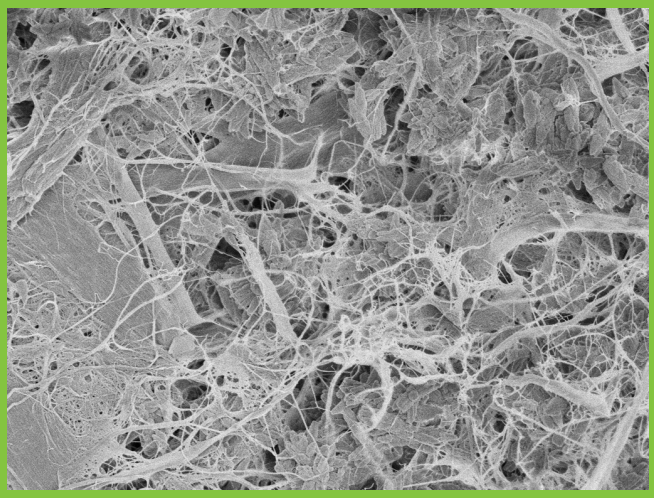
Department of Forest Products Technology

The manufacturing potential of micro and nanofibrillated cellulose composite papers

Juuso Rantanen



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The manufacturing potential of micro and nanofibrillated cellulose composite papers

Juuso Rantanen

A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Chemical Technology, at a public examination held at the lecture hall P1 of the Department of Forest Products Technology on 15 July 2016 at 12.

Aalto University
School of Chemical Technology
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Bio-based Materials Technology

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Abstract

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Abstract

This study presents a novel approach for producing composite papers that have fundamentally different properties to the traditional products in the paper industry. The main focus of this work was to evaluate the use of micro and nanofibrillated celluloses (MNFCs) as a component in paper in conjunction with traditional fillers and pulp fibers. The main hypothesis of this thesis work was that it is possible to form and subsequently dewater furnishes that contain considerable amounts of MNFC. Moreover, the properties of these new MNFC composite papers were expected to differ from traditional paper characteristics.

The properties of MNFC composite papers were studied with different compositions of pulp fibers, MNFC, and filler. It was concluded that the optical properties of the composite papers were excellent and that the use of fillers together with MNFC results in a unique micro and nanoporous network structure of the paper. The in-situ precipitation of calcium carbonate directly on the MNFC fibrils was also shown to be a promising method for adjusting the water uptake of the MNFC and the resulting paper properties. The cost structure of the MNFC composite proved to be very attractive due to a reduction in the level of more expensive fibers required.

The shear thinning behavior of the MNFC composite suspension was shown to enable 5-10 % solids content in forming, and subsequent wire dewatering to 33 % solids content. In addition, this work demonstrated that a wet pressing process can be used for the efficient dewatering of the MNFC composite furnishes if long enough press pulses are used. Under some conditions the dewatering was found to be better than with kraft pulp fibers alone. This thesis work clearly establishes that a wide range of high value MNFC based products can be formed using a feasible, efficient and economical process – a critically important step towards the next generation of products and processes based on forest resources.

Keywords Nanocellulose, MNFC, papermaking, dewatering, composite, PCC

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Tekijä
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Tiivistelmä

Työn tavoitteena oli kehittää uudenlainen lähestymistapa valmistaa komposiittipapereita, joiden ominaisuudet eroavat huomattavasti perinteisistä paperilajeista. Pääpainopisteenä työssä tutkittiin mikro- ja nanofibrilloidun selluloosan (MNFC) käyttöä uudentyyppisten komposiittipapereiden komponenttina yhdessä perinteisten täyteaineiden ja kemiallisen massan kuitujen kanssa. Erityisesti tavoitteena oli selvittää, mitä haasteita ja mahdollisuuksia nämä paljon vettä sitovat materiaalit asettavat paperin ominaisuuksien sekä mahdollisen valmistusmenetelmän kannalta. Keskeisenä hypoteesina työssä oli, että huomattavia määriä MNFC:tä sisältävien komposiittipapereiden rainaus ja vedenpoisto on mahdollista. Lisäksi näiden komposiittipapereiden ominaisuuksien odotettiin olevan erilaisia kuin perinteisillä paperilajeilla.

MNFC-komposiittipapereiden ominaisuuksia tutkittiin eri täyteaine, kuitu- sekä MNFC seossuhteilla. Näiden papereiden optisten ominaisuuksien todettiin olevan erinomaisia, ja MNFC:n sekä täyteaineen ominaisuuksista johtuen paperin nano- ja mikrohuokoisen rakenteen todettiin olevan hyvin ainutlaatuinen. Kalsiumkarbonaatin kerasaostusta MNFC:n kanssa voitiin hyödyntää sekä MNFC:n vedensitomiskyvyn alentamiseen että komposiittipaperin ominaisuuksien säätämiseen. Myös komposiittipapereiden kustannusrakenteen todettiin olevan houkutteleva korkean täyteainepitoisuuden vuoksi.

MNFC-komposiittisuspension leikkausohenevuus mahdollisti rainanmuodostuksen 5-10 prosentin sakeudessa, viiranjälkeisen kuiva-ainepitoisuuden noustessa jopa 33 prosenttiin. Lisäksi todettiin, että märkäpuristus on yksikköoperaationa soveltuva rainan vedenpoistoon viiran jälkeen, mikäli käytetään riittävän pitkiä puristuspulsseja. Eräissä olosuhteissa MNFC-komposiittirainan vedenpoisto oli jopa tehokkaampaa kuin pelkillä kemiallisen massan kuiduilla. Tässä työssä osoitettiin, että MNFC-pohjaisia tuotteita on mahdollista valmistaa tehokkaasti ja taloudellisesti, ja tutkimus on siksi tärkeä edistysaskel kohti uuden sukupolven biopohjaisia tuotteita ja prosesseja.

Avainsanat Nanoselluloosa, MNFC, paperin valmistus, vedenpoisto, komposiitti, PCC

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Preface

The research work done during the course of this thesis was carried out at the Department of Forest Products Technology in Aalto University School of Chemical Technology in 2010 - 2015. During this work, I have had the opportunity to work with a number of professionals from the industry and academic community around the world. I want to express my thanks to UPM-Kymmene, EffNet, FIBIC, Paper Engineer's Association, and PaPSaT for providing financial support for completing this work. The support from Omya AG and Ahlstrom Oyj in providing raw materials and funding the research group is also highly appreciated.

I am extremely grateful for my instructor, Professor Thad Maloney. In his guidance I have learned the important truth that thinking outside the box is often the key to success, and that one can never be too patient in turning every stone while carrying out scientific research. Without his detailed advice especially with my article manuscripts the publication processes wouldn't have been as successful and fluent. Special thanks also go to Professor Emeritus Hannu Paulapuro for introducing me to the world of academic research by employing me as a Master's thesis student back in 2009, and Eero Hiltunen for instructing and helping me with my first scientific publication. The support from the technical personnel of the department was of the highest quality, and I personally want to thank Tuyen Nguyen, Leena Nolvi, and Christian Orassaari for the professional and always so helpful attitude even when confronting difficult questions or tasks. I am also very thankful for the support I had from my research group members during the work, your support has been extremely valuable. I want to also thank my co-authors Jonna Kuusisto, Katarina Dimic-Misic, Panu Lahtinen, Teresa Paulig, Erkki Laiti, Jukka Pirttiniemi, Petri Kuosmanen, and Kaarlo Nieminen for helping me with my manuscripts.

Apart from the professional support, I want to thank my colleagues from the Department of Forest Products Technology for the fruitful and often very unscientific (some may even say inappropriate) coffee table discussions. A coffee break between the endless hours of writing manuscripts and analyzing data often saved the day. Special thanks to Tuomo and Pekka for the nice conversations about pretty much everything!

Most of all I want to thank my family who has always believed in me and supported me whenever in need. My parents Anne and Jukka, my brothers Tuomo and Antti, and my sister Elina, thank you for your love and support!

Espoo, June 10, 2016
Juuso Rantanen

List of abbreviations

BSKP	Bleached softwood kraft pulp
DCS	Dissolved and colloidal substances
FE-SEM	Field emission scanning electron microscope
HW	Hardwood
MFC	Microfibrillated cellulose
MNFC	Micro and nanofibrillated celluloses
MR	Moisture ratio
MTS	Material testing system
NFC	Nanofibrillated cellulose
PCC	Precipitated calcium carbonate
PET	Polyethylene terephtalate
PSD	Pore size distribution
RW	Rewetted water
SED	Specific sedimentation
SEM	Scanning electron microscope
SR	Schopper-Riegler number
SW	Softwood
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl radical
WRV	Water retention value

LIST OF PUBLICATIONS

This thesis is mainly based on the results presented in six publications mentioned below which are referred to as Roman numerals in the text.

Paper I Rantanen, J., Lahtinen, P., and Maloney, T. (2013): Property Space for Fibre, Microfibrillar Cellulose and Precipitated $CaCO_3$ Composite Sheets, *Int.Paperworld IPW*,(5), 46-51.

Paper II Rantanen, J., Paulig, T., Laiti, E., and Maloney, T. C. (2015): Dewatering and Physical Properties of a Nonwoven Composite Material with Microfibrillated Cellulose, Submitted.

Paper III Rantanen, J., and Maloney, T. (2013): Press Dewatering and Nip Rewetting of Paper Containing Nano- and Microfibril Cellulose, *Nord Pulp Pap Res J*, 28(4), 582-587. DOI 10.3183/NPPRJ-2013-28-04-p582-587.

Paper IV Rantanen, J., and Maloney, T. C. (2015): Consolidation and dewatering of a microfibrillated cellulose fiber composite paper in wet pressing. *Eur Polym J,* 68, 585-591. DOI: 10.1016/j.eurpolymj.2015.03.045.

Paper V Rantanen, J., Dimic-Misic, K., Kuusisto, J., and Maloney, T. C. (2015): The Water Uptake of Microfibrillated Cellulose - Effect on Furnish Dewatering and Composite Paper Properties, *Cellulose*, 22(6), 4003-4015. DOI: 10.1007/s10570-015-0777-x.

Paper VI Rantanen, J., Dimic-Misic, K., Pirttiniemi, J., Kuosmanen, P., and Maloney, T. C. (2015): Forming and dewatering of a microfibrillated cellulose composite paper, *BioRes*. 10(2), 3492-3506. DOI: 10.15376/biores.10.2.3492-3506.

Author's contribution

Paper I: *Property Space for Fibre, Microfibrillar Cellulose and Precipitated CaCO3 Composite Sheets*.
Juuso Rantanen was responsible for the experimental design, development of the sheet preparation method, part of the sheet preparations and measurement of properties, statistical analysis, and writing the manuscript.

Paper II: *Dewatering and Physical Properties of a Nonwoven Composite with Microfibrillated Cellulose*.
Juuso Rantanen was responsible for designing all wet pressing experiments and designing handsheet experiments in co-operation with the co-authors, conducted the wet pressing measurements, analyzed the wet pressing results, and wrote the manuscript.

Paper III: *Press Dewatering and Nip Rewetting of Paper Containing Nano- and Microfibril Cellulose*.
Juuso Rantanen was responsible for developing the wet pressing method and procedure, experimental design, all sheet preparations and measurements, analyzing the results, and writing the manuscript.

Paper IV: *Consolidation and dewatering of a microfibrillated cellulose fiber composite paper in wet pressing*.
Juuso Rantanen was responsible for the experimental design, preparation of samples, conducted the wet pressing experiments, developed the algorithm for thickness measurement in the press simulator, measured all sample properties except for mercury porosimetry, made the SEM –imaging of the samples, analyzed the results, and wrote the manuscript.

Paper V: *The effect of micro and nanofibrillated cellulose water uptake on high filler content composite paper properties and furnish dewatering*.
Juuso Rantanen was responsible for the experimental design, preparation of the samples for wet pressing, wet pressing experiments, measuring the sheet properties, SEM –imaging, analyzing the results, and writing the manuscript.

Paper VI: *Forming and dewatering of a microfibrillated cellulose composite paper*.
Juuso Rantanen was responsible for building the first version of the laboratory headbox, participated in the design of the high consistency pilot paper machine and headbox, analyzed the data, and wrote the manuscript.

Table of Contents

1 Introduction and thesis objective

The Finnish paper industry has for over a century relied on the profound understanding of paper making processes and the renewable bio-based raw material, cellulose, from forests. Advances in digital media have had a negative impact on the forest industry resulting in a decreased demand for printed paper products and closure of several paper making plants in Finland and the rest of the Europe. On the other hand, the increased demand for long fiber reinforcement pulp which is used in board and packaging applications has led to new investments in existing paper machines and even to the building a new bio-product factory to improve the competitiveness of the Finnish forest sector (Metsä Fibre Homepage 2015). As a result, the basis of the cellulose based industry is increasingly strong in Finland.

Although paper products and processes have been intensively studied for a long time, the focus has been mostly on improving machine runnability and developing the raw material base in small increments to improve properties of the end product. Only recently have a few innovations been made that have significantly changed this traditional industry. Probably the most promising materials studied in this field of research nowadays are the micro and nanofibrillated celluloses (MFC and NFC, or commonly MNFC, or nanocelluloses) that were first introduced already in the 1980's (Turbak et al. 1983; Herrick et al. 1983). These are most commonly produced by disintegrating macroscopic cellulose fibers by mechanical treatment with or without chemical pre-treatments. Recent review papers describe the various manufacturing routes and potential uses of MNFC in detail (Abdul Khalil et al. 2014; Siró and Plackett 2010; Klemm et al. 2006).

