



# MONASH University

***Biorefinery Opportunities in a Thermomechanical Pulping Mill***

*Wickramarachchige Don Thilina Lakmal Gunawardhana*

MS (Biological Systems Engineering), B.Sc. (Chemical & Process Engineering)

A thesis submitted for the degree of *Doctor of Philosophy* at  
Monash University in 2019  
*Department of Chemical Engineering*

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***Dedicated to my loving parents, brother and sister***

*For their boundless love and support*

*Without you, none of this would have been possible*

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## Abstract

Some sectors of the pulp and paper industry has been facing severe economic hardships over the last few decades. The newsprint industry has been worst affected because of the advent and propagation of electronic media. This has led to closures, mergers and downsizing of many thermomechanical pulping mills across the world. Unfortunately, all these actions only provide short-term, unsustainable fixes. Novel approaches are needed in order to find long-term solutions. Implementing biorefineries is one such approach and it was the focus of this thesis.

An Australian newsprint mill with three thermomechanical pulping mills was analysed for possible biorefinery opportunities. Following constraints were presented prior to the initial analysis: any biorefinery must not disrupt the current production volumes and they should be implementable in the near future. Therefore, waste streams were analysed for potential value-addition. Initial analysis identified four waste streams and three potential bio-products: microfibrillated cellulose, resin acids and terpenes.

Whitewater fines collected using a dissolved air flotation unit was selected as the raw material for microfibrillated cellulose production. These whitewater fines are considered as waste due to their low strength and sparingly used in papermaking process. Their low strength is primarily caused by the enrichment of extractives on the surface, which hinders fibre-fibre bonding. Another objective was to upgrade these whitewater fines, which are a significant 10 o.d. tonnes per day waste stream, back to the desired quality of TMP newsprint so that they can be added back to the papermaking process. Refining energy of 3000 kWh/tonne improved the tensile strength from 28 Nm/g to 40.5 Nm/g. Further homogenization of these refined fines generated microfibrillated cellulose with median diameter of 14 – 19 nm, which exhibited hydrophobic characteristics possibly enabling them to be used as composite materials in non-polar matrices. Whitewater fines can be significantly upgraded via a simple high-yield caustic washing process that resulted in a tensile strength of 48.8 Nm/g, a remarkable ~75% increase. This process also allows recovering extractives from black liquor, from which resin acids could be separated.

Resin acids were successfully isolated and concentrated using a two-stage ultrafiltration process combined with pH manipulation. This process enables ~ 64% recovery of resin acids and generates a concentrated resin acid with ~ 77% purity. These efficiencies could be further improved in an industrial scale membrane filtration system. Recovered resin acids could then be further purified into individual resin acids with potential high-value

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applications as pharmaceuticals and anti-oxidants. Ultrafiltration was successfully applied to the plug screw pressate to isolate and concentrate terpenes. It was evident that terpenes could be isolated in the retentate with 100% recovery. This retentate could be processed using a commercially available reboiler-condenser unit to recover terpenes. Terpenes recovered from thermomechanical pulping mills are superior to kraft turpentine, as they are not contaminated with sulphur. They could have valuable applications as a precursor to biopharmaceuticals such as paracetamol, fragrances and biopolymers.

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## Publications during enrolment

### Peer-Reviewed Journal Papers

1. “Upgrading waste whitewater fines from a *pinus radiata* thermomechanical pulping mill”, Thilina Gunawardhana, Paul Banham, Desmond Richardson, Antonio Patti, Warren Batchelor. Nordic Pulp & Paper Research Journal, Vol 32 no 4, 2017 – **Published**
2. “Development of cellulose nanofibre quality with mechanical energy: effect of starting chemical composition”, Thilina Gunawardhana, Praveena Raj, Swambabu Varanasi, Gil Garnier, Antonio Patti, Warren Batchelor. Sixteenth Fundamental Research Symposium of the Pulp and Paper Fundamental Research Society, September 2017, Oxford, United Kingdom. – **Published**
3. “Homogenizing fines to microfibrillated cellulose – reducing energy consumption at higher consistencies”. Thilina Gunawardhana, Paul Banham, Desmond Richardson, Antonio Patti, Warren Batchelor. – **Manuscript under review by Cellulose Journal**
4. “Upgrading Thermomechanical Pulping Whitewater Fines through Chemical Treatment”, Thilina Gunawardhana, Paul Banham, Desmond E. Richardson, Antonio F. Patti, Warren Batchelor. - **Manuscript to be submitted to Nordic Pulp & Paper Research Journal**
5. “Recovery of Resin Acids and Terpenes from Thermomechanical Pulping Mill Process Water Using Membrane Filtration”, Thilina Gunawardhana, Alicia Reynolds, Vince Verheyen, Desmond E. Richardson, Antonio F. Patti, Warren Batchelor. - **Manuscript to be submitted to Nordic Pulp & Paper Research Journal**

### Related Co-Authored Journal Papers

1. “Effects of fibre dimension and charge density on nanocellulose gels”, Llyza Mendoza, Thilina Gunawardhana, Warren Batchelor, Gil Garnier, Journal of Colloid and Interface Science, Vol 525, 2018 – **Published**
2. “Nanocellulose for gel electrophoresis”, Llyza Mendoza, Thilina Gunawardhana, Warren Batchelor, Gil Garnier, Journal of Colloid and Interface Science, Vol 540, 2019 - **Published**

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## Thesis including published works declaration

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This thesis includes 1 original paper published in peer reviewed journals, Chapter 6. The core theme of the thesis is value addition to waste process streams in a thermomechanical pulping mill. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the student, working within the Department of Chemical Engineering, Monash University under the supervision of Assoc. Prof. Warren Batchelor and Prof. Antonio Patti.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

In the case of Chapter 6, my contribution to the work involved the following:

Thesis Chapter	Publication Title	Status (published, in press, accepted or returned for revision, submitted)	Nature and % of student contribution	Co-author name(s) Nature and % of Co-author's contribution*	Co-author(s), Monash student Y/N*
Chapter 6	Upgrading waste whitewater fines from a pinus radiata thermomechanical pulping mill	Published in <a href="#">Nordic Pulp &amp; Paper Research Journal</a>	60% Experimental design, collecting data and writing	1) <b>Paul Banham</b> , collecting data, data analysis, input into the manuscript, 10% 2) <b>Desmond Richardson</b> , input into the manuscript, 10% 3) <b>Antonio Patti</b> , input into the manuscript, 10% 4) <b>Warren Batchelor</b> , input into the manuscript, 10%	N

I have renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

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The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author I have consulted with the responsible author to agree on the respective contributions of the authors.

