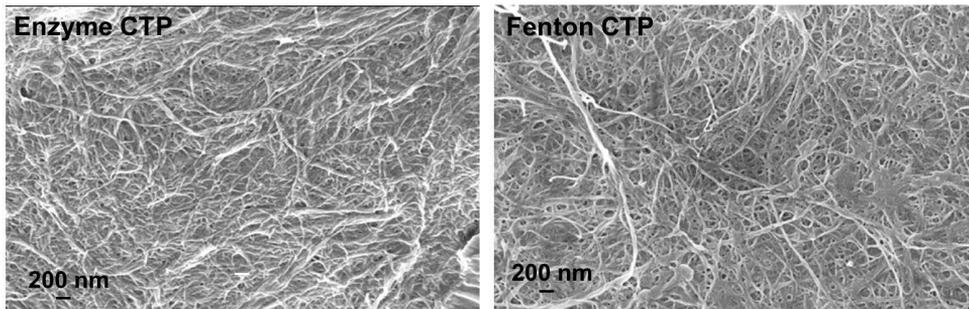


Figure 18. Scanning electron microscope images of enzymatic and Fenton pre-treated birch kraft pulps after five passes (P5) through the high-pressure homogeniser. For explanation of sample denotations, see *Table 2*.

#### 4.4 Comparison between the mechanical treatments in the colloid mill and in the high-pressure homogeniser

Prolonged mechanical treatments in the laboratory colloid mill (*Figure 11*) as well as in the high-pressure pilot homogeniser (*Figure 16*) resulted in an increased amount of small sized elements and also in an increase in surface charge as new charges were exposed. *Figure 19* shows the relationship between the amount of elements  $<112 \mu\text{m}$  measured by size fractionation and the surface charge after mechanical processing. As can be seen, the MFCs prepared by mechanical treatment in the colloid mill and in the high-pressure homogeniser develop in the same way despite the different pre-treatment methods used or

the different approaches for processing the fibres. The MFC produced after Fenton pre-treatment and with the subsequent mechanical treatment stage performed in the colloid mill for 53 minutes seems to be comparable with Fenton pre-treatment followed by refining and one pass through the high-pressure homogeniser, *Figure 19*.

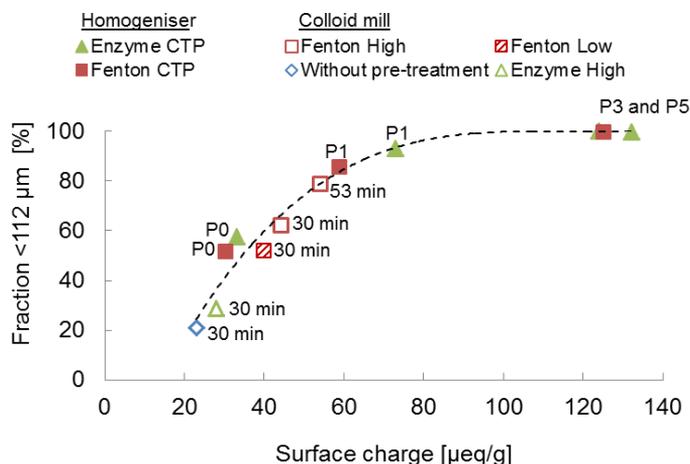


Figure 19. The amount of fraction <112 µm as a function of surface charge for untreated and pre-treated birch kraft pulps mechanically treated in a laboratory colloid mill for 30 or 53 minutes, refined before entering the pilot homogeniser (P0) and after one (P1), three (P3) and five (P5) passes through the homogeniser. The mechanical treatment time 30 and 53 minutes in the colloid mill are depicted beside the sample points. For an explanation of sample denotations, see *Table 2*.

#### 4.5 Evaluation of MFC as a strength enhancer in the middle ply of paperboard

Fenton- and enzymatically pre-treated MFCs prepared after mechanical treatment in the colloid mill were evaluated as strength enhancers in test sheets representing the middle ply of paperboard. The furnish consisted of hydrogen peroxide bleached high temperature spruce (*Picea abies*) chemithermomechanical pulp (HT-CTMP), MFC and a retention aid system containing cationic starch and an anionic silica sol. Test sheets with the addition of Fenton pre-treated MFCs improved the strength properties more than test sheets with the addition of MFCs produced with enzymatic pre-treatment. The addition of 5% MFC (*Fenton High*) to the furnish resulted in an increase in z-directional strength of about 50%, an increase in tensile stiffness index of about 25% and an increase in tensile index of 35% compared to HT-CTMP test sheets prepared without MFC addition. Deviations in both sheet preparation and furnish composition make it difficult to compare the result obtained in this investigation with earlier published findings. However, Taipale et al. (2010) reported a 60% increase in Scott bond and an 8% increase in tensile index when 5% of an MFC produced from bleached softwood kraft pulp, pre-refined and mechanically treated to

MFC in a fluidiser was charged to a bleached softwood kraft pulp furnish containing 1.5% cationic starch. da Silva Perez et al. (2010) reported a tensile index increase of 20-25% when 5% MFC produced from bleached hardwood and softwood kraft pulps, pre-refined before enzymatic treatment and finally mechanically treated in a micro fluidiser was added to hardwood and softwood kraft pulp furnishes.