Revealing the nanostructure of cellulose fibrils results in increased surface area and therefore enables their use as a reinforcing raw material in composites. There has been an exponential increase in the area of MNFC research during the last decade, especially in composites that utilize MNFC as a reinforcing element have been of particular interest for scientists recently. Figure 1

shows the increase in published research related to MNFC and their composites in the 21st century.

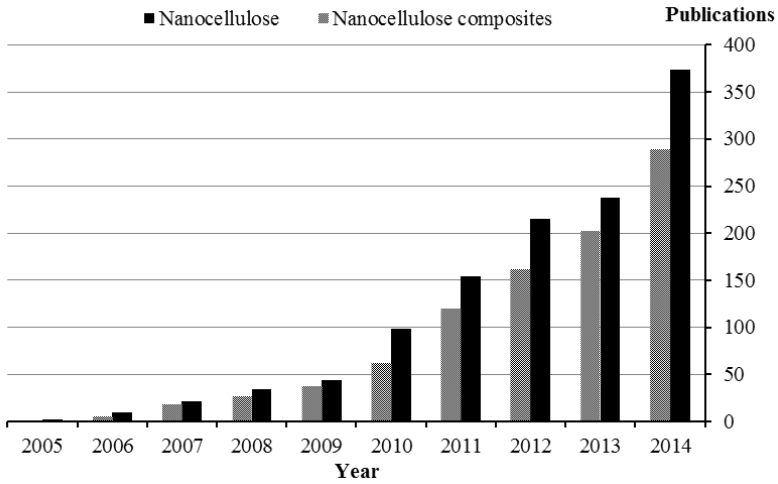

Figure 1. The amount of annual publications related to MNFC and MNFC composites as indexed by Scopus (www.scopus.com).

Although paper is commonly considered as a thin layer of pulp fibers in contact with each other, it can also be defined as a composite that usually contains wood based fibers (chemically or mechanically manufactured), fillers, and a number of different chemicals (Kiyoung et al. 2007; Torgnysdotter et al. 2007; Balankin et al. 2000; Dwan 1987). The strength of paper is a result of hydrogen bonding between hydroxyl groups of the outer surface of individual fibers together with Van der Waals and electrostatic interactions between the fibers (Torgnysdotter and Wågberg 2004; Wågberg and Annergren 1997; Marais and Wågberg 2012). Producing MNFC increases the contact area between the fibers/fibrils considerably which results in increased bonding and eventually higher strength properties (González et al. 2012; Rezayati Charani et al. 2013a; Kajanto and Kosonen 2012; Sehaqui et al. 2013). Nevertheless, this intrinsic property also results in a higher affinity to water and difficulties in the dewatering of the MNFC during the manufacturing process. Therefore, this issue must be considered if composites that contain MNFC are to be produced in an industrial scale.

The objective of this thesis is to answer two main research questions:

1. Which physical properties of a composite paper sheet can be achieved by using MNFC together with traditionally used fillers and chemical pulp fibers that will give added value to the resulting composite paper?
2. How could these new composite papers that have a hierarchical network structure from the nano/microscale (MNFC and fillers) to macroscopic scale (kraft pulp fibers) be manufactured, considering the challenges that MNFC imposes to the dewatering processes.

The first research question was considered in the work detailed in **Paper I and Paper II**, where the resulting sheet properties (property space) when using different mixtures of MNFC/filler/fiber structure was thoroughly examined by using statistical regression analysis and response surface methods. It was shown that a wide range of different strength and optical properties could be achieved by changing the proportions of different components in the furnish. The results from **Paper I** were utilized in creating a composition for the "model furnish" for the research presented in **Papers IV-VI** that aim to give answers to the second research question.

In **Paper III**, a method was developed to study the wet pressing and re-wetting phenomena with a modified material testing system device. It was shown that low amounts of MNFC could be added to a fiber-based furnish without significantly decreasing the dewatering efficiency in wet pressing.

The unique porous structure and its development during the consolidation process in the dewatering of an MNFC composite paper were shown in **Paper IV.** It was also concluded that the wet pressing could be used as a unit operation in the manufacturing of a MNFC composite paper with suitable pressing parameters.

In **Paper V**, the effect of MNFC water uptake on the press dewatering was studied in more detail. It was shown that the increased MNFC water binding decreased the dewatering efficiency considerably without significantly improving critical material properties. An in-situ precipitation of calcium carbonate on the MNFC surface was shown to be a promising method to decrease the water uptake and to manipulate the nano-scale structure of the composite paper.

The work reported in **Paper VI** demonstrates a unique pilot scale forming unit designed for producing webs from MNFC composite furnishes. From the trial runs it was concluded that a high

consistency forming method could be used in the manufacturing of an MNFC composite paper, with solids content of up to 33% after forming. The intrinsic gel-like behavior of the furnish was shown to be beneficial for the processing due to the shear thinning effect and plasticity of the web, even at relatively high solids contents.

2 Background

2.1 Cellulose fibers and chemical pulping

Cellulose is a natural organic polymer that consists of repeated units of β (1→4) linked D-glucose. It is the most abundant bio-based polymer in the world and is commonly utilized for the manufacturing of paper and paperboard products in the form of wood based pulp (Klemm et al. 2005). The renewability of cellulose also makes it a promising material to replace oil-based plastic polymers, especially in composite structures (Pandey et al. 2005; Mohanty et al. 2002; Ashori 2008).

Cellulose provides mechanical strength and structural support for wood and other plants such as cotton, hemp, and flax. The cellulose polymer chains are organized in the plant cell wall as microfibrils or fibril bundles that are in the region of 3-20 nm in diameter. These fibrils aggregate and form the macroscopic cellulose fibers. A schematic illustration of the supramolecular structure of the cellulose fiber is shown in Figure 1. For paper and board production the cellulose fibers are separated from the wood matrix either by a mechanical (Sundholm et al. 1999) or a chemical pulping process (Gullichsen and Fogelholm 1999). The chemical pulping process was first introduced by Hugh Burgess and Charles Watt in 1851 (Digby et al. 1907). It was based on using caustic soda as a chemical agent for isolating the wood fibers, hence it is known as the soda process. The kraft (sulphate) pulping process was further developed from the soda process by Carl Dahl in 1884 (Dahl 1884), who replaced soda ash in the recovery system by sodium sulphate. The resulting pulp was darker in color compared to the soda process, therefore the kraft method started to prevail only after the development of efficient bleaching methods later in the mid- 20th century (Sixta 2008).

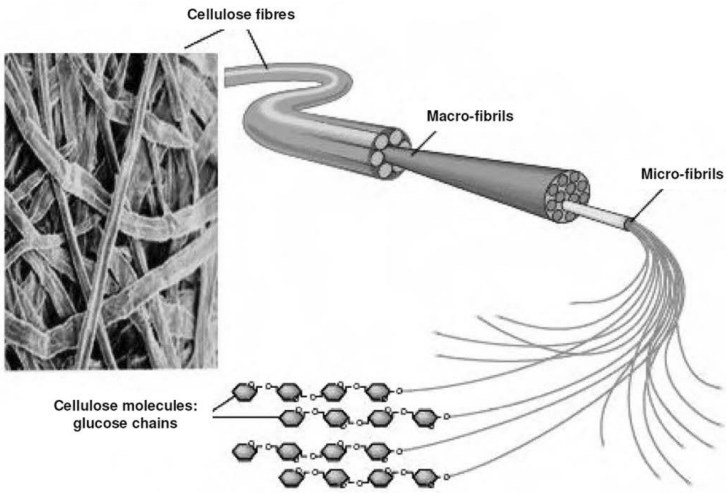

Figure 2. The structure of cellulose from D-glucose units to the macroscopic pulp fiber (Egal 2006).

2.2 Micro and nanofibrillated celluloses (MNFC)

The unique properties of micro and nanofibrillated celluloses (MNFC) and their potential commercial significance were discovered already in the 1980s' (Herrick et al. 1983; Turbak et al. 1983). The processes to produce MNFC can be divided into purely mechanical or a combination of chemical and mechanical treatments, and in most cases they are manufactured in aqueous suspensions. The resulting MNFC-water suspension is typically gel-like due to the high surface area and hydrophilic nature of the fibrils/fibril bundles. The most common methods to produce MNFC are presented in the following sections.

2.2.1 Grinding

A device with rotor-stator configuration can be used to produce MNFC. The idea of applying shear forces on the pulp fibers in order to disintegrate them into smaller fiber fragments and fibril bundles resembles the process of chemical pulp refining. A fine ceramic construction of the rotor and stator has been adopted in the grinding process to produce MNFC (Taniguchi and Okamura 1998; Solala et al. 2012; Hoeger et al. 2013; Wang et al. 2012). The properties of the resulting MNFC can be controlled by the load and the amount of passes through the grinder, and the resulting diameter range of the MNFC was reported to be 20-90 nm with lengths of up to several micrometers.

2.2.2 Homogenization and microfluidization

A high pressure homogenizing process is a method where cellulose fibers are disintegrated by subjecting them to high pressure drop caused by a small flow channel with a spring loaded valve (Dufresne et al. 2000; Nakagaito and Yano 2004; Liimatainen et al. 2013; Qua et al. 2011). A pre-refining step is commonly used to expose the inner layer of the fiber (S2) by peeling of the outer layers (P and S1) and to avoid clogging of the device during the homogenization process (Siró and Plackett 2010).

The resulting MNFC particles commonly have diameters of 5-30 nm and lengths of several μm (Henriksson et al. 2008; Pääkko et al. 2007). Another method that utilizes high pressure to produce MNFC is the microfluidization process. The difference in this method in comparison with homogenization is that the pulp suspension is fed through a fixed flow channel without a valve, however, the dimensions of the resulting MNFC particles seem to be similar to the ones produced by homogenization (Spence et al. 2011; Rezayati Charani et al. 2013a; Li et al. 2014).

2.2.3 TEMPO-mediated oxidation

One of the most studied methods for producing MNFC is the oxidation of chemical pulp by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) -mediated oxidation and mild disintegration in water suspension using NaBr and NaClO as additional reagents. This method was first presented by Saito et al. (2006) for wood based cellulose material.

As a result of the TEMPO –mediated oxidation, C6 hydroxyl groups of native cellulose are converted to carboxyl groups via aldehydes as proposed by de Nooy et al. (1995). This process results in very fine fibrils with diameters of 3-4 nm and lengths of at least several μm (Isogai et al. 2011). The resulting water suspension typically exhibits stronger gel-like properties than any other MNFC grade due to the high fibrillation and surface charge caused by the TEMPO –mediated oxidation.

2.2.4 Enzymatic pre-treatments

Enzymes have been found useful in many applications in the pulp and paper industry. Specific uses have been identified for mechanical and chemical pulping (Messner and Srebotnik 1994), pre-bleaching of kraft pulp (Bajpai and Bajpai 1992), and the improvement of the drainage rate in the paper making process (Bhardwaj et al. 1995). There are several types of cellulase enzymes which typically originate from fungi such as Trichoderma Reesei (Chaudhary and Tauro 1982;

Teeri et al. 1983; Sheir-Neiss and Montenecourt 1984) and the use of cellulase enzymes in facilitating the mechanical disintegration of kraft pulp fibers has been recently studied by several authors (Cadena et al. 2010; González et al. 2013).

Amongst the range of cellulases, endoglucanase (endo-β -1,4-glucanase) has been shown to effectively defibrillate pulp fibers which results in improved mechanical properties of paper sheets, especially when combined with mechanical refining of the pulp fibers (Singh et al. 2014; Singh et al. 2015; Lecourt et al. 2010; García et al. 2002). Its mechanism is primarily based on enhanced hydrolysis of the accessible amorphous parts that results in reduction of the cellulose chain length. Other known cellulase types include exoglucanase which disrupts the crystalline regions of cellulose and β-glucosidase that hydrolyses the exocglucanase product into individual monosaccharides (Singh et al. 2015; Kostylev and Wilson 2012; Lynd et al. 2002).

It has also been shown that the energy consumption can be decreased in MNFC production by the use of enzymes on pulp fibers before mechanical treatment (Henriksson et al. 2007). In addition, the use of enzymatic pretreatment in MNFC production was reported to result in improved tensile strength and elongation with the same number of grinding passes in comparison with mechanical treatment only (Yoo and Hsieh 2010).

2.3 Commercial and pilot scale production of MNFC

Due to the wide array of potential applications for MNFC, production has steadily increased towards the large scale during recent years. Many of the large companies operating in the forest sector have announced their own pilot scale activities for the production of MNFC, and a number of smaller commercial pilot plants have been assembled recently (Skuse 2015; Nelson and Retsina 2014; Bilodeau 2015; Tolnai 2015).

Most of these pilot scale production plants are targeted to produce coarse grades of MNFC rather than a fine fibrillated product. This results from the fact that the production costs are much higher for highly fibrillated MNFC grades, and without an actual high value application it is not feasible to move in that direction due to increased energy consumption (Spence et al. 2011). Nevertheless there is a limited amount of data about the properties of the resulting materials available due to the proprietary nature of the process and patent issues.