Main Supervisor signature: 

Date: 11-09-2018

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## Abbreviations

AcGGM	-	Acetyl-galactoglucomannan
AOX	-	Adsorbable Organic Halides
ARC	-	Australian Research Council
BC	-	Bacterial Cellulose
BDDJ	-	Brit Dynamic Drainage Jar
BEK	-	Bleached Eucalyptus Kraft
BKP	-	Bleached Kraft Pulp
CHP	-	Combined Heat & Power
CMF	-	Cellulose Microfibrils
CNC	-	Cellulose Nano Crystals
CNF	-	Cellulose Nanofibrils
COD	-	Chemical Oxygen Demand
CSF	-	Canadian Standard Freeness
CTMP	-	Chemi-Thermomechanical Pulping
CTO	-	Crude Tall Oil
DAF	-	Dissolved Air Flotation
EMT	-	Effective Medium Theory
ETP	-	Effluent Treatment Plant
FID	-	Flame Ionisation Detector
GC	-	Gas Chromatography
GCMS	-	Gas Chromatography - Mass Spectrometry
L&W	-	Lorentzen & Wettre
MBR	-	Membrane BioReactor
MCC	-	Micro Crystalline Cellulose
MCEM	-	Monash Centre for Electron Microscopy
MDF	-	Medium-Density Fibreboard
MF	-	Microfiltration
MFC	-	Microfibrillated Cellulose
MWCO	-	Molecular Weight Cut-Off
NA	-	Not Applicable
NC	-	Nanocellulose
NFC	-	Nanofibrillated Cellulose
NFC	-	Nano-Fibrillated Cellulose

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NLC	-	Nano-lignocellulose
OCA	-	Optical Contact Angle
PES	-	Polyethersulfone
PFI	-	Paper and Fibre Research Institute
PHA	-	Polyhydroxyalkanoates
PM	-	Paper Machine
PSF	-	Plug Screw Pressate
R&D	-	Research & Development
RC	-	Regenerated Cellulose
RH	-	Relative Humidity
RO	-	Reverse Osmosis
SBPK	-	Softwood Bleached Pine Kraft
SEM	-	Scanning Electron Microscopy
SPME	-	Solid-Phase Micro-Extraction
TAPPI	-	Technical Association of the Pulp and Paper Industry
tBME	-	tertiary-butyl methyl ether
TEMPO	-	2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
TMP	-	Thermomechanical Pulping
TMP2	-	Thermomechanical Pulp Mill #2
UF	-	Ultrafiltration
VOC	-	Volatile Organic Compounds
VPP	-	Value-Prior-Pulping
VSEP	-	Vibratory Shear Enhanced Processing

---

## Nomenclature

%	-	percentage
°C	-	degrees Celcius
bar	-	bar, pressure
C <sub>c</sub>	-	Critical Concentration
g	-	gram
g	-	Gravity Coefficient
gsm	-	grams per metre squared
kDa	-	kilo Dalton
kg	-	kilogram
kPa	-	kilo Pascal
kV	-	kilo Volts
kWh	-	kilo Watt hour
L/D	-	Aspect Ratio
l <sub>f</sub>	-	Length of the fibre
min	-	minutes
mL	-	millilitre
mm	-	milimetre
MPa	-	Mega Pascal
MT	-	Metric Tonne
N	-	Netwon
nm	-	nanometre
o.d.	-	Oven dried (weight)
P	-	Pressure
Patm	-	Atmospheric Pressure
pKa	-	Dissociation constant
RBA	-	Relative Bonding Area
Rev	-	Revolutions
rpm	-	revolutions per minute
s	-	seconds
T	-	Tensile Strength/Index
W	-	Watt
wf	-	Width of the fibre
wt%	-	weight percentage

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wt. %	-	weight percentage
Z	-	Zero-span strength
$\mu\text{m}$	-	micrometre
$\rho$	-	Density
tb	-	Fibre-fibre bonding

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# Chapter 1

## Introduction & Literature Review

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# Chapter 1 – Introduction & Literature Review

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# Chapter 1 - Introduction & Literature Review

## 1.1. Introduction

The pulp and paper industry is a well-established industry with significant contributions to the world economy, delivering a range of products from tissue papers to cardboard packaging. In Australia, pulp and paper industry is a highly invested industry with total capital assets of AUD \$ 5.0 billion [1], consisting of 9 mills, and direct employment of more than 5800 [1]. Pulp and paper industry is also a mature industry with almost all the key pulping technologies at least few decades old and the possibilities of significant breakthroughs in are minimal.

### 1.1.1. Current challenges in the pulp and paper industry

Over recent decades, the pulp and paper industry has faced severe economic challenges, not only in Australia, but also globally. Profits have dwindled, some mills have been restructured, some big companies have merged to reduce cost, several mills have been shut down, and many people have lost employment [1-8]. This has resulted in lack of investment in both capital and R&D investment [1, 2]. The lack of capital investment is worrying when you consider the fact that pulp and paper industry is one of the three most capital-intensive industries in the whole world, along with the petroleum and petrochemical industries [2].

The main reason for dwindling profits is the reduced demand for some paper grades, especially newsprint, with the rise of electronic media. The demand for newspapers in Australia [1, 3, 9-11] and the world [3, 12] has fallen significantly. In fact, the demand for paper products such as newsprint and copy paper is unlikely to improve in the future; indeed the demand for newsprint is predicted to continue sharp declines over the coming years [1, 13]. This is in contrast to packaging and hygiene papers such as tissue products that have continued to grow [14].

The traditional survival strategy undertaken by the pulp and paper industry is often focussed on company mergers, downsizing, and restructuring but these business approaches have proved insufficient. In fact, we need a solution, which is creates value-adding opportunities for the industry separate from making conventional grades of paper.

Many pulp and paper mills have pursued increasing energy efficiency and energy self-sufficiency as possible technological solutions to reduce operating costs. But as pointed

out by Thorp et. al [15], a majority of the chemical pulping mills have achieved energy self-sufficiency and a small number of mills are not using fossil fuels at all, instead they export heat and power. Therefore, it is almost impossible to achieve any further significant results across the whole industry by the means of increasing energy efficiency. This further emphasizes the previous argument that we need innovative and value adding solution to sustain the pulp and paper industry. The most promoted solution is integrating a biorefinery within the pulp and paper mills [5, 7, 8, 15-25].