The improvement in strength properties was proportional to sheet density, surface area (BET), surface charge and the amount of fraction <112  $\mu\text{m}$  for all produced MFCs regardless of the pre-treatment method employed (Figures 3 and 4 in Paper 2). Figure 20 (A-C) presents the clear linear correlation between the weight in percent of the MFC products that passes a 112  $\mu\text{m}$  nylon net and the z-directional strength, tensile index and tensile stiffness index. The bending resistance index is not affected by the amount of material within this fraction, Figure 20 (D). For sheets prepared without MFC, the fraction <112  $\mu\text{m}$  is considered to be zero since no small-sized particles have been added. The strength improvement as a consequence of MFC addition is most likely due to an increased number of bonds between the stiff HT-CTMP fibres where the MFC acts as a binding phase in between.

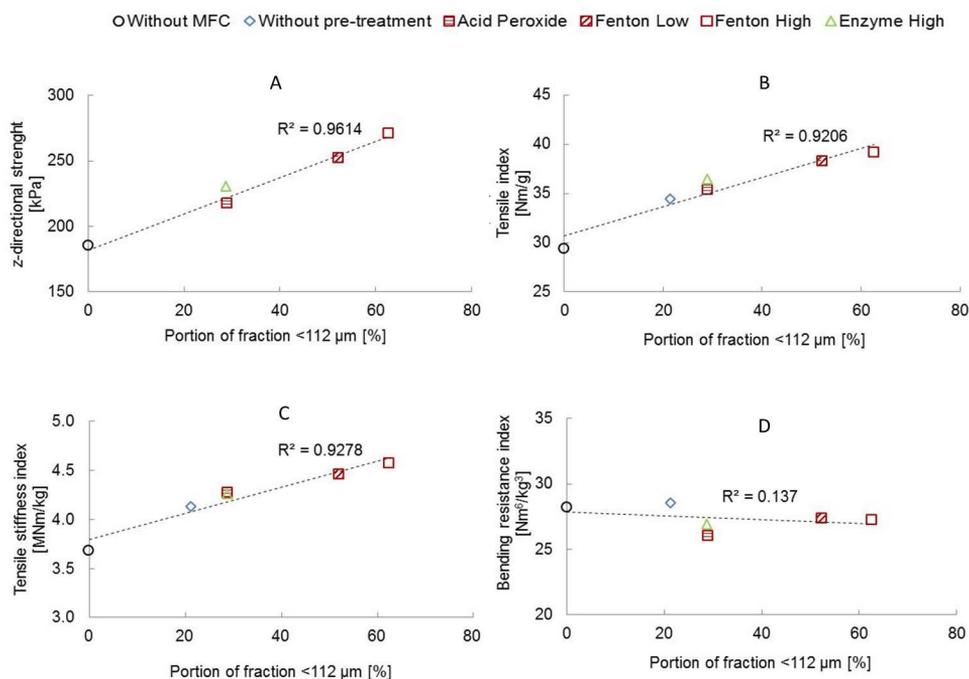


Figure 20. Z-directional strength (A), tensile index (B), tensile stiffness index (C) and bending resistance index (D) for test sheets prepared with and without MFC (5%) as a function of the weight in percent of the MFC products that pass through a 112  $\mu\text{m}$  nylon net. For an explanation of sample denotations, see Table 2.



## 5. Conclusions

Fenton pre-treatment, i.e. the use acidic hydrogen peroxide in the presence of ferrous ions when producing microfibrillar cellulose (MFC) from a fully bleached birch (*Betula verucosa*) kraft pulp was shown to produce a pulp that was easier to process mechanically in a laboratory colloid mill as well as in a pilot high-pressure homogeniser i.e. contained a significantly higher amount of small fibrillated elements and a higher specific surface area at a given mechanical treatment time compared to MFC produced with an enzymatic pre-treatment with endoglucanase. Examination with scanning electron microscopy, rheological measurements and size fractionation confirmed a higher degree of fibrillation after Fenton pre-treatment. Chemically and morphologically, the Fenton pre-treatment resulted in a decreased pulp viscosity and a significant increase in carbonyl groups situated along the cellulose chains.