2.4 MNFC films and composites

As outlined earlier, research on the potential uses of MNFC has been focused mainly on composites, but many studies have also concentrated on forming films from pure MNFC for high oxygen barrier materials (Sehaqui et al. 2010; Nogi et al. 2009; Varanasi and Batchelor 2013; Syverud and Stenius 2009). Manufacturing bio-based films that could replace plastic is one of the key issues when moving towards more sustainable products. The hydrophilic nature of MNFC however, can cause difficulties in the moisture barrier properties of films, and also impair the compatibility with hydrophobic matrices. This is evidently the biggest limitation that prevents large scale adoption of MNFC as a plastic replacement.

Controlling the compatibility of hydrophilic MNFC with the hydrophobic matrix polymer and achieving good dispersion has been shown to be critical for achieving a reinforcement effect in MNFC-polymer composites (Boissard et al. 2012; Huang et al. 2012; Nakagaito et al. 2009; Nyström et al. 2010; Plummer et al. 2013; Qiu and Netravali 2012; Tanpichai et al. 2012). Lee et al. (2014) concluded that the highest potential for reinforcement is with relatively high amounts (> 30%-vol) of MNFC within a polymer matrix in plastic composites. Nonetheless, there are also several studies showing that even lower MNFC addition levels result in significantly increased composite strength when mixed with polylactic acid matrix (Suryanegara et al. 2009; Bulota et al. 2012; Liu et al. 2010; Herrera et al. 2015; Okubo et al. 2009).

In the paper industry, MNFC research has been focused on several areas. Improving the optical properties and/or cost structure of the end product by increasing the filler content of paper has been one of the main motivations to add MNFC into a paper making furnish (Torvinen et al. 2011; Subramanian et al. 2008). For paper grades that do not contain fillers, adding MNFC will result in increased sheet strength, especially in the z-direction (Manninen et al. 2011; Kajanto and Kosonen 2012; González et al. 2012). This is due to the large amount of hydroxyl groups on the surface of MNFC that are able to form hydrogen bonds and thus increase the strength of the composite material.

In addition to improving traditional products there are also attempts to expand the properties of paper-like materials with the addition of MNFC. One example is the substrate for printed electronics which utilizes the nano-scale size of the MNFC and morphology of kaolin clay to produce the smooth surface required for printing conducting materials (Penttilä et al. 2013; Torvinen et al. 2012). Different “nanofilters” that utilize the unique microporous structure of

dried MNFC have also been developed recently (Mautner et al. 2015; Mautner et al. 2014; Metreveli et al. 2014).

2.5 MNFC water binding capability and relation to rheology and dewatering of suspensions

The water binding capability of MNFC can be divided to the water located between (interparticle) and inside (intraparticle) of the MNFC particles (Maloney 2015). A higher water binding capability of MNFC suspension is generally connected to a higher apparent viscosity and shear thinning behavior due to the gel-like network forming ability of the entangled fibrils (Tanaka et al. 2014; Dimic-Misic et al. 2013d; Rezayati Charani et al. 2013b; Suopajärvi et al. 2015). This intrinsic property can be beneficial for certain applications where the gel-like properties are favorable, such as using MNFCs as viscosity modifiers or as water binding additives.

The high water binding capability of the MNFC inevitably result in difficulties for water removal processes, such as wire section dewatering, wet pressing and drying of paper. Recent studies on drainage (Taipale et al. 2010; Djafari Petroudy et al. 2014) and wet pressing (Hii et al. 2012; Kajanto and Kosonen 2012) of MNFC containing furnishes have shown however, that at low contents (≤ 5% of total dry weight) good dewatering can be maintained by proper design of the retention systems, furnish composition and pressing conditions.

Varanasi and Batchelor (2013) have shown that the required time for preparing an MNFC sheet can be significantly decreased by increasing the consistency of the MNFC suspension. Increasing the solids content changes the dynamic rheological characteristics of the suspension dramatically. As shown by Dimic-Misic et al. (2013b), the rheological behavior of a furnish that contains 20-30% MNFC with 70% PCC with or without pulp fibers is governed only by that of the MNFC regardless of the other components. The dewatering of such furnishes was also shown to be controlled by the water binding capability of the MNFC, but it was improved by simultaneous application of vacuum and shear during the dewatering (Dimic-Misic et al. 2013c). At solids contents between 5-15%, this type of composite furnish differs greatly from a typical paper making furnish by having shear thinning gel-like properties.

2.6 Fillers in the paper industry

There are several inorganic pigments/fillers used in the paper manufacturing industry, most common ones being calcium carbonate, kaolin clay, talc, and titanium dioxide. The two terms pigment and filler are used alternatively depending on the intended purpose and their role as a filler is related to the cost structure of the paper. The significantly lower price of common fillers in comparison with pulp fibers makes it economical to have as high filler content as possible. This is however limited by the sheet strength decrease which is a result of the inability of the fillers to form bonds with pulp fibers, for this reason the amount of fillers is typically below 40 wt-% of the total paper making furnish.

Another positive result from increased filler content, is the improved dewatering of the furnish. In contrast to pulp fibers, fillers are not able to bind significant amounts of water which results in improved drainage, wet pressing efficiency, and drying rate of a highly filled paper grade. The term pigment is related to the ability to affect optical properties of paper by changing the light scattering and adsorption coefficients (Bundy and Ishley 1991) of the materials. Due to their smaller size compared to fibers, pigments are also able to fill the spaces between fibers, thus improving surface smoothness for better paper printability.

2.6.1 Precipitated $CaCO_3$ (PCC)

Probably the most versatile of the filler materials is $CaCO_3$ that in nature can be found in rocks as limestone, shells of marine organisms and pearls. The most common form of $CaCO_3$ is the mineral calcite, but it can be also found in aragonite and vaterite forms (Ropp 2013). Calcium Oxide (CaO), which is the starting material of the PCC manufacturing process, is prepared by burning crushed limestone in an oven at temperatures of around 1000 °C. CaO is mixed with water to form a milk-of-lime [$Ca(OH)_2$] slurry that is subsequently treated with CO_2 gas. This is a common method used by the pigment industry to manufacture precipitated $CaCO_3$ (PCC) with different morphologies:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

2.6.2 Biomineralization approach for cellulose – filler composite structures

In nature, especially in marine organisms such as seashells, the formation of $CaCO_3$ in the presence of biopolymers is often referred to as biomineralization. This is a complex cell-mediated process where each organism has adapted to their environment by forming certain nanostructures within their hard tissue (Mann et al. 1993). Many scientists have been trying to understand and mimic these processes in search for superior material properties for tailored biocomposites (Heuer et al. 1992; Sommerdijk and de With 2008; Olszta et al. 2007).

Application of the biomineralization method for cellulose-$CaCO_3$ composites by deposition of calcite on the surface of cellulose via heterogeneous nucleation was reported by Dalas et al. (2000). Cellulose-$CaCO_3$ nanocomposites have also been prepared by the controlled reaction of calcium chloride with dimethyl carbonate in an alkaline medium by Vilela et al. (2010).

Several authors have studied the precipitation of $CaCO_3$ in the presence of pulp fibers with reported cost savings due to the increased filler content of the paper, a so called "lumen loading" or "fiber loading" method (Green et al. 1982; Middleton and Scallan 1989; Middleton and Scallan 1985; Miller and Paliwal 1985; Klungness et al. 1996; Klungness et al. 2000) . Silenius (2003) and Subramanian et al. (2005; 2006) used an in-situ precipitation of $CaCO_3$ on pulp fines and fibrils by using CO_2 gas after fibrillating the pulp and mixing it with $Ca(OH)_2$ to produce a composite cellulose-$CaCO_3$ material for papermaking applications. Their target was to increase the strength of typical paper grades with constant filler amount to gain savings in furnish costs while improving optical properties of paper.

Ciobanu et al. (2010) have also compared two other fiber loading methods with the one mentioned above. They concluded that a double exchange reaction of calcium chloride ($CaCl_2$) with $CaCO_3$ will result in the highest yield of $CaCO_3$ into the fiber wall pores and lumen, although it also results in a lower tensile strength of the paper when compared to normal filler loading. However, they showed that the previously presented carbonation of $Ca(OH)_2$ provided the optimum combination of optical and strength properties of paper. A third method that they investigated was the reaction of $CaCl_2$ with sodium hydroxide (NaOH), followed by carbonation with CO_2. The results showed however, that the yield of $CaCO_3$ and the resulting paper properties were generally poorer compared to other filler loading methods.

3 Materials and methods

3.1 Raw materials

3.1.1 Chemical pulp fibers

Pulp fibers used in the experiments were all bleached fibers prepared by the sulfate pulping (kraft) process delivered as dried sheets. The Schopper Riegler (SR˚) value indicates the drainage resistance of the diluted pulp suspension and was measured according to standard ISO-5267/1 and is usually measured as an indication of the amount of refining. Length weighted average fiber length was measured with FiberLab –analyzer (Metso Automation). All pulps and their relevant properties related to each publication are listed in Table 1.

Table 1. The pulp fibers used in the experiments for each publication and their relevant properties.

Paper	Pulp source	Pre-treatment	SR	Average fiber length
I	Birch	Refining (Sprout-Waldron)	22°	0.81 mm
II	50% softwood/ 50% eucalyptus	None	N/A	2.58 mm (sw)/ 0.78 mm (euca)
III	25% softwood/ 75% hardwood	Refining (Paper mill)	48°	1.12 mm (combined)
IV&VI	Softwood	Refining (Conical pilot refiner)	18°	2.24 mm
V	Softwood	None	N/A	2.24 mm

3.1.2 Synthetic fibers

Synthetic polyethylene terephthalate (PET) fibers with a linear density of 1.7 dtex and a fiber length of 10 mm and a diameteter of 10 μm (supplied by Teijin) were used in **Paper II**.

3.1.3 MNFC grades and their preparation

Several different grades of MNFC were used during the research related to this thesis. The methods for producing these are described in the following section and more detailed information can be found from the corresponding publications.

In the research related to **paper I**, the MNFC was prepared from once dried bleached hardwood kraft pulp. The fiber/water suspension was first dispersed at 3 wt-% by a high shear mixer (Diaf) for 10 minutes at 700 RPM. After dispersion the suspension was fed through a "supermasscolloider" (Masuko Sangyo CO, Japan, see Figure 3), which is a mechanical grinder with ceramic stones commonly used to produce fibrillated cellulosic materials (Taniguchi and Okamura 1998; Solala et al. 2012; Hoeger et al. 2013). A viscous MNFC suspension was formed as a result of the treatment.

In **Paper II**, the MNFC was produced in similar conditions with the exception that the pulp was first pre-refined with a laboratory Hollander refiner to SR° 31 in order to facilitate fibrillation during the grinding. In addition, the solids content of the suspension was slightly lower (2.5 wt-%).

Figure 3. The "supermasscolloider" grinder used in the production of MNFC (Papers I and II).

The MFC used in **paper III** was produced from never-dried bleached birch kraft pulp. The pulp was pre-refined with the supermasscolloider, and subsequently treated with a microfluidizer (model M7115, Microfluidics, USA) for 5 passes at 2.3 wt-% solids content. For the first pass, the

microfluidizer was equipped with a 200 μm flow channel and for the last four passes with a 100 μm flow channel. The NFC for **paper III** was manufactured from once dried bleached birch kraft pulp by a TEMPO-oxidation method as described by Saito et al. (2006) at 1.4 wt% solids content with a NaClO dosage of 5 mmol/g dry fibers and the carboxyl content of the resulting NFC was 1.02 mmol/g.

In **papers IV** and **VI**, the MNFC was a commercial grade Daicel Celish KY-100G, delivered at 10 wt-% solids content.

The MNFC used in **paper V** was prepared from never-dried bleached birch kraft pulp. It was treated to sodium form and washed with de-ionized water before subjecting it to an enzymatic pre-treatment. 3 mg of the enzyme (Ecopulp® R) per gram of pulp was added to a 2.5 wt-% suspension and the temperature was increased to 57 °C. The suspension was agitated for two hours while maintaining the temperature.

To terminate the activity of the enzyme, the suspension pH was increased to 9-10 by sodium carbonate and the temperature was increased to 90 °C. The suspension was then cooled overnight in cold storage and subsequently refined in a Valley Hollander for 30 min. The pre-refined pulp was then treated in a microfluidizer (model M-110P, Microfluidics, USA) with a 100 μm flow channel for one and two passes at 2000 bar pressure (see Figure 4). The solids content of the resulting MNFC was 1.7 wt-% and pH 6.9.

Figure 4. The microfluidizer used in the MNFC preparation for the experiments in paper V.

3.1.4 PCC

Two different grades of PCC with scalenohedral morphology were used in the experiments, both were obtained from Omya AG, Switzerland. In **papers I and II** the PCC was a commercial grade FS 260 with a nominal particle size of 2.6 μm. In **papers IV – VI**, the PCC was a commercial grade FS 240 with a nominal particle size of 2.4 μm. These PCC grades are non-dispersed and slightly cationic.