The pulp and paper industry needs more innovative and economically feasible novel solutions rather than short-term management solutions. Creating novel products and value addition to existing products is key to realize this goal and implementing biorefinery concepts in pulp and paper industry is the most powerful route to achieve long-term sustainability of the industry [16-18, 26-29]. We could expect that 'newsprint' would continue to survive despite the predictions of a gloomy future which doesn't necessarily mean the end of the road for TMP plants. TMP plants would continue to supply light-weight coated paper. One could also predict that TMP plants would continue to make inroads to packaging products such as food contact materials where non-chemically treated TMP fibres would be preferable to chemically treated pulp. Also, some TMP plants are thriving as board manufacturers, for example, WPI in New Zealand. Therefore, the biorefinery explored in this thesis is still relevant and applicable for TMP industry.

In this thesis, we work closely with a thermomechanical pulping (TMP) mill and investigate the possible value-adding opportunities. The rest of this chapter is dedicated to literature review in which we summarize the key findings on existing and possible biorefinery opportunities in the pulp and paper industry, with emphasis on newsprint industry. Chapter 2 describes the TMP newsprint mill in focus of this study. Chapter 3 details the research objectives and outlines each chapter. The Chapters 4 to 8 illustrates the results from the experimental work while Chapter 9 provides the conclusions and the recommendations of this study.

### 1.2. Literature Review

Our key findings on existing biorefinery opportunities in the pulp and paper industry is detailed in this section. We also look into the literature for possible biorefinery opportunities in pulp and paper industry, more specifically in TMP newsprint mills. This section is divided into six sub-sections for clarity. Lignocellulosic biomass is introduced in the first sub-section with further sub-sections on key components of biomass: cellulose, hemicellulose, lignin and extractives. The second sub-section introduces the basics of

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thermomechanical pulping with emphasis on primary processing of wood chips into fibres. The aim of these two sub-sections is to provide basic level knowledge on TMP newsprint industry and lignocellulosic biomass.

The next sub-section discusses existing and novel biorefinery concepts in pulp and paper industry. The next two sub-sections describes two important biorefinery concepts: production of microfibrillated cellulose and extraction of phytochemicals, in detail. These two sub-sections are further divided into sub-section accordingly. The last sub-section discusses the gaps in the existing literature and identifies the areas that we could work in this project and sets up the objectives of this thesis, which can be found in Chapter 3.

### 1.2.1. Lignocellulosic Biomass

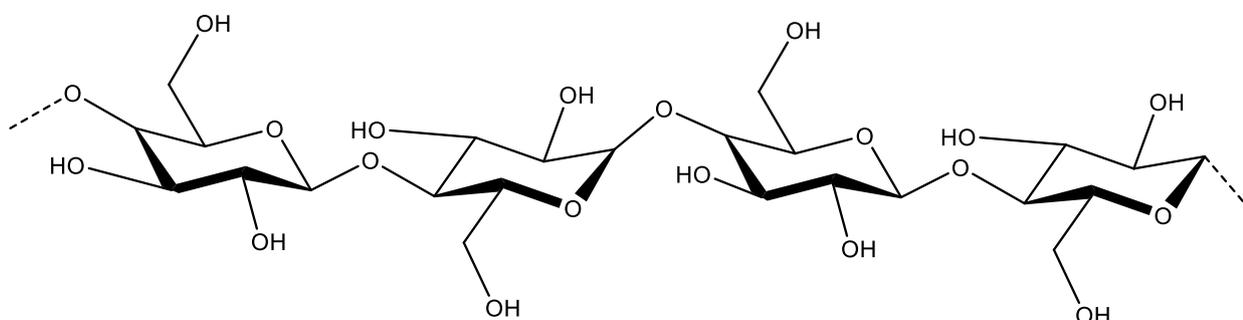
Biomass is the most abundant natural and renewable resource in the world of which the lignocellulosic biomass contributes a significant portion [30]. Trees and herbaceous plants are the major sources of lignocellulosic biomass while algae and bacterial cellulose contribute lesser amounts [31].

Woody biomass from trees is made of two main components as implied by the term, “lignocellulose”, which are lignin and holocellulose [32]. Holocellulose is the fraction made of sugars and is further divided into cellulose and hemicellulose [32]. Extractives or more technically referred to as ‘phytochemicals’ and ash makes up the rest of the dry plant biomass [33]. Ash mainly consists of inorganic chemicals and elements such as SiO<sub>2</sub>, Ca and P, and is not a significant fraction of woody biomass [34, 35]. However, ash can be significant fraction in herbaceous biomass [36]. The metals which are naturally present in lignocellulosic biomass might interact with retention aids and other chemicals during papermaking. However, their effects would be largely overshadowed by the effects of the other metal ions introduced via pH adjustment, for example, Na<sup>+</sup> and Ca<sup>2+</sup>. The amount of cellulose, hemicellulose, and lignin depends on the type of tree, tree species, part of the tree, and age of the tree [37]. The amount of extractives changes with the season in addition to the above-mentioned variables [33].