When the MFCs were evaluated as strength enhancers in test sheets produced from a furnish consisting of a spruce (*Picea abies*) chemithermomechanical pulp, MFC and a retention aid system containing cationic starch and an anionic silica sol, the Fenton pre-treated MFC (50 kg/t hydrogen peroxide, 0.2 kg/t Fe, pH 3.5, 150 minutes, 90°C) increased the strength properties more than the enzymatic pre-treated MFC (4 ECU/g). The addition of 5 wt% Fenton pre-treated MFC resulted in an increase in z-directional strength of about 50%, an increase in tensile stiffness index of about 25% and an increase in tensile index of 35% compared to test sheets prepared without MFC addition. The strength improvement obtained with MFC produced after pre-treatment with a lower charge of Fenton's reagent (10 kg/t hydrogen peroxide, 0.04 kg/t Fe) was almost in the same range and indicate a possibility to reduce the chemical charges.

The findings of this thesis indicate the potential to reduce the energy requirement in the production of MFC by the use of Fenton's reagent compared to enzymatic pre-treatment (endoglucanase) and that such a pre-treatment may be of commercial interest. However, the Fenton pre-treatment can be further optimised and correct assessments of its merits are still premature.



## 6. Recommendations for future work

This thesis work has indicated that the use of Fenton pre-treatment for the preparation of microfibrillar cellulose may be of commercial interest by reducing the energy consumption in the mechanical processing stage. However, the method can be further optimised. For example optimisation of the conditions during Fenton treatment (pH, time, temperature and charge of hydrogen peroxide and ferrous ions) to minimise cellulose depolymerisation and increase the carbonyl- and carboxyl groups in the cellulose chain and eventually convert the carbonyl groups to carboxyl groups. To be able to obtain information about the carbonyl nature (aldehyde, ketone, hydrate and hemiacetal) it would be interesting to use the carbonyl selective fluorescence labelling method combined with UV resonance Raman spectroscopy and molecular weight distribution described by Potthast et al. (2005) on Fenton pre-treated pulps.

The optimal quality of the MFC i.e. size distribution, fibrillation degree, surface area, total charge etc. is dependent on the application area. One issue is to produce an MFC with the “right quality” for the intended application and optimise the conditions during pre-treatment and the subsequent mechanical treatment to produce this MFC. In line with this, it would be interesting to evaluate the MFCs produced in this study by homogenisation as strength enhancers in a paperboard application. The study should be designed to include various charges of the MFCs from pre-refining and in each pass through the homogeniser to be able to relate the obtained strength properties with MFC quality and the addition level and to calculate the best economics between increased product charge or product quality.



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## 8. References

- Aaltio, E. (1962) The effect of highly beaten birch pulp fraction on the properties of Kraft paper. *Paperi Puu* 44(4a):217-222.
- Abdul Khalil, H. P. S., Bhat, A. H., Ireana Yusra, A. F. (2012) Green composites from sustainable cellulose nanofibrils. A review. *Carbohydr Polym* 87(2):963-979.
- Abdul Khalil, H. P. S., Davoudpour, Y., Islam, M. N., Mustapha, A., Sudesh, K., Dungani, R., Jawaid, M. (2014) Production and modification of nanofibrillated cellulose using various mechanical processes: A review. *Carbohydr Polym* 99(0):649-665
- Abe, K., Iwamoto, S., Yano, H. (2007) Obtaining cellulose nanofibers with a uniform width of 15 nm from wood. *Biomacromolecules* 8(10):3276-3278.
- Abe, K., Nakatsubo, F., Yano, H. (2009) High-strength nanocomposite based on fibrillated chemi-thermomechanical pulp. *Compos Sci Technol* 69(14):2434-2437.
- Ahola, S., Österberg, M., Laine, J. (2008a) Cellulose nanofibrils – adsorption with poly(amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive. *Cellulose* 15(2):303-314.
- Ankerfors, M. (2012) Microfibrillated cellulose: Energy-efficient preparation techniques and key properties. Licentiate thesis, TRITA-CHE-Report 2013:38, Royal Institute of Technology, Stockholm, Sweden.
- Barb, W. G., Baxendale, J. H., George, P., Hargrave, H. G. (1951) Reactions of ferrous and ferric ions with hydrogen peroxide. *J Chem Soc Faraday Trans* 47:462-500.
- Bhandari, P. N., Jones, D. D., Hanna, M. A. (2012) Carboxymethylation of cellulose using reactive extrusion. *Carbohydr Polym* 87(3):2246-2254.
- Bhardwaj, N. K., Duong, T. D., Hoang, V., Nguyen, K. L. (2004): Determination of fiber charge components of lo-solids unbleached kraft pulps. *J Colloid Interface Sci* 274(2):543-549.
- Bilbao-Sainz, C., Bras, J., Williams, T., Sénechal, T., Orts, W. (2011) HPMC reinforced with different cellulose nano-particles. *Carbohydr Polym* 86(4):1549-1557.
- Brodin, F. W., Gregersen, Ø. W., Syverud, K. (2014) Cellulose nanofibrils: challenges and possibilities as paper additive or coating material: a review. *Nord Pulp Pap Res J* 29(1):156-166.
- Brown, R. M. (2004) Cellulose structure and biosynthesis: What is in store for the 21st century?. *J Polym Sci Part A: Polym Chem* 42(3):487-495.
- Brown Jr., R. M., Saxena, I. M. (2000) Cellulose biosynthesis: A model for understanding the assembly of biopolymers. *Plant Physiol Biochem* 38(1-2):57-67.
- Brändström, J. (2001) Micro- and ultrastructural aspects of Norway spruce tracheids: a review. *Inter Assoc Wood Anatom* 22(4):333-353.
- Bäckström, M., Kolar, M.-C., Htun, M. (2008) Characterisation of fines from unbleached kraft pulps and their impact on sheet properties. *Holzforschung* 62(5):546-552.
- Cao, Y., Tan, H. (2002) Effects of cellulase on the modification of cellulose. *Carbohydr Res* 337(14):1291-1296.