3.2 In-situ precipitation of $CaCO_3$ on MNFC

To adjust the water binding capability of the MNFC, an in-situ precipitation method of $CaCO_3$ on the surface of MNFC was applied (**paper V**). CaO was first slaked by mixing it with water in a ratio of 1:8 for 10 minutes at 50°C to produce $Ca(OH)_2$. PCC was formed in-situ on the 2 pass MNFC in a batch reactor with a volume of 3 dm^3. The reactor was equipped with a high shear mixer and a CO_2 gas feed nozzle with the MNFC and $Ca(OH)_2$ mixed in the reactor for 5 minutes prior to starting to feed CO_2 into the reactor. The initial pH of the mixtures was 12 and starting temperature was 23 °C.

Two different levels of $CaCO_3$ were precipitated on the MNFC, corresponding to 10.6 wt-% (2P-LOW) and 75.5 wt-% (2P-HIGH) of the total MNFC/PCC amount with CO_2 flow rates of 0.2 dm^3/min and 1.0 dm^3/min respectively. A schematic illustration of the in-situ PCC process is shown in Figure 5.

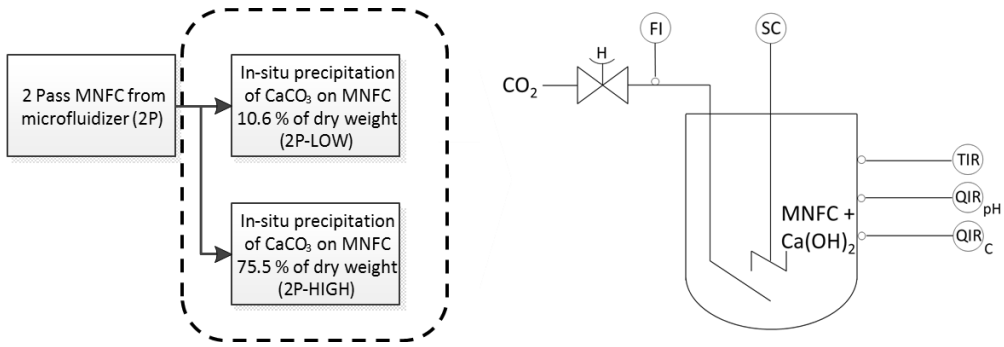

Figure 5. A schematic illustration of the in-situ $CaCO_3$ precipitation process (left) and a technical drawing of the reactor (right) (paper V).

3.3 Preparation of laboratory handsheets

3.3.1 MNFC-PCC-fiber composite sheets

All furnish components were first mixed with a high shear mixer while diluting to the target sheet forming consistency (0.27-1.5 wt-%). A modified sheet forming mould with a pressurized top chamber was used for the sheet forming using a 50 kPa overpressure. The standard wire was covered with a nylon membrane (Sefar Nitex 03-10/2, Sefar AG, Switzerland) with 10 µm mesh openings in order to retain the fine MNFC and filler material. Drainage time to prepare one sheet was between 2-22 min depending on the amount and type of MNFC in the furnish

After forming, the sheets were removed from the membrane and wet pressed for 260 s at 0.42 MPa, or put inside plastic bags for press simulator experiments. After wet pressing, the sheets were press dried four sheets at a time for 2-5 min depending on the furnish composition. The temperature of the top and bottom plates was 130 °C during the drying. A simplified process diagram of the handsheet preparation procedure is presented in Figure 6.

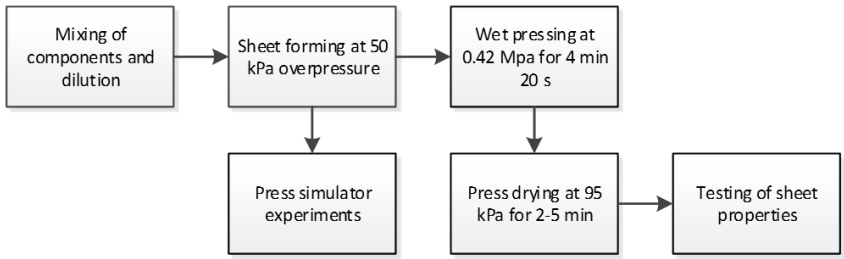

Figure 6. A simplified process diagram of the preparation of MNFC composite sheets.

3.3.2 Sheets with low amounts of MNFC mixed with fibers (paper III)

The sheets with low amounts of MNFC (1-5 wt-%) in the furnish were prepared with a standard wire and handsheet mould. The MNFC was first dispersed by diluting it to 0.2 wt-% and mixing by magnetic stirring for 15 min at 600 RPM. Pulp suspensions were diluted to 0.5 wt-% and the MNFC was added followed by 10 min agitation. The final solids content in the sheet forming was 0.41 wt-% and target grammages of the handsheets varied between 30-120 g/m^2. No retention chemicals were used during the handsheet forming but measurement of the dewatering time and air permeability of the quick dried sheets were used as an indication of MNFC retention. After forming, the sheets were put inside plastic bags for wet pressing experiments.

3.4 Statistical analysis by response surface method (papers I and II)

A three component mixture design and response surface method was applied in the handsheet preparation experiments described in **papers I and II** using a statistical analysis software (Minitab 16). This method enables the analysis of synergistic effect of the components by creating a statistical model based on the measured values, and has been also implemented in recently published chemical engineering publications (Chen et al. 2010; Salem and Akbari Sene 2011). The models for each property were created by a stepwise regression method with $\alpha = 0.15$, and if all the predictors are present the model can be expressed as:

$$Y = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{123} X_1 X_2 X_3$$

, where X_i = component proportion and

β_{ijk} = corresponding coefficient.

3.5 Wet press simulator

A press simulator (see Figure 7) was used in the experiments in order to study the dynamic dewatering and re-wetting phenomena in wet pressing. The simulator was built on a universal material testing system frame (Saukko 2006), and it is capable of producing repeatable press pulses that simulate real pressing conditions. In this work, the pulse durations were varied between 25-250 ms and the maximum pressure was varied between 2-10 MPa. The maximum pressure was varied in **papers II and IV**, the pulse duration was varied in **paper V**, and both parameters were kept constant in **paper III**.

The sample was pressed between a polished stainless steel top plate operated with a hydraulic piston, and a permeable sintered steel lower plate that acted as the water permeable media. The edge of the lower plate had three eddy current distance sensors (Micro-epsilon EddyNCDT 3300) at 120° intervals for accurate measurement of minimum sample thickness during the press pulse.

All samples were wet pressed with the wire side facing the sintered plate. After the press pulse the sample adhered to the polished top plate, preventing possible post-nip rewetting. The sintered steel plate had an average pore size of 20 µm and the vacuum level in the chamber under the sintered plate was set to 60 kPa below atmospheric pressure.

Sample dry weight (m_{dry}) and weight after pressing (m_{out}) were used to calculate the moisture ratio after pressing, $MR_{out} = (m_{out} - m_{dry}) / m_{dry}$. An accurate 3 – point eddy current measurement

was utilized to measure the minimum thickness of the sample at compression (b). Using the sample area ($A = 4.54 \cdot 10^{-3}\ m^2$), densities of water ($\rho_{H2O} = 1.0 \cdot 10^6\ g/m^3$), cellulose ($\rho_c = 1.55 \cdot 10^6\ g/m^3$) and calcium carbonate ($\rho_{PCC} = 2.71 \cdot 10^6\ g/m^3$), the minimum moisture ratio can be calculated from:

$$MR_{min} = \frac{\left[b \cdot A - \frac{m_{dry}}{(0.3 \cdot \rho_C + 0.7 \cdot \rho_{PCC})}\right] \cdot \rho_{H_2O}}{m_{dry}} = \frac{\left[4.54 \cdot 10^{-3} \cdot b - \frac{m_{dry}}{(2.36 \cdot 10^6)}\right] \cdot 10^6}{m_{dry}}$$

The amount of rewetted water (nip rewetting) was calculated as $RW = MR_{out} - MR_{min}$.

To be able to accurately measure the sample thickness during pressing, aluminum plates of 40 – 100 µm thickness were used for calibration. During pressing, the MNFC composite furnish material partly penetrated into the sintered bottom plate and this factor was accounted for by measuring the surface topography of a freeze-dried sample that contained an imprint of the sintered plate taken immediately after pressing. From this topography map, an average penetration thickness was estimated by calculating the standard deviation (σ). By adding this to the measured thickness (b_m) the actual minimum thickness could be calculated as $b = b_m + \sigma$.

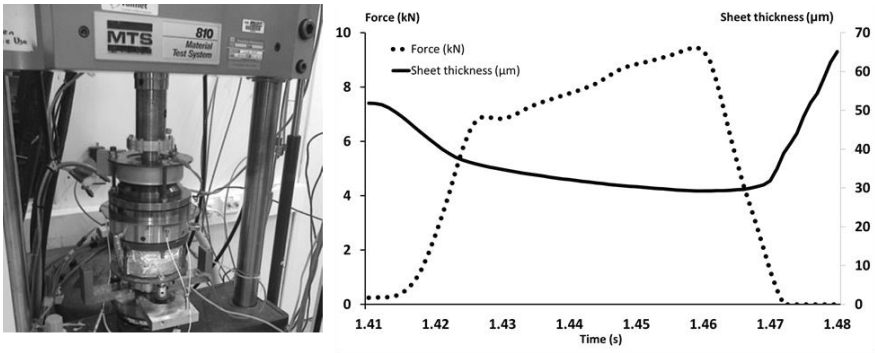

Figure 7. The press simulator built on a universal material testing system (MTS-810) frame (left) and an example of the press pulse and thickness data (right).

3.6 Pilot forming unit

The work presented in **paper VI** shows the development of a pilot scale forming unit and high consistency headbox for studying the forming of MNFC composite paper furnishes in the solids content range of 5-10 wt-%. The system consisted of a storage tank equipped with a high consistency mixer, a pump with flexible impeller (model 10490, ITT Jabsco), an in-line mixer

(model 0835 P, HEG Engineering), and a specifically designed headbox. The headbox was designed based on earlier studies of ultra-high consistency forming of pulp fibers (Hietaniemi and Gullichsen 1996; Cichoracki et al. 2001; Manninen et al. 2007; Gullichsen and Härkönen 1981). Figure 8 shows the approach flow system and the design principle of the headbox.

3.7 Rheological measurements

Before the pilot scale trials, the rheological properties of the furnish were evaluated by methods developed for shear thinning materials in order to understand the gel-like properties and the effect of shear on the dynamic viscosity recovery with the following measurements (Dimic-Misic et al. 2013c; Dimic-Misic et al. 2013a).

Dynamic viscoelastic moduli, storage modulus (G') and loss modulus (G''), were measured as a function of angular frequency (ω = 0.1 – 100 s^{-1}) by oscillatory methods. Frequency sweep test was performed by obtaining the linear viscoelastic range of the sample (LVE) from an amplitude sweep using constant angular frequency (ω = 1 s^{-1}). The strain amplitude was varied between 0.01 and 500%. The influence of shear rate ($\dot{\gamma}$) on the dynamic viscosity (η) was measured at a steady state flow by increasing the shear rate from 0.01 to 1000 s^{-1}.

To determine how the furnish consistency affects the recovery of the dynamic elastic network structure after removal of high shear, 3ITT (3 Interval Thixotropy Test) measurements were conducted. First, the samples were subjected to low shear rate (0.1 s^{-1}), then subsequently high shear rate (500 s^{-1}), and finally once again low shear rate (0.1 s^{-1}). Structure recovery was traced in respect to recovery of dynamic transient viscosity (η^+) in the third interval, expressed as percentage (%) of ratio η^+/η_0 after 300 s of measurements, where η_0 is the low shear viscosity at the beginning of first interval (Dimic-Misic *et al.* 2013a).

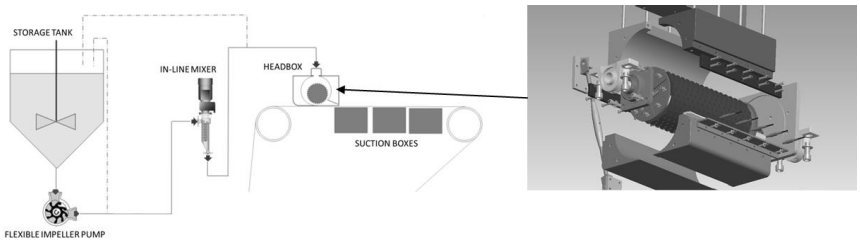

Figure 8. The approach flow system of the forming unit and the design principle of the headbox designed for forming of high consistency MNFC containing furnishes.

3.8 The water binding capability of MNFC (paper (V)

3.8.1 Water Retention Value

A modified Water Retention Value (WRV) measurement was used in measuring the network level water binding capability of the MNFC in **paper V**. The method was modified from the standard SCAN-C 62:00 by mixing 90% never-dried bleached hardwood (WRV_0 = 1.8 ml g^{-1}) with 10% MNFC. The WRV of the MNFC can then be calculated from the measured WRV of the mixture:

$$WRV_{MNFC} = \frac{WRV_{mix} - WRV_0 \cdot 0.9}{0.1} \text{ [ml g}^{-1}\text{]}$$

An average of four measurements was reported in the results. The in-situ precipitated samples also contained calcium carbonate in addition to the MNFC (1.2% and 30.8% of total weight). In this case the WRV was calculated, assuming the water binding capability of the PCC to be 0 ml g^{-1}, as follows:

$$WRV_{2P-LOW} = \frac{WRV_{mix} - WRV_0 \cdot (1-0.012)}{0.1} \text{ [ml g}^{-1}\text{]}$$

$$WRV_{2P-HIGH} = \frac{WRV_{mix} - WRV_0 \cdot (1-0.308)}{0.1} \text{ [ml g}^{-1}\text{]}$$

It should be noted that the previous equations are used to calculate the water binding capability of the MNFC itself, therefore they are reported on the basis of ml of water per gram of MNFC. Nevertheless, in the in-situ PCC containing sample some water can be held between the $CaCO_3$

particles and in addition, interactions of the MNFC with the fiber network both have an impact on the final result.