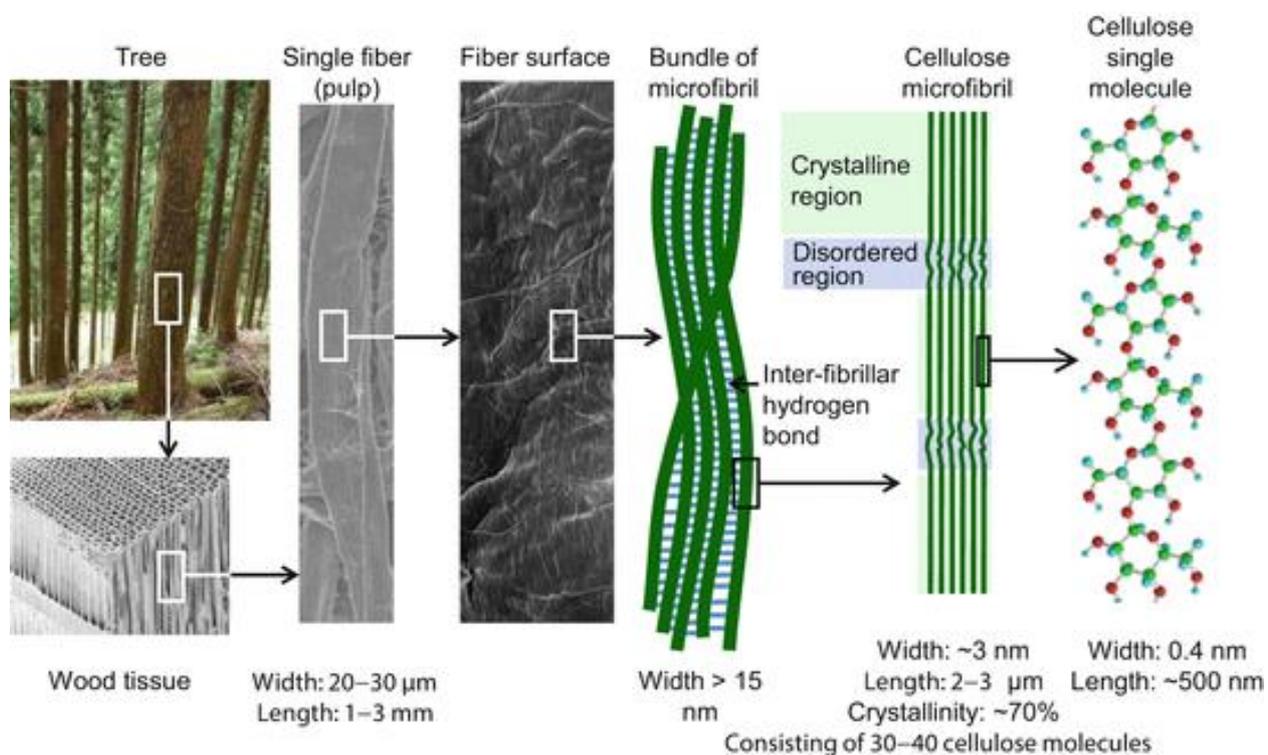
#### 1.2.1.1. Cellulose

Cellulose is the primary product of plant photosynthesis and it is the most abundant natural biopolymer on the earth [30]. Cellulose is entirely made of glucose, which is the primary C<sub>6</sub>-sugar. The primary building block of cellulose chain consists of two glucose units bonded via a β-1, 4-glycosidic bond [38]. Individual cellulose polymer chains bond to each other using hydrogen bonds [38]. See Figure 1.1 for the molecular structure of cellulose.

Cellulose is the main components in plant cell walls and gives structure to the cell [39, 40]. Individual polymer chains of cellulose are bundled together to make microfibrils and microfibrils are further bundled together to make microfibril bundles [39, 40]. These microfibril bundles eventually come together to make cellulose fibres which gives the structure to the cell and subsequently to the tree [39-41]. See Figure 1.2.



**Figure 1.1.** Molecular structure of the cellulose polymer



**Figure 1.2.** Cellulose Microfibril Arrangement in Plant Cell Wall. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer, [High-Performance and Specialty Fibers](#), Cellulose Nanofibers as New Bio-Based Nanomaterials, Akira Isogai, © Springer (2016) [40]

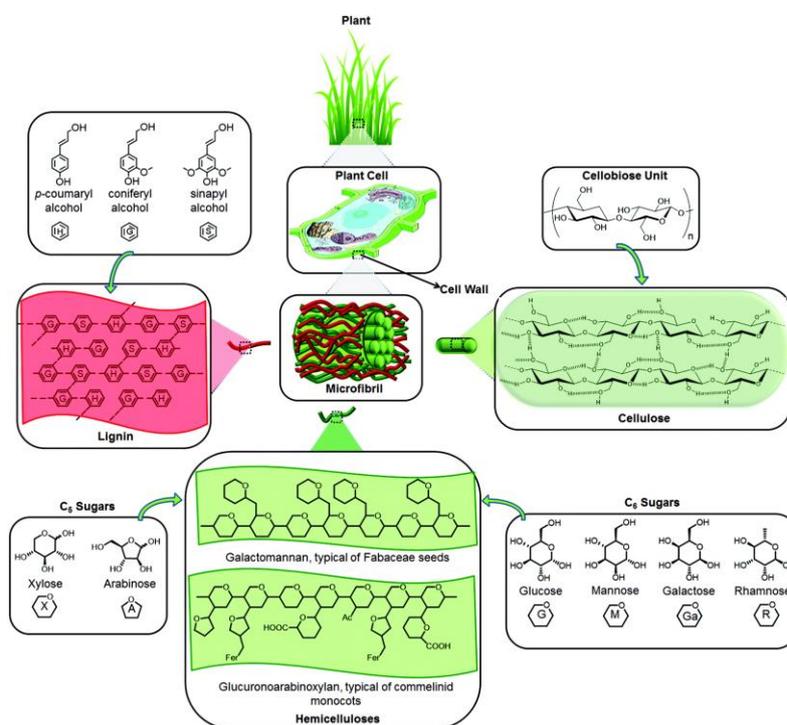
Separation of these cellulose microfibril bundles and individual microfibrils have received much attention over the last few years, as means to produce nano-scale cellulose fibres [39].

### 1.2.1.2. Hemicellulose

Hemicellulose are also polymers of sugar similar to cellulose. However, hemicellulose is not made of glucose entirely [41]. Instead, it is a mixture of both C5 and C6 – sugars [41]. The composition of sugars dependent on the tree type, hardwood or softwood and tree species [42]. Hemicellulose serves the purpose of binding cellulose microfibrils and microfibril bundles together [41].

### 1.2.1.3. Lignin

Lignin is also a biopolymer similar to cellulose and hemicellulose [43]. However, the structure and the purpose of lignin is completely different from that of cellulose and hemicellulose [43]. Lignin is not made of sugars instead of aromatic building blocks. These building blocks are arranged in random ways through many complex bonds [43]. This random nature of bonds and aromatic groups makes lignin ever harder to break down by microorganisms and chemicals. Aromatic nature of lignin also results in hydrophobicity [41]. This purpose of lignin in plant cell wall is to protect the plant from microbial attacks and weather [41]. Figure 1.3 shows how lignin exists in plant cell wall along with cellulose and hemicellulose. It also shows a general representation of building blocks of cellulose, hemicellulose and lignin.