- Charreau, H., Foreseti, M., Vazquez, A. (2013) Nanocellulose patents trends: A comprehensive review on patents on cellulose nanocrystals, microfibrillated and bacterial cellulose. *Rec Pat Nanotechnol* 7(1):56-80.
- Chinga-Carrasco, G. (2011) Cellulose fibres, nanofibril and microfibrils: The morphological sequence of MFC components from a plant physiology and fibre technology point of view. *Nanoscale Res Lett* 6(417):1-7.
- Chinga-Carrasco, G., Syverud, K. (2014) Pretreatment-dependent surface chemistry of wood nanocellulose for pH-sensitive hydrogels. *J Biomater Appl* 29(3):423-432.
- Cranston, E. D., Gray, D. G. (2006) Morphological and optical characterization of polyelectrolyte multilayers incorporating nanocrystalline cellulose. *Biomacromolecules* 7(9):2522-2530.
- da Silva Perez, D., Tapin-Lingua, S., Petit-Conil, M., Braz, J., Siquera, G., Dufresne, A. (2009) Production of cellulose micro- and nanofibers: State of the art. 42nd Pulp Pap Int Congress Exhibition, Sao Paulo, Brazil, October 26-29, 12pp.
- da Silva Perez, D., Tapin-Lingua, S., Lavalette, A., Barbosa, T., Gonzalez, I., Siqueira, G., Bras, J., Dufresne, A. (2010) Impact of micro/nanofibrillated cellulose preparation on the reinforcement properties of paper and composites films. *Int Conf Nanotechnol Forest Prod Ind*, Espoo, Finland, September 26-29, pp 1-20.
- Ding, S.-Y., Himmel, M. E. (2006) The maize primary cell wall microfibril: A new model derived from direct visualization. *J Agric Food Chem* 54(3):597-606.
- Dufresne, A. (2012) Preparation of microfibrillated cellulose. In: Dufresne, A (ed) *Nanocellulose: From Nature to High Performance Tailored Materials*. ISBN 978-3-11-025460-0, Walter de Gruyter, München, Germany, pp 43-81.
- Engström, A.-C., Ek, M., Henriksson, G. (2006) Improved accessibility and reactivity of dissolving pulp for the viscose process: Pretreatment with monocomponent endoglucanase. *Biomacromolecules* 7(6):2027-2031.
- Eriksen, Ø., Syverud, K., Gregersen, Ø. (2008) The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper. *Nord Pulp Pap Res J* 23(3):299-303.
- Fengel, D., Wegener, G. (1989a) Structure and ultra structure In: *Wood Chemistry, Ultrastructure, Reactions*. ISBN 3-11-012059-3, Walter de Gruyter, Berlin, Germany, pp 6-25.
- Fengel, D., Wegener, G. (1989b) Cellulose In: *Wood Chemistry, Ultrastructure, Reactions*. ISBN 3-11-012059-3, Walter de Gruyter, Berlin, Germany, pp 66-105.
- Fengel, D., Wegener, G. (1989c) Lignin In: *Wood Chemistry, Ultrastructure, Reactions*. ISBN 3-11-012059-3, Walter de Gruyter, Berlin, Germany, pp 132-174.
- Fengel, D., Wegener, G. (1989d) Extractives In: *Wood Chemistry, Ultrastructure, Reactions*. ISBN 3-11-012059-3, Walter de Gruyter, Berlin, Germany, pp 182-222.
- Fenton, H. J. H. (1894) Oxidation of tartaric acid in presence of iron. *J Chem Soc Faraday Trans* 65:899-910.