3.8.2 DCS - Dissolved and Colloidal Substances and specific sedimentation

The dissolved and colloidal substances (DCS) were determined by first centrifuging 50 g of the furnish at 1.3 wt-% at 3500 G for 10 min. The consistency of the precipitated samples were adjusted to 1.4 wt% (2P-LOW) and 4.9 wt% (2P-HIGH) in order to have the same amount of cellulose material per sample. The supernatant and sediment volume were measured and consequently oven dried for 16 h. The concentration of DCS was then calculated:

$$DCS = \frac{m_{SN}}{V_{SN}} \text{ [g l}^{-1}\text{]}$$

, where m_{SN} is the oven dry weight of the supernatant
V_{SN} is the volume of the supernatant after centrifugation.

It should be mentioned here that nano-sized particles of PCC can still be present in the supernatant, and can slightly influence the results.

The suspension sedimentation after centrifuging was also measured. In this study, we used a specific sedimentation value calculated as the amount of water in the sediment per gram of cellulose:

$$SED = \frac{V_{SED} - \left(\frac{m_{cell} \cdot X_{cell}}{\rho_{cell}} + \frac{m_{PCC} \cdot X_{PCC}}{\rho_{PCC}}\right)}{m_{cell}} \text{ [ml g}^{-1}\text{]}$$

, where V_{SED} is the sedimented volume
V_{dry} is the dry volume of the sediment
m_{cell} is the oven dry weight of cellulose in the sedimented material
X_{cell} is the proportion of cellulose in the suspension
ρ_{cell} is the density of cellulose ($1.55 \cdot 10^6$ g m^{-3})
m_{PCC} is the oven dry weight of PCC in the sedimented material
X_{PCC} is the proportion of PCC in the suspension
ρ_{PCC} is the density of PCC ($2.71 \cdot 10^6$ g m^{-3}).

3.9 Composite paper characterization

3.9.1 Consolidation of the pore structure (paper IV)

Calculating the density of the samples outside the press simulator was performed manually by measuring the sample thickness. Due to the high compressibility of the samples, two aluminum plates with known thickness (b_{Al}) were placed on each side of a 4 sample stack. A micrometer screw was then used to measure the thickness of the stack (b_{st}) at 4 different points. After weighing the stack of samples (m_s), density was calculated, $\rho = [m_s / (b_{st} - b_{Al}) \cdot A]$.

Mercury intrusion porosimetry was used to measure the porosity of samples before pressing, after pressing, and after press drying. Wet samples from various stages of the dewatering process were freeze dried by immersing them in liquid nitrogen, followed by vacuum drying. As a result, dried samples suitable for porosimetry measurements were produced, which resemble the structure of the sample in the water saturated state. Pore size distribution (PSD) and sample apparent density were measured at 400 MPa maximum pressure.

3.9.2 Scanning electron microscopy

A field emission scanning electron microscope (FE-SEM, Zeiss Sigma) was used to characterize the morphology of the samples. Prior to their characterization, the samples were sputtered with a gold layer and the acceleration voltage of the microscope was set to 2.5 kV. In order to preserve their structure, samples before and after pressing in **paper IV** were freeze dried by immersing them in liquid nitrogen, followed by vacuum drying.

3.9.3 Paper properties

The measured paper properties and their corresponding standards or methods are listed in Table 2.

Table 2. Material properties measured from the samples and their corresponding standards.

Property	Standard	Remarks
Tensile index	ISO 1924-2	12 mm/min elongation rate, 50 mm gauge length
Elastic modulus	ISO 1924-2	
Tear strength	ISO 1974	1 sample (paper I) and 2 samples (paper II) per measurement
Bending stiffness	SCAN-P 29:84	15° angle, 10 mm length, sample size 38 X 76 mm
ISO-Brightness	TAPPI T452	

Opacity	TAPPI T519	
Light scattering coefficient	SCA-C 27:76	
Light absorption coefficient	SCA-C 27:76	
Air permeability	ISO-5636-3	

4 Results

4.1 Property space of composite papers with MNFC addition

The traditional paper industry is mainly based on products that contain pulp fibers (mechanically or chemically produced), fillers, and chemical additives for increased strength, retention, or other purposes. Limitations set by the manufacturing process and raw material base also define the resulting range of properties of the end product, the so called property space. The work presented in **papers I and II** shows that by adding MNFC as a component in a composite paper structure together with fibers and structured filler/pigment ($CaCO_3$), this property space can be expanded considerably.

A response surface method was used in the analysis of the results. Based on statistical models, the interdependent effects between the components were found for the sheet properties. According to the results presented in **paper I**, pulp fibers and MNFC were shown to have a synergistic effect in increasing sheet tensile properties. This is probably due to the increased hydrogen bonding together with the ability of the smaller sized fibrils of the MNFC to form bridging bonds in void areas between relatively large and rigid fibers.

Another significant finding from the study was the remarkably high optical synergy of the MNFC together with PCC. This is due to the fact that these materials, when formed as a composite, are able to form optically active micropores that are very effective at scattering light. These pores are in the size of few hundred nanometers (half of the wavelength of visible light), and scatter light due to their optimal size for reflecting the incident light. The same phenomenon has also been observed in previous studies with cellulosic microfines and PCC containing composite papers (Subramanian et al. 2008; Sodagam 2010). Figure 9 shows the response surface contours of tensile index and opacity.

It was also shown in **paper I** that bending stiffness of the material had a maximum value in the three-component region, which is a result of the combined synergistic effect of all three components. It would seem logical that the addition of a non-bonding filler material would also reduce the bending stiffness of the resulting composite, however, it seems that PCC can increase the thickness of the composite without deteriorating the elastic modulus. Increasing material thickness is a very effective way to improve bending stiffness, as is shown in the equation (Niskanen 2008):

$$S_b = \frac{E \cdot d^3}{12} \quad [\mathrm{N}]$$

, where E = Elastic modulus [Pa] and
d = Sheet thickness [m].

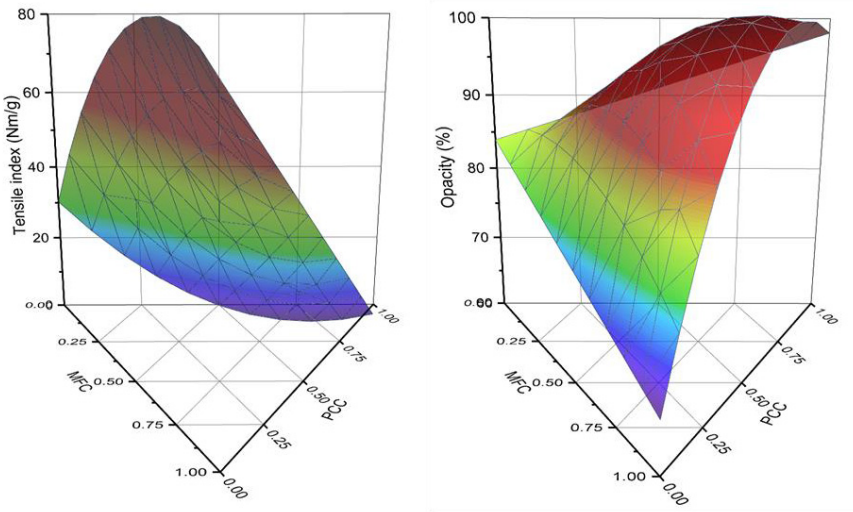

Figure 9. Examples of tensile index (left) and opacity (right) surface contours created from the statistical models. Non-linearity of the surface indicates a synergistic effect between two or more components (paper I).

In addition, MNFC was shown to decrease the air permeability of the composite papers considerably, which is due to the film forming ability of MNFC which results in blocking of pores in the paper structure. This phenomenon could be seen already at low amounts of MNFC in a sheet of pulp fibres as shown in Figure 10 (**paper III**).

Unpublished results showed that a sheet that contains 17 wt-% of MNFC produced by Masuko –grinding method mixed with birch fibers resulted in air permeability of zero. With composite papers that contain PCC, the structure became almost impermeable to air when the amount of MNFC in the structure was around 30 wt-% (**paper II**). The low permeability of MNFC containing films and composites has also been observed in several previous studies (Rezayati Charani et al. 2013a; Taipale et al. 2010; Missoum et al. 2013)

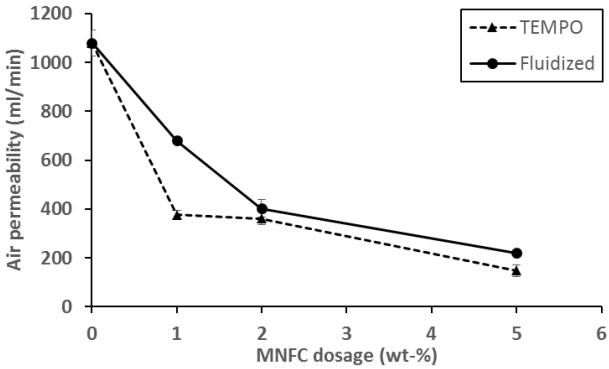

Figure 10. Air permeability of sheets containing variable dosages of TEMPO-oxidized and fluidized MNFC. Sheets were quick dried and their basis weight was 70 g/m² (paper III).

The work presented in **paper II** was also targeted to evaluate the suitability of a MNFC composite paper for non-woven applications. It was concluded that the improved strength provided by the MNFC enabled an extremely high filler content, which improved the optical properties - like opacity - significantly in comparison with a reference industrial material used for wall cover application. The environmental impact of the MNFC composite was also shown to be significantly lower than that of the reference due to the more ecological raw material base.

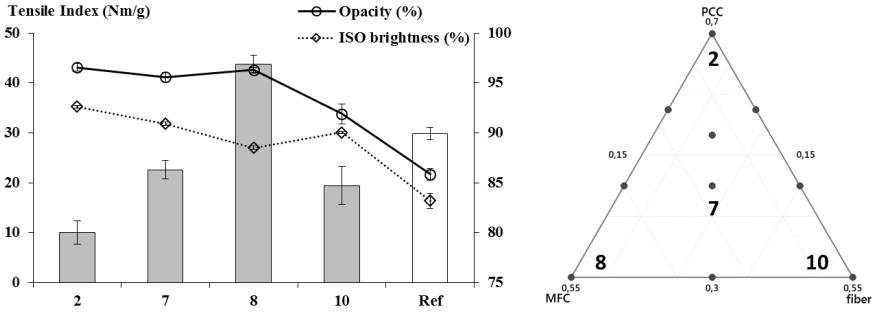

Figure 11. Comparison of the non-woven composite sheet properties with an industrial wall cover reference material (left), and the location of test points in the mixture design (right). All samples contained 15 wt-% of synthetic PET –fibers in addition to other three components.

4.2 The effect of MNFC water binding capability on dewatering and sheet properties (paper V)

The aim of this work was to show how the fluidization and the application of an in-situ precipitation method will affect the water binding capability and press dewatering of the MNFC and the resulting composite paper properties. The composite papers consisted of 70% PCC, 20% MNFC, and 10% softwood bleached kraft pulp (SBKP) fibers. The fluidized MNFC was loaded at two different levels of $CaCO_3$ by a carbonation method which was described in detail in section 3.2. The compositions of the resulting composite papers are shown in Table 3.

Table 3. Test point labels and compositions.

Test point	Composition (SBKP fibers / MNFC (type) / in-situ PCC / scalenohedral PCC)
0P	10% / 20% (enzyme treated and refined pulp) / 0% / 70%
1P	10% / 20% (1 pass) / 0% / 70%
2P	10% / 20% (2 pass) / 0% / 70%
2P-LOW	10% / 20% (2 pass) / 2.3% / 67.7%
2P-HIGH	10% / 20% (2 pass) / 61.6% / 8.4%

The MNFC water binding capability increased with increasing passes in fluidizator, which can be observed from the increased DCS and sedimentation values shown in Figure 12. When the suspension is subjected to increasing amount of mechanical energy the fibrils are further separated and the water holding capability of the material is increased. This correlates well with previous observations on the interaction of MNFC with water (Carrillo et al. 2014; Hoeger et al. 2013; Dimic-Misic et al. 2013c; Zhang et al. 2012a).

Surface structure and chemistry also influence the water binding capability of MNFC. Fibrils and hemicelluloses are present on the surface of the MNFC particles and increase the water binding ability of the MNFC. The precipitation of a low amount of PCC on the surface of the 2P MNFC effectively decreases the amount of DCS and the sedimentation volume. This is likely due to the removal of sugar residues and other colloidal substances from the suspension as a result of

the nucleation of PCC, since it tends to nucleate on high surface area material encapsulating and adsorbing DCS from the suspension.