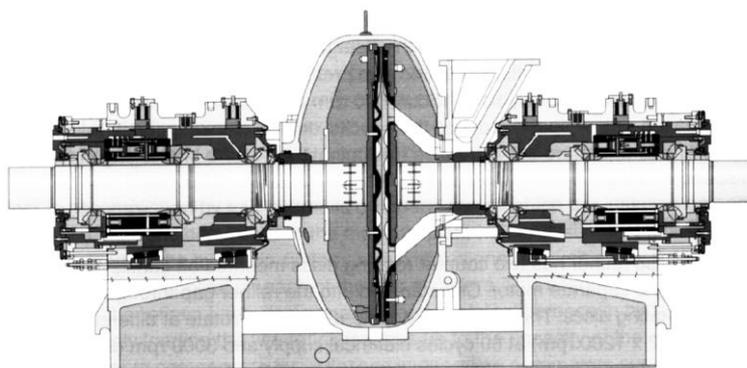
**Figure 1.3.** Cellulose, Hemicellulose and Lignin: Existence in Plant Cell Wall and Building Blocks, Reproduced from [44] with permission from the Royal Society of Chemistry, under Creative Commons Attribution 3.0 Unported Licence, © Royal Society of Chemistry (2015)

#### 1.2.1.4. Extractives

Extractives are naturally occurring chemicals in plants and they are often referred to as phytochemicals in literature [33]. Extractives exist in plants to protect the plant from microbial and fungal infections [45]. There are two major classes of extractives in plants: volatile extractives and non-volatile extractives [33]. Volatile extractives usually consists of terpenes such as  $\alpha$ - and  $\beta$ -pinenes and limonene [33]. The major classes of non-volatile extractives include resin acids, fatty acids, sterols and triglycerides [33]. Extractives will be discussed in detail in section 1.2.5 of this chapter.

#### 1.2.2. Thermomechanical Pulping

Thermomechanical pulping is the use of heat and mechanical shear energy to break down wood into fibres [46]. TMP is made from softwood owing to the presence of long fibres which results in higher strength properties, as opposed to hardwood. Wood chips are fed into a large refiner in which they are refined while being heated up to around 130 °C [46]. The high temperature helps the lignin to soften and help the fibrillation process [46]. It is important to point out that there is no delignification during this process and the majority of the lignin and hemicellulose is retained in fibres, unlike chemical pulping methods in which lignin and hemicellulose are chemically converted and dissolved away, and only cellulose fraction is retained [46]. This makes TMP a high yield process with values up to ~95%. In contrast, chemical pulping results in much lower yields, ~ 45 - 60%, depending on the chemical composition of the wood and pulping method [46]. This high yield is a major advantage of TMP compared to chemical pulping. High shear crushing of wood in primary refining and fibres in secondary refining induce significant fibrillation generating a significant weight fraction of fines (200P, < 74  $\mu$ m in length) in thermomechanical pulp [46].



**Figure 1.4.** The double-disc refiner (Metso RGP 68 DD). Reprinted by permission from John Wiley and Sons: Wiley Books, [Handbook of Pulp](#), Mechanical Pulping Processes, Jürgen Blechschmidt & Sabine Heinemann, © John Wiley and Sons (2008) [47]

Primary refining of wood incorporates steam to heat up the wood fibres. This leads to some extractives in the wood (extractives will be discussed later in section 1.2.5 of this chapter) being steam distilled and escaping through the steam outlet and this steam may be captured as a condensate in the heat recovery systems [33, 48]. This steam contains a significant portion of volatile extractives, and some resin acids. Mechanical refining of wood also releases significant amount of extractives into the process water system, which is known as 'whitewater' in pulping terminology [33]. The composition of extractives and their effects on pulping and papermaking will be discussed later in section 1.2.5 of this chapter.

Pulp from the TMP mills can be used further used with or without bleaching for paper making purposes depending on the application and intended paper quality. Bleaching is usually done by treatment with hydrogen peroxide and sodium hydrosulfite [46]. The upstream unit operations, however, remain unchanged irrespective of the bleaching chemicals used.

### 1.2.3. Biorefineries

A biorefinery can be defined as a facility which integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass, as proposed by the National Renewable Energy Laboratory of the USA [49]. This is quite analogous to a petroleum refinery, which uses petroleum crude oil to produce fuels, polymers and other commodities. A biorefinery will use food, agricultural wastes and forestry resources to produce biofuels, chemicals and many other products [50].

#### 1.2.3.1. Biorefineries in the pulp and paper industry

The forest biorefinery can be described as a subset of biorefineries, which uses wood, as the primary feedstock, but is not necessarily based on a paper mill. On the other hand, a paper mill based biorefinery is a subset of forest biorefineries, which is based on a paper mill, utilizing pulp or other by-products of the mill to produce fuels or chemicals. The terms, forest biorefinery and paper mill based biorefinery, have been used interchangeably in the literature, even though a forest biorefinery does not have to be part of a paper mill. Sometimes "integrated forest biorefinery", has been used to identify pulp mill based biorefineries [16, 26, 51, 52]. Although this is quite understandable since the paper industry is the biggest forest based industry and pulp mills are regarded as providing the best way to prepare wood for further biorefining [16].

Axegard 2005 defines a pulp mill based biorefinery as “Full utilization of the incoming biomass and other raw materials, including energy, for simultaneous production of fibres for paper products, chemicals and energy” [26].

Therefore, a pulp and paper mill based biorefinery can be identified as an integrated facility, which produces energy, chemicals, and fuels in addition to its traditional products; pulp and paper, based on the above definitions.

As Bajpai [16] points out, most modern pulp mills are operated as basic biorefineries. Waste materials from the pulping processes, such as bark and black liquor are combusted or gasified to produce heat and power. Also, some by-products such as tall oil and terpenes, (known as turpentine), which are generated in the kraft pulping process have valuable applications. Biorefinery concepts in the pulp and paper industry can be categorised into two broad thermochemical platforms and biochemical platforms. Kraft pulping process is a special instance where the process inherently produces three valuable by-products: lignin, tall oil and kraft-turpentine [51].

In the thermochemical platform, gasification and combustion to produce combined heat and power (CHP) are the most widely researched and implemented options [19, 25, 53-56], while in the biochemical platform anaerobic digestion to produce bio-methane, which is then combusted to produce heat and power, is the most popular biorefinery option [53, 56].