- Ferrer, A., Quintana, E., Filpponen, I., Solala, I., Vidal, T., Rodríguez, A., Laine, J., Rojas, O. (2012): Effect of residual lignin and heteropolysaccharides in nanofibrillar cellulose and nanopaper from wood fibers. *Cellulose* 19(6):2179-2193.
- Festucci-Buselli, R. A., Otoni, W. C., Joshi, C. P. (2007) Structure, organization, and functions of cellulose synthase complexes in higher plants. *Braz J Plant Physiol* 19(1):1-13.
- Gellerstedt, G. (2009) Pulp and paper chemistry and technology. In: Ek, M (ed) *Pulp and Paper Chemistry and Technology*, vol 2. ISBN 978-3-11-021342-3, Walter de Gruyter, Berlin, Germany, pp 91-120.
- Haber, F., Weiss, J. (1934) The catalytic decomposition of hydrogen peroxide by iron salts. *Proc R Soc* 147, Ser. A.:332-351.
- Heijnesson-Hultén, A. (2007) Method for preparing microfibrillar polysaccharide. WO2007001229A1.
- Henniges, U., Okubayashi, S., Rosenau, T., Potthast, A. (2012) Irradiation of cellulosic pulps: Understanding its impact on cellulose oxidation. *Biomacromolecules* 13(12):4171-4178.
- Henniges, U., Veigel, S., Lems, E.-M., Bauer, A., Keckes, J., Pinkl, S., Gindl-Altmutter, W. (2014) Microfibrillated cellulose and cellulose nanopaper from *Miscanthus* biogas production residue. *Cellulose* 21(3):1601-1610.
- Henriksson, G., Christiernin, M., Agnemo, R. (2005) Monocomponent endoglucanase treatment increases the reactivity of softwood sulphite dissolving pulp. *J Ind Microbiol Biotechnol* 32(5):211-214.
- Henriksson, M., Henriksson, G., Berglund, L. A., Lindström, T. (2007) An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers. *Eur Polym J* 43(8):3434-3441.
- Henriksson, G., Lennholm, H. (2009) Cellulose and carbohydrate chemistry. In: Ek, M., Gellerstedt, G., Henriksson, G. (eds) *Pulp and Paper Chemistry and Technology*, vol 1. ISBN 978-3-11-021339-3, Walter de Gruyter GmbH & Co. KG, Berlin, Germany, pp 71-100.
- Horn, S., Vaaje-Kolstad, G., Westereng, B., Eijsink, V. G. (2012) Novel enzymes for the degradation of cellulose. *Biotechnol Biofuels* 5(1):45, pp12.
- Isogai, A. (2009) Individualization of nano-sized plant cellulose fibrils achieved by direct surface carboxylation using TEMPO catalyst. *Int Conf Nanotechnol Forest Prod Ind*, Edmonton, Canada, June 23-26, pp 49-72.
- Isogai, A., Atalla, R. H. (1998) Dissolution of cellulose in aqueous NaOH solutions. *Cellulose* 5(4):309-319.
- Isogai, A., Saito, T., Fukuzumi, H. (2011) TEMPO-oxidized cellulose nanofibers. *Nanoscale* 3(1):71-85.
- Iwamoto, S., Kai, W., Isogai, T., Saito, T., Isogai, A., Iwata, T. (2010) Comparison study of TEMPO-analogous compounds on oxidation efficiency of wood cellulose for preparation of cellulose nanofibrils. *Polym Degrad Stabil* 95(8):1394-1398.