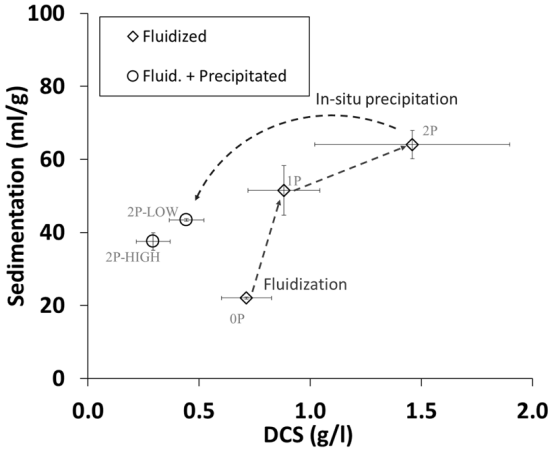

Figure 12. Water binding capability of the different MNFC grades as measured by the sedimentation after centrifuging for 10 min at 3500 x g plotted against the DCS from the supernatant. Error bars represent 95% confidence limits.

The wet pressing of the composite papers were compared by using a press impulse of 265 kPa•s with a duration of 250 ms and maximum pressure of 2.1 MPa. It was shown that the WRV values correlated with the after press moisture ratio quite well (see Figure 13). The increased water binding capability of the MNFC also had a negative effect on the after press MR.

A low amount of the in-situ PCC clearly improved the after press MR, which could be a result of the decreased amount of DCS in the MNFC. These substances are known to cause problems in dewatering processes due to their film-forming ability which can prevent the flow of water from the furnish during wet pressing. Despite that, when higher amounts of PCC are precipitated in-situ, the structure of the composite sheet becomes closed due to extremely fine PCC crystals in the size region of 30-100 nm (Figure 14).

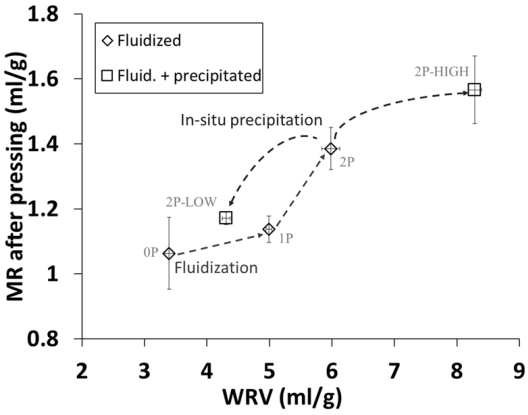

Figure 13. Moisture ratio of the composite paper samples after pressing at 265 kPas as a function of WRV of the MNFC. Error bars represent 95% confidence intervals.

The sheet properties (see Table 4) showed a significant increase in sheet tensile index and elastic modulus when the enzymatically pre-treated (0P) pulp was subjected to the fluidization process. In contrast, a second fluidization step only slightly decreased the sheet air permeability without significant changes in other sheet properties. Probably the most significant finding from this study was the fact that a low amount of in-situ PCC in the structure improved dewatering properties of the composite paper without a negative impact on sheet properties. In fact, a slight increase in tensile properties was seen when compared to the 2P sample.

Although the high level of in-situ PCC resulted in poor press dewatering, it was interesting to observe the positive effects on tensile index and elastic modulus of the composite paper. In-situ PCC has previously been shown to decrease paper strength when compared to normal filler loading of pulp fibers (Ciobanu et al. 2010; Fortuna et al. 2013). This effect was apparently caused by the fact that the in-situ PCC interrupts the formation of bonds between the fibers. However, in this study an opposite effect was determined as the tensile index of the papers increased by around 50%, and the elastic modulus by almost 100% as a result of the in-situ process.

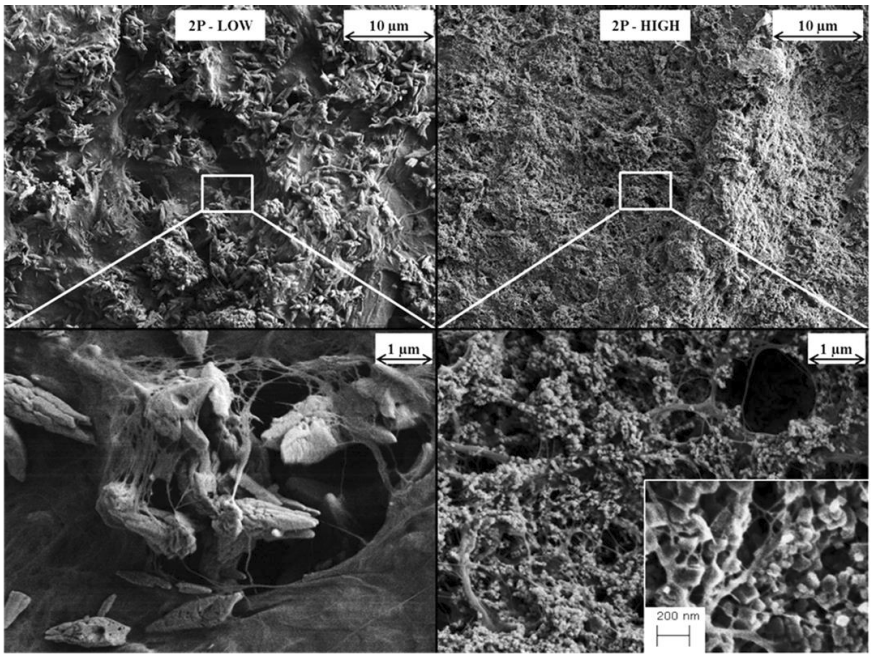

Figure 14. SEM -microscope image of the composite paper surfaces that contain mostly commercial PCC (left) and in-situ PCC (right). Note the large size of the commercial grade in comparison with PCC crystallites of 30-100 nm diameter in the in-situ formed PCC.

Table 4. The measured composite paper properties with 95% confidence limits.

Measurement	0P	1P	2P	2P-LOW	2P-HIGH
Bulk (cm^3/g)	1.76 ± .06	1.61 ± .02	1.62 ± .04	1.57 ± .05	1.26 ± .05
Tensile Index (Nm/g)	3.36 ± .55	11.7 ± 1.24	10.6 ± .69	10.7 ± .42	15.9 ± .66
Elastic Modulus (GPa)	0.36 ± .05	0.82 ± .07	0.83 ± .04	0.93 ± .04	1.77 ± .07
Air Permeability (ml/min)	374 ± 40.8	38.6 ± 4.39	29.6 ± 2.01	28.6 ± 1.07	11.6 ± .90
ISO-Brightness (%)	93.9 ± .15	94.4 ± .25	93.2 ± .05	93.2 ± .28	92.4 ± .14
Opacity (%)	96.9 ± .39	97.4 ± .25	97.4 ± .26	97.8 ± .17	96.1 ± .67
Light Scattering Coeff. (m^2/g)	145 ± 10.0	174 ± 13.3	161 ± 4.97	161 ± 5.87	107 ± 9.65
Light Absorption Coeff. (m^2/g)	0.14 ± .01	0.14 ± .01	0.16 ± .01	0.19 ± .01	0.21 ± .02

4.3 Press dewatering and re-wetting (paper III)

The results presented in this paper showed that low amounts of MNFC can be added to a paper manufacturing process without causing a significant effect on wet pressing performance, as long as it is operated under pressure controlled pressing conditions. As expected, the addition of MNFC prepared by the TEMPO–oxidation method had a slightly larger negative influence on the press dewatering than adding a coarser grade prepared by the fluidization process (see Figure 15). In both cases, however, a 5 wt-% addition of MNFC in the furnish deteriorated the dewatering performance, indicating a blocking of the inter-fiber pores.

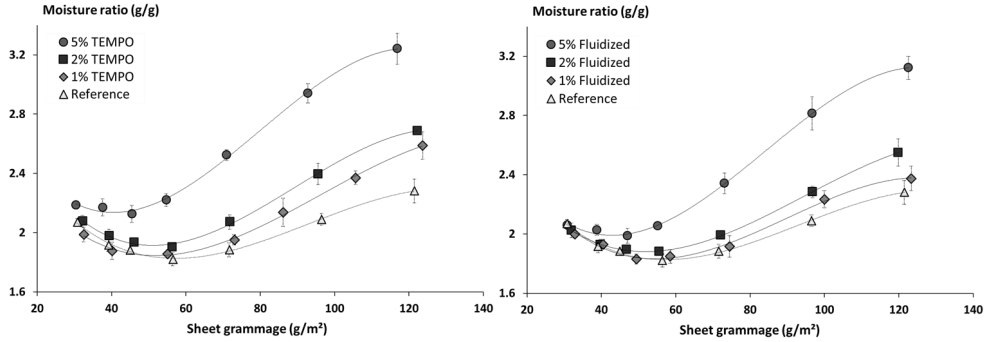

Figure 15. The effect of TEMPO -oxidized and fluidized MNFC on the after press MR with varying sheet grammages and dosage levels. Error bars represent 95% confidence limits.

Re-wetting can be defined as the difference between the minimum theoretical MR during the press pulse and actual after press MR. The minimum MR occurs at the peak pressure in the press nip when the structural resistance of the paper web is the primary force opposing the pressing force (pressure controlled pressing), or right after the point of peak pressure due to the resistance against water flow out of the paper (flow controlled pressing). Increasing the grammage also increases the amount of water in the structure, and flow controlled pressing starts to dominate. If rewetting after the press impulse is constant, as in this case at lower grammage area, the higher amount of fibers in the sheet contribute to lower after press MR until the flow controlled regime starts to contribute with higher grammage sheets. For the furnishes studied in this paper, we observed that the minimum MR approached values of around 0.6-0.7 ml/g for lower grammage sheets, which equals to the amount of water located in the micropores of fibers (Maloney et al. 1998). This indicates that under these conditions, all of the available water from between the fibers and larger macropores within the cell wall is removed during the maximum pressure.

It was also observed that re-wetting, i.e. the water that is transferred back to the paper structure after pressing, varied between 40 and 65 g/m² in this experiment. This is in agreement with other values reported in the literature (Hoyland and Wheeldon 1980; Jaavidaan et al. 1988). A new observation was that re-wetting increased significantly after the sheet grammage reached around 70 g/m², and for samples containing TEMPO this phenomenon was more pronounced than for the samples containing fluidized MNFC. This finding indicates that in addition to decreasing the water flow from the structure, any changes in the network water binding capability may also affect the potential sheet re-wetting. The results also showed that both the amount of water and higher re-wetting tendency are contributing to the high after press moisture ratio at higher sheet grammages.

4.4 Press dewatering and consolidation during dewatering (paper IV)

The wet pressing and consolidation of an MNFC composite sheet with 70 wt-% PCC, 20 wt-% MNFC (commercial grade), and 10 wt-% pulp fibers (SBKP) was compared with a sheet made of 100% SBKP fibers in **paper IV**. It was shown that the wet pressing performance of the MNFC composite sheet was excellent, with MR after press values of approximately 0.1 ml/g lower than that of the SBKP fibers (see Figure 16).

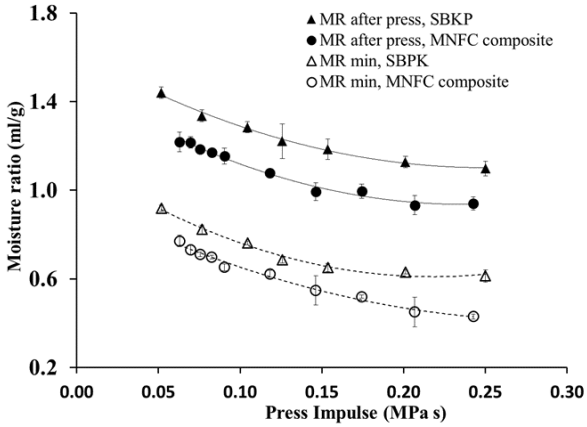

Figure 16. The effect of press impulse on the after press and minimum MR of the samples.

Although somewhat surprising at first, this result can be explained by the location of water within the sheet structure. It has been shown earlier that the water held inside the fiber wall is the

limiting factor in press dewatering (Wahlström 1990). This is due to the small size of the pores in the cell wall, which are around 1-30 nm in diameter and can restrict water removal rate in wet pressing.

Another important factor in press dewatering is that the permeability of the sample, particularly on the exit layer, must be maintained (MacGregor 1983). SEM -images of the freeze dried MNFC composite samples before and after pressing showed pores in the exit layer in the range of 1-5 μm, which seems to be sufficient for good press dewatering (see Figure 17 C1-C2).