There is an inherent weakness in the above-mentioned approaches, especially thermochemical platform technologies such as gasification and combustion. They are incorporated into the system to reduce externally sourced energy, and reduce costs. They do not produce any new products, which can bring in more revenue, but rather generate virtual profits via cost offsetting. Therefore, this fails to realize key objective of implementing biorefineries in pulp and paper industry, which is value addition, and generating new income sources, which could help towards the long-term sustainability of the industry. It should be noted that several researchers have looked at the potential of integrating the Fisher-Tropsch platform in pulp and paper mills [16, 25, 51, 57-60]. On the other hand, Hytonen et al [61] state that syn-gas can also be converted to a range of alcohols via chemical and biochemical catalytic reactions. However the Fisher-Tropsch platform has been there for over a century, therefore it cannot be considered as a novel biorefinery avenue, and it has not been more widely applied due to various reasons such as high capital cost and risk associated with large scale reactors, issues with catalyst

development, and issues with catalyst deactivation during processing [62]. Therefore, it has so far failed to become a mainstream biorefinery platform.

Biochemical platform suffers from a different issue. The biochemical platform is mainly based on fermentation to convert pretreated/non-pretreated lignocellulosic biomass to ethanol and other organic products such as biofuels [63]. However, the efficiencies and economies of converting lignocellulosic biomass via microbial fermentation are relatively low and often hampered by the low yields of conversion compared to fermentation of starch or starch containing grains to ethanol [64]. However, the yields could be improved thanks to the many advances achieved in genomic engineering [65]. While the biochemical platform has so far focussed heavily on how to convert cellulose to a bioproducts, some researchers have looked into ways to utilize hemicellulose. One emerging research in this area is to ferment hemicellulose into polyhydroxyalkanoates (PHA) [66-69]. PHA can be a biorenewable alternative for many petroleum-based polymers [67, 69].

### 1.2.3.2. Novel products in pulp and paper industry – current research

The mostly widely researched biorefinery options in pulp and paper industry are separation of phytochemicals or extractives, lignin extraction, hemicellulose extraction (often referred to as value-prior-to-pulping or VPP), and MFC or nanocellulose production. Production of MFC will be discussed in section 1.2.4, while the existing research on phytochemical extractions and hemicellulose extraction will be discussed here.

#### 1.2.3.2.1. Extraction of phytochemicals

Extraction of phytochemicals from trees, rather woody biomass, is not a novel concept. In fact, there are dedicated industries, which use woody biomass to extract chemicals, e.g. eucalyptus oil production in Spain and Australia. In addition, extracting chemicals from pine trees is a well-developed industry with much on-going research, e.g. Forest Chemicals Review Journal. This industry has been operating as a distinctively separate industry from the pulp and paper industry [70-74]. In fact, a majority of the industry uses only the bark of the pine tree instead of the wood. However, there has been growing interest and research into integrating the extraction of phytochemicals to the pulp mill.

There are numerous research articles on extracting phytochemicals from various parts of trees. One example is the extraction of oregonin (a diarylheptanoid, which has anti-ageing and anti-inflammatory properties) using organic solvents from Alder wood [53]. The extraction of phytochemicals from the bark of various species has also been widely

research [20, 21, 75-78]. Holmbom et al. 2010 [77] draws attention to the current industrial production of resin and fatty acids; kraft pulping process produces 'sulphated soap' which can be further processed into 'crude tall oil' (CTO). CTO can be vacuum distilled to produce tall oil resin, tall oil fatty acid and distilled tall oil. Other research reports present a pathway to integrate production of phytochemicals from wood bark, within an existing pulp mill [79].

Extracting chemicals from the bark and leaves is obviously the preferred choice since the concentration of phytochemicals is higher in the bark than in sapwood and heartwood [75, 76, 79]. In fact, few researchers have looked into extraction of phytochemicals from wood or wood fibres. Demirbas et al [80] describe a method to extract fatty acids from beech wood via supercritical acetone extraction, while Conde et al [81] have studied the extraction of bioactive compounds in *Pinus pinaster* wood through acetone extraction [80, 81]. Suckling et al studied the composition of volatile organic compounds in steam discharge of TMP pulp mills using *Pinus radiata* (Radiata Pine) and stated the concentration of some chemicals such as terpenes, methanol and acetic acid are quite significant [48]. This report did not discuss the recovery of those chemicals from steam or steam condensates. However, this suggests that the steam and steam condensates are possible sources for phytochemicals in TMP pulping mills.

### 1.2.3.2.2. Lignin extraction

Lignin has been a valuable yet, under-utilized by product of chemical pulping [51]. Recently, lignin has been receiving increased attention as a raw material for a plethora of high-valued chemicals [82]. Lignin can be converted into aromatic sub-units by pyrolysis and catalysis [82]. Lignoboost process, which was invented by Valmet, is also making it easier to utilize lignin into value-added products [83]. Membrane filtration has been increasingly used to recover high-value lignin, especially low molecular level lignin [84, 85].

### 1.2.3.2.3. Hemicellulose extraction

Recently, researchers have looked into the possibility of removing hemicelluloses prior to the pulping process and diverting them in to other value added products. This is also called as "value-prior-to-pulping" (VPP) by some authors [86]. The most popular method of hemicellulose extraction uses hot or superheated water [86-90]. Jeaidi et al [86], and Lloyd et al [91] discuss the potential of integrating pre-extraction of hemicellulose into a TMP mill. Other techniques include steam explosion [92], and extraction from TMP whitewater streams [93, 94]).

Extracted hemicelluloses are mainly fermented into ethanol and other biochemicals such as xylitol [86, 95-98]. Other end products of hemicellulose include production of acetylated galactoglucomannan (AcGGM) which can be used as a hydrocolloid [99], and production of polyhydroxyalkanoates (PHAs) via fermentation of pentose sugars as mentioned in section 1.2.3.1.

### 1.2.3.3. Kraft vs TMP mills – Asymmetry in research

There is a major gap in the current research into biorefineries in pulp and paper industry. Majority of the research is being done in kraft mill based biorefineries [17, 25, 51, 53, 87-90, 92, 95, 96, 100, 101], and only a few researchers discuss the potential of biorefineries in TMP mills, even though these mills face the greatest economic difficulties [86]. This is reflective of the relative market sizes of kraft pulp vs TMP pulp. In fact, Jeaidi et al. 2011 [86] is the only research article which comprehensively looks into implementing biorefineries in TMP mills. The other articles listed in that column looks at either hemicellulose extraction prior to pulping [91, 93, 94] or gasification to produce combined heat and power [55].