- Jain, P., Vigneshwaran, N. (2012) Effect of Fenton's pretreatment on cotton cellulosic substrates to enhance its enzymatic hydrolysis response. *Bioresour Technol* 103(1):219-226.
- Jeong, M.-J., Dupont, A.-L., de la Rie, E. R. (2014) Degradation of cellulose at the wet-dry interface. II. Study of oxidation reactions and effect of antioxidants. *Carbohydr Polym* 101(0):671-683.
- Johansson, L.-S., Tammelin, T., Campbell, J. M., Setälä, H., Österberg, M. (2011) Experimental evidence on medium driven cellulose surface adaptation demonstrated using nanofibrillated cellulose. *Soft Matter* 7(22):10917-10924.
- John, M. J., Thomas, S. (2008) Biofibres and biocomposites. *Carbohydr Polym* 71(3):343-364.
- Kajanto, I., Kosonen, M. (2012): The potential use of micro- and nano-fibrillated cellulose as reinforcing element in paper, *J Sci Technol For Prod Processes* 2 (6):42-48.
- Kangas, H., Lahtinen, P., Saariaho, A.-M., Laitinen, O., Hellen, E. (2014) Characterization of fibrillated celluloses. A short review and evaluation of characteristics with a combination of methods. *Nord Pulp Pap Res J* 29(1):129-143.
- Kaushik, M., Chen, W. C., van de Ven, T. G. M., Moores, A. (2014) An improved methodology for imaging cellulose nanocrystals by transmission electron microscopy. *Nord Pulp Pap Res J* 29(1):77-84.
- Klemm, D., B. P., T. Henze, U. Heinze, W. Wagenknecht (1998) *Comprehensive Cellulose Chemistry. Volume 1. Fundamentals and Analytical Methods.* ISBN 3-527-29413-9, Wiley-VCH Verlag GmbH, Weinheim, Germany, pp 9-21.
- Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D., Dorris, A. (2011) Nanocelluloses: A new family of nature-based materials. *Angew Chem Int Ed* 50(24):5438-5466.
- Koyama, M., William, H., Tomoya, I., Junji, S., Henrissat, B. (1997) Parallel-up structure evidences the molecular directionality during biosynthesis of bacterial cellulose. *P Natl Acad Sci* 94(17):9091-9095.
- Lai, Y.-Z. (2001) Chemical degradation. In: Hon, D. N.-S., Shiraishi, N. (eds) *Wood and Cellulosic Chemistry.* 2nd edn. ISBN 0-8247-0024-4, Marcel Dekker, Inc., New York, NY, USA, pp 443-512.
- Laitinen, O., Kempainen, K., Niinimäki, J. (2011) Fractionation of pulp and paper particles selectively by size. *BioResources* 6(1):672-385.
- Lavoine, N., Desloges, I., Dufresne, A., Bras, J. (2012) Microfibrillated cellulose – Its barrier properties and applications in cellulosic materials: A review. *Carbohydr Polym* 90(2):735-764.
- Lindström, T., Winter, L. (1988) Mikrofibrillär cellulosa som komponent vid papperstillverkning. Internal STFI report C159. Public research report and can be obtained from <http://www.innventia.com>
- Lynd, L. R., Weimer, P. J., van Zyl, W. H., Pretorius, I. S. (2002) Microbial cellulose utilization: Fundamentals and biotechnology. *Microbiol Mol Biol R* 66(3):506-577.