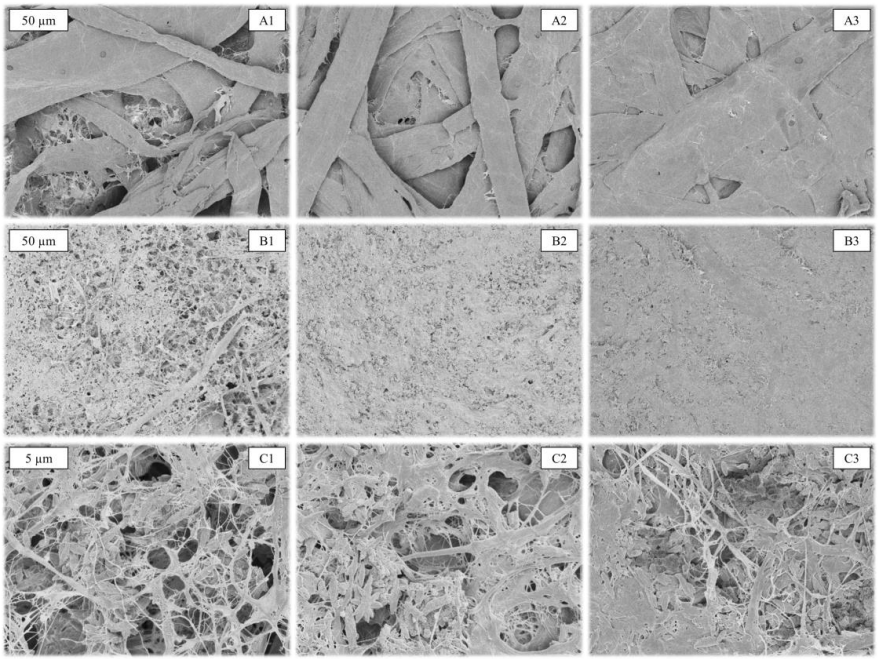

Figure 17. Development of surface morphology of the SBKP fibers (A) and MNFC composite paper (B) before pressing (1), after pressing at 10 MPa (2) and after press drying at 0.57 MPa and 130 °C (3). Higher magnification images of the MNFC composite surfaces are shown in C1-C3 which reveal the packing of PCC and MNFC during consolidation.

Similar values for the re-wetting were obtained for both the SBKP and MNFC composite sheets, of 0.48 ml/g and 0.51 ml/g respectively. These values are very close to those obtained in **paper III** with 1-5 wt-% of MNFC in the structure. This is an interesting observation since one would expect to have different amount of re-wetting with varying sheet microstructure due to capillary forces.

Calculating the (volumetric) porosity of the samples shows that the dry MNFC composite sheet has a porosity of 0.63 compared to a porosity of 0.36 of the dry SBKP fibers, although, the porosity of both samples was similar in all other consolidation stages (see Figure 18). This shows that the MNFC composite has distinctive characteristics in consolidation of the structure during drying. While the SBKP fibers collapse as a result of the drying process, the MNFC-PCC structure is able to maintain much of its volume.

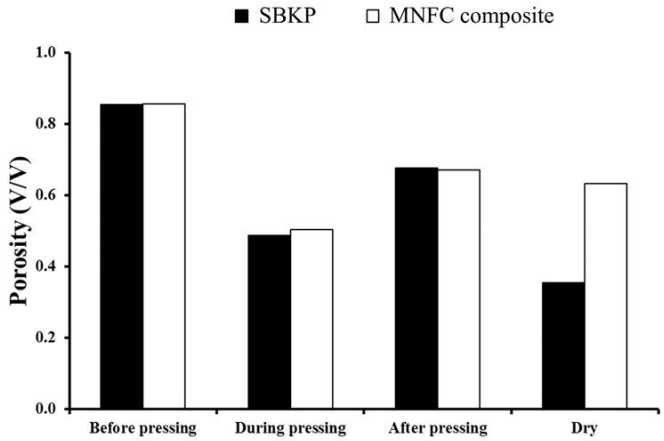

Figure 18. The volumetric porosity of the samples during different consolidation stages measured by mercury intrusion porosimetry, except for porosity during pressing which was based on the inline measurement of thickness during press pulse.

Figure 19 shows the pore size distributions of the MNFC composite and SBKP sheets in wet pressing and in press drying. As the dewatering proceeds, sheet structure consolidates and the water filled pores are closed. In the MNFC composite, most of the water is distributed in pores smaller than 10 μm in diameter before wet pressing, while in the SBKP fiber network most of the water is located in pores larger than 10 μm in diameter. More water seems to be located in the MNFC composite structure within a pore volume diameter range of 0.1 – 1 μm after wet pressing than before pressing. This suggests that the PCC particles form an open structure with voids between them where most of the water is held after pressing.

In press drying, the pore size distribution stays almost unchanged compared to the situation after pressing, which further supports the view that for the MNFC composite paper, the structured PCC packs to a threshold density which resists even the significant consolidation forces imposed by press drying. The fact that the MNFC composite furnish resists pore collapse in the later stages

of water removal is a significant advantage compared to SBKP sheet. One reason is that the open structure provided by the high PCC content may help maintain a high evaporation rate and good drying efficiency. Timofeev et al. (2014) showed that the drying rate of a sheet that contains 80 wt-% of kaolin pigment with 20 wt-% of Masuko –ground MNFC is comparable to a typical board product with similar external drying conditions. Considering the structural differences of the scalenohedral PCC and plate-like kaolin pigments it is expected that the drying rate of this type of furnish would not become an issue.

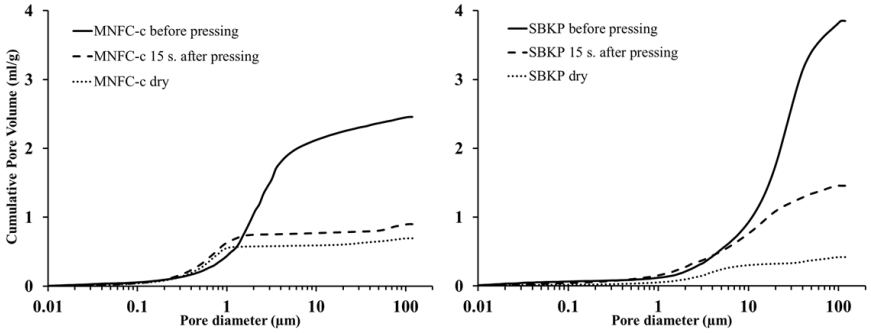

Figure 19. Cumulative pore volumes of the MNFC composite (A) and SBKP fibers (B) measured before pressing, 15 s after pressing at 10 MPa and after press drying at 0.57 MPa and 130 °C. Samples taken before and after pressing were freeze dried, thus the pore distributions correlate with the location of water in the structure.

4.5 Comparative analysis of press dewatering

In order to have an overall understanding about the press dewatering potential of the furnishes used in this thesis work, it is useful to examine them in relation to each other. This is done by plotting moisture ratio data as a function of press impulse from each publication where wet pressing was studied (**papers II-V**). Table 5 shows the compositions of different paper samples and their corresponding publications.

Table 5. Sample codes and furnish compositions of the samples studied in different publications.

Code	Publication	Furnish description
Ref	Paper IV	100% SBKP pulp
A	Paper II	15% PET, 38.3% PCC, 23.4% pulp, 23.4% MNFC (Masuko)
B	Paper III	99% pulp, 1% MNFC (5 pass fluidized)
C	Paper III	99% pulp, 5% MNFC (5 pass fluidized)

D	Paper III	99% pulp, 1% MNFC (TEMPO)
E	Paper III	99% pulp, 5% MNFC (TEMPO)
F	Paper IV	70% PCC, 20% MNFC (Daicel), 10% pulp
G	Paper V	70% PCC, 20% MNFC (1 pass fluidized), 10% pulp
H	Paper V	70% PCC, 20% MNFC (2 pass fluidized), 10% pulp
I	Paper V	70% PCC, 20% MNFC (2 pass fluid.+ low amount of precipitated PCC), 10% pulp
J	Paper V	70% PCC, 20% MNFC (2 pass fluid. + high amount of precipitated PCC), 10% pulp

The results seen in Figure 20 suggest that the wet pressing process can be used in the production of several types of MNFC composite papers with PCC in the furnish, provided that a long enough press pulse is applied. In fact, a sheet with 20 wt-% commercial MNFC, 70 wt-% PCC, and 10 wt-% pulp fibers had the best dewatering performance of all the studied compositions, including the reference (100% SBKP fibers). It seems that the initially large difference in MR after press between most of the samples diminishes as the press impulse is increased. It is interesting to see the comparatively high MR values of the samples studied in **paper III**, considering the low amount of MNFC in those furnishes. This is due to the very intensively refined base pulp, since even the reference pulp had a MR after press value of approximately 2.1 ml/g (see Figure 15), which is still higher than with any other of the studied furnishes.

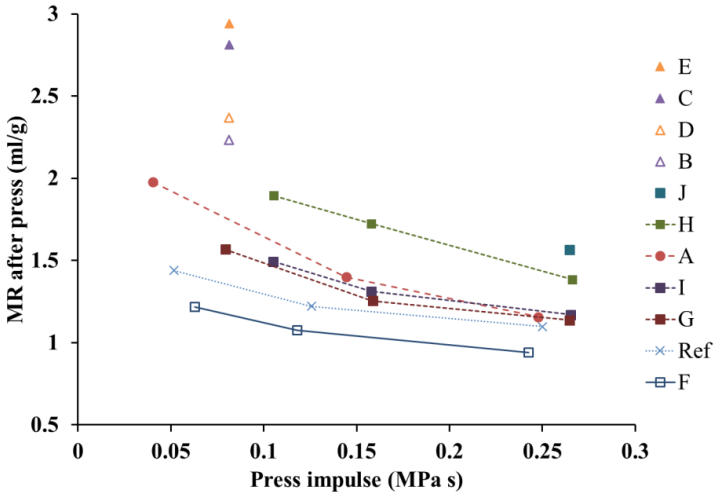

Figure 20. The moisture ratio of different samples after wet pressing as a function of press impulse. The shape of the test point icons corresponds to similar furnishes. Sample codes are explained in Table 5. The basis weight of the studied sheets varied between 90-110 g/m² which may slightly affect the results.

4.6 Pilot scale study on the forming of MNFC composite web (paper VI)

This study presented some initial steps that demonstrate a forming and dewatering strategy for the MNFC composite furnish that was also used in wet pressing studies published in **paper IV**. The furnish consisted of 70 wt-% PCC, 20 wt-% MNFC (Daicel), and 10 wt-% SBKP fibers. The response of this type of furnish to shear, and the gel-like properties were analyzed by dynamic rheological measurements. The purpose was to analyze how dynamic viscosity changes as a function of shear, and how the viscosity recovers after a high shear period.

It can be seen in Figure 21a that the composite furnish is highly shear thinning. The regeneration of the dynamic transient viscosity (η^+) after application of a high shear period is shown in Figure 21b. The results show that the initial viscosity of the 7 wt-% furnish was, as expected, higher than the 4 wt-% furnish. When the shear rate was increased to 500 s^{-1}, the value of η^+ dropped about 3 to 4 orders of magnitude due to the shear thinning behavior of the furnish. After the high shear period, the viscosity recovered to an order of magnitude lower value than in the initial state. This information proved important for the forming experiments, it demonstrated that the furnish could be subjected to high shear in the mixer and with the rotor inside the headbox before forming.

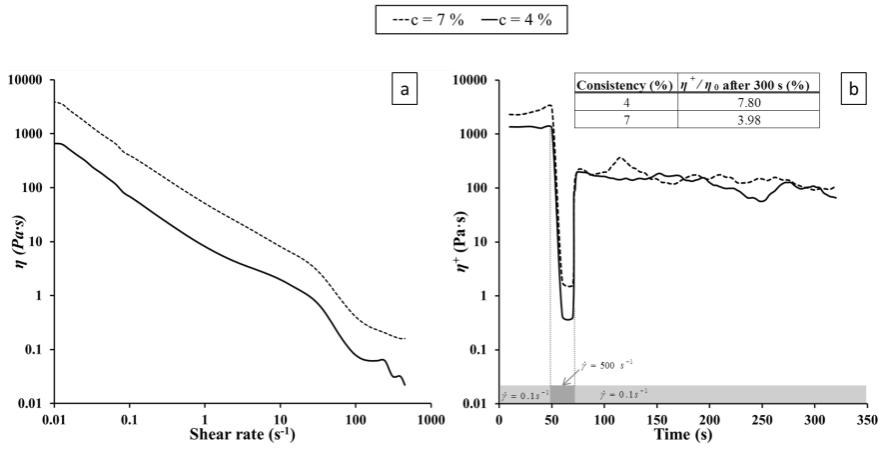

Figure 21. a) Dynamic viscosity of the composite furnish as a function of shear rate, showing the shear thinning behavior. b) Recovery of the dynamic transient viscosity after a high shear period obtained by 3ITT recovery measurements. The green area represents the low shear zone and red area represents the high shear zone.

Studying the web coherence with a smaller scale laboratory headbox showed promising results with formable webs at up to 20% solids content, although the consequent pilot trials were conducted over a three day period with solids content range of 6-8% due to processability reasons, such as pumping and mixing. The lower solids content limit was due to the fact that the retention of the fine PCC and MNFC was shown to be nearly 100% for furnishes with over 5% solids content, therefore, no special wires were needed in the trials.

The dewatering of the composite furnish was shown to be excellent. For a web with a basis weight of 207 g/m^2, an operating speed of 20 m/min and a headbox solids content of 6%, the final solids content after forming was 33%. An important factor for good dewatering was the use of a bent plastic blade after the headbox (see Figure 22a), which was used to apply pressure and shear on the furnish. The solids content after forming could be as low as 10% without use of the blade. The wet strength of the composite web was also remarkably high, which could be seen by the fact that the web could be removed from the couch intact (see Figure 22b). The high wet strength is likely due to the small pores between the fibers and a relatively high surface area for the air-water interface of the MNFC composite web.