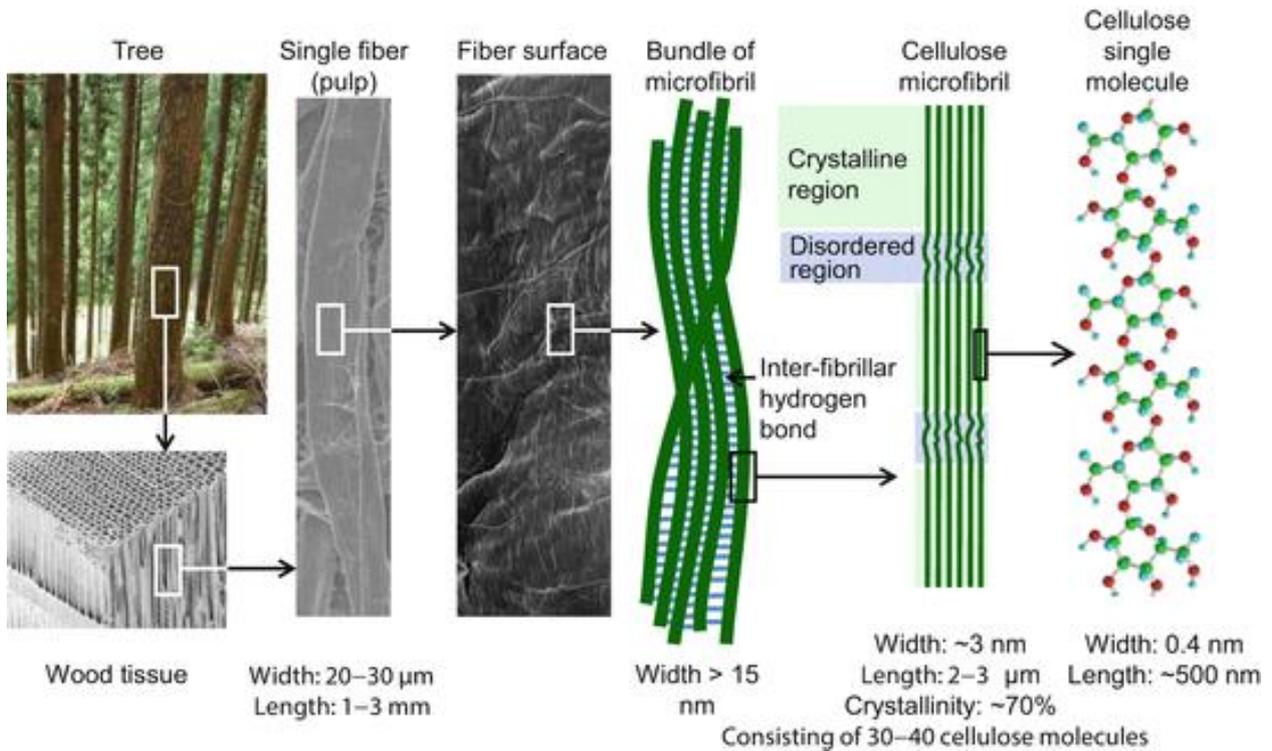
This fact is quite concerning and surprising especially when the TMP mills are the most affected mills with the declining demand of newsprint which is the major market for paper produced from TMP. Therefore, it is evident that, we need to put more effort into research in biorefinery concepts in TMP mills. However, the higher number of research into biorefinery opportunities in Kraft pulping mills is expected as the Kraft pulping mills have a larger market share in the pulp and paper industry [46]. In addition, TMP is a high yield process, which has made it a less suitable candidate for biorefinery implementation, due to the greatly reduced fraction of the biomass available as waste.

### 1.2.4. Microfibrillated cellulose

MFC, often termed as nanocellulose, has attracted a lot of attention as high strength polymer with many novel applications. Its potential has been multiplied by the fact that MFC can be generated from almost any source of cellulose, which is the most abundant, natural or synthetic, polymer on earth. MFC is primarily the end product of separation of fibrils in the secondary cell walls of cellulose containing fibres (See Figure 1.5. [39]), and first introduced by Turbak and Herrick in 1983 [102-104], as a non-calorific food additive and rheological additive to paints and formulations.

MFC is generally classified as a nanomaterial with a very high aspect ratio (length to width, L/D). On average MFC has a width range of 10-100 nm and length range of 0.5 –

50  $\mu\text{m}$  [105]. The different terminology used in the field of MFC and nanocellulose arises from the different size ranges of different materials, as shown in Table 1.1 [105].



**Figure 1.5.** Hierarchical structure of wood cellulose, forming crystalline cellulose microfibrils. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer, [High-Performance and Specialty Fibers](#), Cellulose Nanofibers as New Bio-Based Nanomaterials, Akira Isogai, © Springer (2016) [40]

**Table 1.1.** Relative size of cellulose nano-materials [105]

Particle type/terminology	Length ( $\mu\text{m}$ )	Width (nm)
Wood fibre	> 1000	~ 30000
Microcrystalline cellulose (MCC)	10-50	10-50
Microfibrillated cellulose (MFC)	0.5-50	10-100
Nanofibrillated cellulose (NFC)	0.5-2	4-20
Cellulose nanocrystals (CNC)	0.05-0.5	3-5
Bacterial cellulose (BC)	>1	30-50

A range of raw materials from bacterial cellulose to kraft pulp has been used by researchers to produce MFC or nanocellulose, using a variety of treatments such as homogenization and microgrinding, with or without pretreatment. Most of the research into producing MFC has used chemical pulp, mainly kraft pulp as the feedstock [106-113].

The small diameters and high aspect ratios of MFC leads to increased surface area, which in turn results in, increased strength [114, 115]. Therefore, MFC sheets inherently has higher tensile strength than normal fibres, depending on the quality and source of MFC. For example, commercially available MFC produced via homogenization of cotton fibres can have a tensile index around 85 Nm/g [116]. The higher tensile strength of MFC means that even small amounts of them can be added to unrefined or recycled pulp resulting in significant reinforcement [117-119]. The small diameters of MFC means that they will be closely packed when made into a sheet. This results in decreased air and water vapour permeability [120, 121], to the point where nanocellulose films are being developed as barrier layers to make renewable, recyclable packaging [105, 121]. Also, there is an increased hydrophilicity in MFC because of higher amounts of exposed hydroxyl groups from increased surface area [112, 121]. Sheets made from nanocellulose of diameters less than 10 nm, especially TEMPO oxidised nanocellulose, show significant optical transparency and can be quite strong [39, 122-124]. This opens a whole new range of applications such as transparent structures for electronic applications and novel packaging with nano-composites [111, 120, 121, 124-127].