- Marx-Figini, M. (1978): Significance of the intrinsic viscosity ratio of unsubstituted and nitrated cellulose in different solvents. *Die Angew Makrom Chem* 72(1):161-171.
- Missoum, K., Belgacem, M., Bras, J. (2013) Nanofibrillated cellulose surface modification: A review. *Materials* 6(5):1745-1766.
- Norimoto, M. (2001) Chemical modification of wood. In: Hon, D. N.-S., Shiraishi, N. (eds) *Wood and Cellulosic Chemistry*. 2nd edn. ISBN 0-8247-0024-4, Marcel Dekker, Inc., New York, NY, USA, p 600.
- Oliva, J. M., Manzanares, P., Ballesteros, I., Negro, M. J., González, A., Ballesteros, M. (2005) Application of Fenton's reaction to steam explosion prehydrolysates from poplar biomass. *Appl Biochem Biotechnol* 124(1-3):887-899.
- Osong, S. H., Norgren, S., Engstrand, P. (2013) An approach to produce nano-ligno-cellulose from mechanical pulp fine materials. *Nord Pulp Pap Res J* 28(4):472-479.
- Osong, S. H., Norgren, S., Engstrand, P. (2014) Paper strength improvement by inclusion of nano-ligno-cellulose to chemi-thermomechanical pulp. *Nord Pulp Pap Res J* 29(2):309-316.
- Page, D. (1969) A theory for the tensile strength of paper. *Tappi* 52(4):647.
- Peng, Y., Gardner, D., Han, Y. (2012) Drying cellulose nanofibrils: in search of a suitable method. *Cellulose* 19(1):91-102.
- Peng, Y., Gardner, D., Han, Y., Kiziltas, A., Cai, Z., Tshabalala, M. (2013) Influence of drying method on the material properties of nanocellulose I: Thermostability and crystallinity. *Cellulose* 20(5):2379-2392.
- Potthast, A., Rosenau, T., Kosma, P., Saariaho, A.-M., Vuorinen, T. (2005): On the nature of carbonyl groups in cellulosic pulps. *Cellulose* 12(1):43-50.
- Pouyet, F., Chirat, C., Potthast, A., Lachenal, D. (2014): Formation of carbonyl groups on cellulose during ozone treatment of pulp: Consequences for pulp bleaching. *Carbohydr Polym* 109(0):85-91.
- Pääkkö, M., Ankerfors, M., Kosonen, H., Nykänen, A., Ahola, S., Österberg, M., Ruokolainen, J., Laine, J., Larsson, P. T., Ikkala, O., Lindström, T. (2007) Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. *Biomacromolecules* 8(6):1934-1941.
- Qing, Y., Sabo, R., Zhu, J. Y., Agarwal, U., Cai, Z., Wu, Y. (2013) A comparative study of cellulose nanofibrils disintegrated via multiple processing approaches. *Carbohydr Polym* 97(1):226-234.
- Ramiro, R., Berglund, L. (2013) Processing of mechanical pulps to obtain new microfibrillated cellulose. 17th Int Symp Wood fibre Pulp Chem, Vancouver, Canada, June 12-14.
- Retulainen, E., Moss, P., Nieminen, K. (1993): Effect of fines on the properties of fibre networks. *Prod Paperm – 10th Fund Res Symp*, Oxford, UK, pp 727-769.
- Samir, M. A. S. A., Alloin, F., Paillet, M., Dufresne, A. (2004): Tangling effect in fibrillated cellulose reinforced nanocomposites. *Macromolecules* 37(11):4313-4316.

- Samir, M. A. S. A., Alloin, F., Dufresne, A. (2005) Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules* 6(2):612-626.
- Shatkin, J. A., Wegner, T. H., Bilek, E. M., Cowie, J. (2014) Market projections of cellulose nanomaterial-enabled products. Part 1: Applications. *Tappi J* 13(5):9-16.
- Siqueira, G., Bras, J., Dufresne, A. (2010a) Cellulosic bionanocomposites: A review of preparation, properties and applications. *Polymers* 2(4):728-765.
- Siqueira, G., Tapin-Lingua, S., Bras, J., da Silva Perez, D., Dufresne, A. (2010b) Morphological investigation of nanoparticles obtained from combined mechanical shearing, and enzymatic and acid hydrolysis of sisal fibers. *Cellulose* 17(6):1147-1158.
- Siro, I., Plackett, D. (2010) Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose* 17(3):459-494.
- Sjöström, E. (1993a) The structure of wood In: *Wood Chemistry Fundamentals and Applications*. ISBN 0-12-647481-8, Academic Press, San Diego, California, USA, pp 1-20.
- Sjöström, E. (1993b) Wood polysaccharides In: *Wood Chemistry Fundamentals and Applications*. ISBN 0-12-647481-8, Academic Press, San Diego, California, USA, pp 51-70.
- Sjöström, E. (1993c) Extractives In: *Wood Chemistry Fundamentals and Applications*. ISBN 0-12-647481-8, Academic Press, San Diego, California, USA, pp 92-107.
- Sjöström, E. (1993d) Wood pulping In: *Wood Chemistry Fundamentals and Applications*. ISBN 0-12-647481-8, Academic Press, San Diego, California, USA, pp 114-138.
- Sjöström, E. (1993e) Pulp bleaching In: *Wood Chemistry Fundamentals and Applications*. ISBN 0-12-647481-8, Academic Press, San Diego, California, USA, pp 166-201.
- Süss, H., Kronis, J. (1998) The correlation of COD and yield in chemical pulp bleaching. *Tappi Breaking the Pulp Yield Barrier Symposium*, Atlanta, GA, USA, February 17-18, pp 153-162.
- Sychev, A. Y., Isak, V. G. (1995) Iron compounds and the mechanisms of the homogenous catalysis of the activation of O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> and the oxidation of organic substrates. *Russ Chem Rev* 64(12):1105-1129.
- Syverud, K., Chinga-Carrasco, G., Toledo, J., Toledo, P. G. (2011) A comparative study of Eucalyptus and Pinus radiata pulp fibres as raw materials for production of cellulose nanofibrils. *Carbohydr Polym* 84(3):1033-1038.
- Taipale, T., Österberg, M., Nykänen, A., Ruokolainen, J., Laine, J. (2010) Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength. *Cellulose* 17(5):1005-1020.
- Tanaka, A., Seppanen, V., Houni, J., Sneek, A., Pirkonen, P. (2012): Nanocellulose characterization with mechanical fractionation. *Nord Pulp Paper Res J* 27(4):689-694.