The use of the headbox rotor gave somewhat conflicting results in the experiments. The application of shear lowered the viscosity and helped the flow of the web, especially at higher solids. However, the pulsations generated by the rotor propagated through the headbox and were evident in the formed web. Using the high shear mixer without the headbox rotor on allowed a thorough mixing of components, reduction of viscosity, and avoidance of problems with pulsations and headbox flow disturbances. In an industrial application, this would be a preferred solution, since the complex rotor can be eliminated, and a greatly simplified headbox, based on simple laminar flow principles, could be designed.

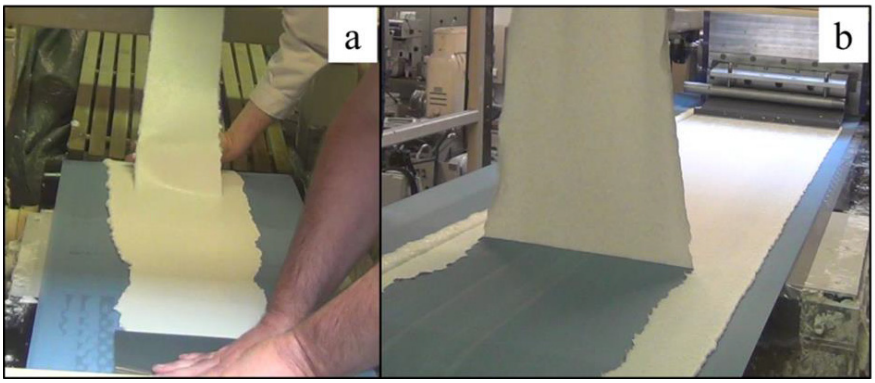

Figure 22. Forming trial of the MNFC composite web. The plasticity of the web enabled deformation in the dewatering zone after forming of the web (a). Wet web strength was high so that the web could be easily lifted from the wire (b).

5 Discussion

5.1 The manufacturing paradigm

As outlined in this thesis, the MNFC composite furnish is inherently different from the processability point of view when compared to traditional paper making furnishes. Especially the gel-like behavior caused by the high water uptake of MNFC presents both challenges and opportunities considering the manufacturing paradigm. This section is intended to give some insights into the possible solutions for the equipment and process conditions required for forming a web and consequently dewatering the composite paper furnish.

5.1.1 Forming

First of all, a full wire retention of fine material such as MNFC and PCC particles can be achieved when the solids content is increased. In our case, solids contents of above 5% resulted in nearly 100% wire retention with a furnish that contains 70% PCC, 20% MNFC, and 10% pulp fibers by weight (**Paper VI**). This phenomenon has been previously linked to the formation of a heterogeneous gel-like fibril network, which is effectively retains the fine material (Zhang et al. 2012b; Varanasi and Batchelor 2013).

To form a coherent web from a suspension that behaves like a gel is actually much easier than forming a traditional pulp fiber based web. This is due to the fact that flocculation of macroscopic pulp fibers suspended in water plays a significant role in the resulting paper formation, as high shear forces are required to break the fiber flocs. In comparison, the high viscosity of the interfiber phase for MNFC containing furnishes prevents reflocculation of fibers on the time scale of forming which promotes good formation. For a high solids content MNFC composite furnish, thorough mixing of the components to a homogeneous suspension should be achieved for even formation of the resulting web. The plastic behavior of the MNFC composite furnish also enables its formability up to relatively high web solids contents. In contrast, only limited deformation of the

web is possible for a traditional pulp fiber based paper after it has been formed on the wire. This is interesting from the perspective that the MNFC composite paper can be imprinted with surface patterns or even formed in three dimensional (3D) shapes at relatively high solids content. Recent results have confirmed the 3D-forming potential of similar compositions of MNFC, PCC, and pulp fibers (Dinh 2016).

The results from rheological measurements showed that applying shear will change the viscosity of the composite furnish, especially at higher solids contents. This is relevant considering the manufacturing process, as different unit operations such as mixing and pumping impart shear to the furnish. This means that it is important to understand, not only the effect of shear, but also the time dependent changes in rheological behavior of the furnish to be able to design suitable process equipment. An important observation related to the furnish rheology was that a coherent web could be formed even up to 20% solids content furnishes with the laboratory headbox, given that enough shear was applied to the furnish (**Paper VI**). At this solids content, the MNFC composite furnish is practically solid at rest. However, based on the visual observations during the laboratory headbox experiments it was seen that forming a web at these solids contents would require that the jet speed of the furnish exiting the headbox slice should be around 250 m/min. Due to the much lower speed of the pilot paper machine it could not be confirmed that an even quality web can be formed at such high solids in a continuous process in these experiments, but the results were definitely promising on the laboratory scale.

Based on the experiments, it is conceivable that a simple forming unit with narrow slice and a component for applying shear on the furnish during initial dewatering would be adequate to form a web for further processing. In the pilot trials a bent plastic blade (wedge) was used above the wire for this purpose. A rotating element inside the headbox did not seem necessary, at least at consistencies up to 6% and in fact, it caused unnecessary basis weight fluctuations on the formed web.

5.1.2 Wet pressing and drying

The solids content of the MNFC composite web after forming was as high as 33%. Based on the results presented in **Paper IV**, it was concluded that a 50 ms single nip press pulse was sufficient for removing water from the MNFC composite paper to achieve an after press solids content of 52%, from an initial solids content of 20%. It was concluded that the efficient water removal of the MNFC composite paper in wet pressing was due to the larger fraction of inter-particle water

in comparison with a paper made of softwood fibers. It has been shown by Wahlström (1990) that the water located inside the fiber wall is a limiting factor in wet pressing, mainly due to the small size of the pores in the cell wall (1 – 30 nm in diameter). Additionally, the high amount of structured PCC (70 wt%) helps to maintain the flow channels required for efficient dewatering. The results in **Paper V** also confirm that press dewatering becomes more difficult without the structured PCC in the furnish.

Although a study of the drying phenomena of the MNFC composite papers was beyond the scope of this thesis, there are some aspects worth mentioning about the behavior of the composite paper during drying. Due to the drying shrinkage caused by the MNFC, the laboratory sheets had to be dried with a hot press as described in **Paper I**. Manninen et al. (2011) have studied the shrinking potential of sheets that contain 20 wt% MNFC with pulp fibers, and noticed that the drying shrinkage can be as high as 10% when the laboratory sheets were freely dried. Although in our case the shrinkage was not quantitatively measured, it was clear based on the early tests that a restrained drying method had to be developed. For an industrial scale production method, the so called condebelt–drying would seem a feasible option, as it utilizes applied pressure for restrained drying and is known to result in drying rates 10 – 15 times higher than conventional cylinder drying (Feller et al. 2005; Lee et al. 2003; Lee et al. 2000; Lehtinen 1995; Lehtinen 1998; Retulainen et al. 1998).

5.2 Cost structure of the MNFC composite papers

One of the most important factors that would promote the development of novel products based on high amount of fillers and MNFC is the predicted cost structure of the end product. The total furnish cost C_{tot} is a function of the raw material costs and, in the case of the three component mixture, can be calculated by:

$$C_{tot} = C_1 \cdot X_1 + C_2 \cdot X_2 + C_3 \cdot X_3$$

, where C_i = cost of a component
X_i = proportion of a component.

The material costs are quite well known for fibers and PCC, but for MNFC the cost is more or less speculative due to low production rates resulting from high energy consumption (Spence et al. 2011; Osong et al. 2016), and lack of current markets. However, some of the big papermaking

companies have already started their pilot-scale and semi-commercial production facilities for MNFC which implies that the production costs are expected to be within reasonable limits (Skuse 2015; Nelson and Retsina 2014; Bilodeau 2015; Tolnai 2015). The basis for the MNFC cost structure is the cost of fibers that are used in the grinding process, in this case birch kraft pulp. In addition to the price of fibers, other costs related to e.g. energy and equipment must be considered. For MNFC, two different cases are compared. In case **a**, additional costs are estimated to be 400 €/ton (total cost of MNFC = 1000 €/ton) and in case **b** they are estimated to be 900 €/ton (total cost of MNFC = 1500 €/ton). The price of fibers used in these calculations is 600 €/ton and price of PCC 110 €/ton. The cost structures of the MNFC composite sheet for these two cases are presented in Figure 23.

It should be emphasized here that this cost model is very simple, and other relevant costs related to production are neglected. The bold lines in the figures represent the speculative price of a fine paper furnish with 20 wt% PCC content with pulp fibers (502 €/ton). The raw material costs for a 3-component sheet are less in the green area of the triangle that is located below this line. It can be seen that the price of MNFC has a large influence on the total price. Nevertheless, in both cases the total cost of furnish with 70 wt% PCC, 20wt% MNFC, and 10 wt% pulp fibers falls below the price of the example fine paper, being 337 €/ton for case a, and 437 €/ton for case b.

Even so, the interesting properties of high MNFC content sheet could potentially justify the higher costs if proper applications can be identified. It is evident that while production costs of MNFC are very likely to decrease in the future, the economically feasible product space will expand. This leads to the situation where the production of traditional paper grades could be replaced with higher filler content materials with unique structural and optical properties resulting from the addition of MNFC. A substrate for printed electronics could be one of the potential applications in the future (Penttilä et al. 2013).

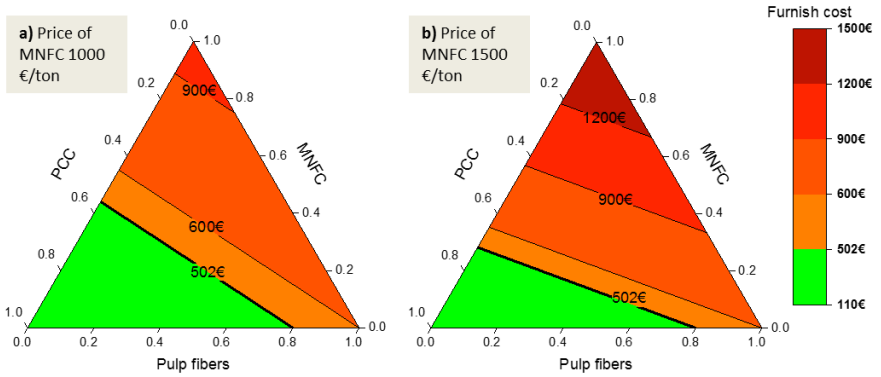

Figure 23. Total furnish cost models for two different MNFC raw material cost. The green color shows the area where the furnish cost is lower than the speculative raw material cost for a fine paper that contains 20 wt% PCC with pulp fibers.

6 Conclusions

6.1 Significance of this work

The significance of this work is based on a number of novel findings. As presented in the introduction, the research made in this thesis work was based on two main research questions. Trying to answer the first question required a set of experiments to analyze the physical properties of the MNFC composite papers. For the first time, the basic sheet properties were determined for a total range of compositions of MNFC, filler, and pulp fibers. Very high optical performance and a unique microstructure of composite papers with very high filler content could enable a totally new range of bio-based products. Comparing the properties of a non-woven MNFC composite to an industrial wall cover material showed the potential of these composite materials in new areas also outside the traditional paper industry. It was also shown that the structure can be fine-tuned by an in-situ precipitation method, which can also be utilized to lower the water binding capability of the MNFC for improved dewatering.

The second research question was set to understand the manufacturing paradigm of the MNFC composite papers in light of the intrinsic water binding properties of MNFC. To the best of the author's knowledge, wet pressing of materials that contain relatively high amounts of various MNFC grades has not been extensively studied previously. The dewatering of furnishes with MNFC is considered as one of the most important challenge in the production MNFC composite papers/materials due to the high affinity of MNFC to water. The pilot scale forming study presented in **Paper VI**, although very qualitative in nature, is one of the first published research in the area of manufacturing continuous webs from MNFC based suspensions. This work shows that it is feasible that a wide range of high value MNFC based products can be formed with an efficient process, and is an important step towards a next generation of products and processes that are based on forest resources.

6.2 Recommendations for future research

In order to increase the range of economically feasible products that are based on MNFC, the production costs need to be reduced considerably. The results in this work have shown that there seems to be no advantage to fibrillate the pulp fibers extensively, as far as the basic sheet properties are considered. To facilitate mechanical disintegration of pulp fibers, it is important to evaluate the effect of different pretreatments (enzymatic and chemical) on the energy required in MNFC production.

The study of the in-situ precipitation of $CaCO_3$ on the MNFC is an interesting subject for further research, particularly the effect of different precipitation conditions on the PCC morphology and composite properties. In fact, the in-situ PCC process could become an integrated part of a unit that produces a wide range of MNFC based products, although, the most important factor for the realization of this will be the identification of applications where the unique interactions of MNFC and PCC would give more value for the end use.

The next technological step would include building a semi-pilot scale research environment that is capable of producing continuous webs of composite papers that contain MNFC. Ideally, also the MNFC production with possibility to include the in-situ precipitation of $CaCO_3$ should also be considered as this would be a critical step towards the industrial production of these novel composite papers.

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