- Tapin-Lingua, S., Meyer, V., Petit-Conil, M. (2013) Correlations between pulp composition and efficiency of M/NFC production TAPPI Int Conf Nanotechn Renew Mat, Stockholm, Sweden, June 24-27, 25pp.
- Taylor, N. G. (2008) Cellulose biosynthesis and deposition in higher plants. *New Phytol* 178(2):239-252.
- Tejado, A., Alam, M., Antal, M., Yang, H., van de Ven, T. (2012) Energy requirements for the disintegration of cellulose fibers into cellulose nanofibers. *Cellulose* 19(3):831-842.
- Teleman, A. (2009) Hemicelluloses and pectins. In: Ek, M., Gellerstedt, G., Henriksson, G. (eds) *Pulp and Paper Chemistry and Technology*, vol 1. ISBN 978-3-11-021339-3, Walter de Gruyter GmbH & Co. KG, Berlin, Germany, pp 101-120.
- Torgnysdotter, A., Kulachenko, A., Gradin, P., Wågberg, L. (2007) Fiber/fiber crosses: Finite element modeling and comparison with experiment. *J Compose Mater* 41(13):1603-1618.
- Turbak, A. F., Snyder, F. W., Sandberg, K. R. (1983) Microfibrillated cellulose, a new cellulose product: Properties, uses, and commercial potential. *J Appl Polym Sci, Appl Polym Symp* 37:815-827.
- Walker, C. (2013): Nanotechnology is ready to transform our industry. *Paper 360°* 8(5):34-36.
- Walter, K., Paulsson, M., Wackerberg, E. (2009) Energy efficient refining of black spruce TMP by using acid hydrogen peroxide: Part 1. A pilot plant study. *Nord Pulp Pap Res J* 24(3):255-265.
- Walter, K., Paulsson, M., Hellström, P. (2013) Acid hydrogen peroxide treatment of Norway spruce TMP: A model study using free ferrous ions and ferric ions chelated with EDTA as catalysts. *J Wood Chem Technol* 33(4):267-285.
- Wang, M., Olszewska, A., Walther, A., Malho, J.-M., Schacher, F. H., Ruokolainen, J., Ankerfors, M., Laine, J., Berglund, L. A., Österberg, M., Ikkala, O. (2011a) Colloidal ionic assembly between anionic native cellulose nanofibrils and cationic block copolymer micelles into biomimetic nanocomposites. *Biomacromolecules* 12(6):2074-2081.
- Wang, Z.-X., Li, G., Yang, F., Chen, Y.-L., Gao, P. (2011b) Electro-Fenton degradation of cellulose using graphite/PTFE electrodes modified by 2-ethylanthraquinone. *Carbohydr Polym* 86(4):1807-1813.
- Zimmermann, T., Pöhler, E., Geiger, T. (2004) Cellulose fibrils for polymer reinforcement. *Adv Eng Mater* 6(9):754-761.
- Zimmermann, T., Bordeanu, N., Strub, E. (2010) Properties of nanofibrillated cellulose from different raw materials and its reinforcement potential. *Carbohydr Polym* 79(4):1086-1093.



# Fenton Pre-treatment of a Birch Kraft Pulp for MFC preparation

The potential to use acidic hydrogen peroxide in the presence of ferrous ions (Fenton's reagent) as a pre-treatment when producing microfibrillar cellulose (MFC) from a bleached birch kraft pulp was investigated and the properties of the produced MFC was compared to the properties of a MFC produced with enzymatic pre-treatment. Additionally, the MFCs evaluated as strength enhancers in test sheets representing the middle ply of paperboard.

From the chemical characterisation, it was concluded that the Fenton pre-treatment caused a decrease in the degree of polymerisation (DP) and an increase in both carboxyl- and carbonyl groups. In the subsequent mechanical treatment in a colloid mill, the Fenton pre-treated pulps were easier to process mechanically indicating a potential to lower the energy consumption.

When the MFCs were evaluated as strength enhancers in test sheets, Fenton pre-treated MFCs increased the strength properties more than the enzymatic pre-treated MFCs at a given mechanical treatment time. Addition of 5 wt% Fenton pre-treated MFC resulted in an increase in z-directional strength of about 50%, an increase in tensile stiffness index of about 25% and an increase in tensile index of 35% compared to test sheets prepared without MFC addition.

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