### 1.2.4.1. MFC from TMP pulp

Many researchers have successfully produced MFC from kraft pulp. Few researchers have explored the possibility of using pulp/fibres from TMP to produce MFC or nanocellulose. The major bottleneck which prevent using TMP is the presence of lignin. Lignin is thought to inhibit fibrillation during homogenization and refining processes [128]. The presence of lignin has led some researchers to use the term “nano-ligno-cellulose” or NLC for MFC like materials produced from TMP [129].

The extractives present in wood might also affect the properties of MFC produced from TMP, if they are not removed from fibres prior to fibrillation. Most of the extractives present are hydrophobic in nature (especially triglycerides and resin acids). Thus, retaining such extractives might help to produce hydrophobic MFC or MFC like material, which will help to overcome the issue of inherent hydrophilicity of MFC produced from pure cellulose or kraft pulp [112, 128].

Nevertheless, several researchers have recently investigated different ways to produce MFC like material from TMP. Some of them have focussed only on mechanical treatment such as homogenization, while other have used various chemical treatment such as TEMPO mediated oxidation and carboxymethylation, followed by mechanical treatment. The following are the summaries of the findings reported in those papers.

### *1.2.4.1.1 Mechanical treatment only*

Spence et al [112, 128] studied the effect of chemical composition of fibres on the physical properties to evaluate the possibility of making more hydrophobic MFC. Their hypothesis was that lignin-containing cellulosic fibres would result in more hydrophobic MFC, making it more dispersive in non-polar media. They compared MFC produced by thermo-mechanical pulp (type of wood is not specified, most probably a softwood) with that of various kraft pulps. Pulp was beaten in a laboratory Valley beater at 2% consistency for 3 hours, and a portion of the beaten pulp was homogenized for 1, 4, 8, 12, 16, and 20 passes at 55 MPa (~550 bar). Sheets (~30 gsm) were made by casting on a petri dish.

Spence et al [112, 128] found that fibril diameter, film density and tensile strength all showing significantly inferior properties to MFC produced by kraft pulp in the same way. Some properties such as water retention value and hard to remove water content were better than that of MFC produced from kraft pulp, suggesting that MFC from TMP is more hydrophobic than MFC from kraft pulp. Water vapour transmission rate was significantly higher than its counterparts from kraft pulp were. The authors and other researchers suggested that even though MFC from TMP is more hydrophobic due to the presence of lignin, the pore size in the sheets made will be higher due to the larger fibril diameter, thus it increases the water vapour transmission rate considerably. Authors also found out that the extractive content in TMP fibres increases the hydrophobicity of the MFC produced.

Osong et al [129] attempted to utilize the less useful reject fines fractions in TMP mills to produce nano-ligno-cellulose (NLC). They used thermomechanical pulp (TMP), bleached kraft pulp (BKP - 75% pine and 25% spruce), and fractionated both pulps using a Bauer-McNett Classifier and a custom-made Britt Dynamic Drainage Jar (BDDJ). Different fibre fractions were then subjected to homogenization at 200-300 bar for 18 passes. There was no mention of BKP being refined in PFI mill or a Valley Beater to generate fines, prior to homogenisation. They claim that the fibres with the lengths in the range of 0.00 – 1.20 mm were the easiest to homogenize, as longer fibres caused clogging in the homogenizer. The authors claimed that they were able to produce TMP-NLC particles

with diameters in the range of 80 – 115 nm. However, the SEM images provided by them are not quite clear and they measured diameters of small fibrils when a significant number of large fibres are also visible. The authors suggested that lignin can act as a gluing agent which can inhibit the fibrillation process.

Lahtinen et al [130] examine how different fibres undergo fibrillation and the impact of lignin on fibrillation. The authors used four different pulps along with thermomechanical pulp (TMP) from spruce (softwood). Fibrillation was brought about by passing fibre suspensions through a friction grinder. TMP fibres were the most resistant to fibrillation and they formed fibre fragments and flake like particles during grinding. On the other hand, CTMP fibres had better fibrillation due to their prior chemical pre-treatment. The authors suggest that the reason for poor fibrillation might be the low processing temperature which might not be high enough to soften the lignin to aid fibre separation and fibrillation.

### *1.2.4.1.2. Chemical and mechanical treatment*

Chemical treatment can be used to increase the fibrillation and generate better quality nanocellulose. 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO) assisted oxidation has been successfully used on various kraft pulp and produced nanocellulose [39, 122, 131-134]. The primary alcohol group in glucose ring can be oxidized into an aldehyde group first and then into a carboxyl group in right conditions [39, 122, 123].

Very little research has been done on the use of TEMPO on TMP fibres. One study from Okita et al investigated the effect of TEMPO assisted oxidation on TMP fibres [123]. They used never-dried softwood TMP and softwood bleached kraft pulp (SBPK) as a reference. Acetone extracted TMP fibres were oxidised in a NaOCl/NaBr/TEMPO solution, before homogenization to fibrillate. The authors [123] reported that carboxyl group formation in TEMPO oxidation of TMP fibres is significantly less efficient than kraft pulp with TMP fibres needing almost 5 times the NaOCl than for kraft pulp. The yield was around 40% corresponding to the cellulose content in TMP fibres. This means there are many side reactions apart from oxidation of primary alcohol of glucose units. Lignin and hemicellulose are oxidized into many water-soluble by-products, and some part of amorphous cellulose is being oxidized which results in increased crystallinity.

Even with the obvious drawback of high oxidant requirements, TEMPO mediated oxidation of TMP fibres resulted in superior quality nanocellulose with diameters in the range of 4.9-6.3 nm and lengths of few microns [123]. This is of similar quality to nanocellulose produced by the similar treatment of kraft pulp and can be considered as

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a viable route to produce nanocellulose from TMP fibres if we could utilize the water-soluble lignin and hemicellulose as usable by-products, thus improving the overall yield.

Sulphonation using  $\text{Na}_2\text{SO}_3$  and carboxymethylation using monochloroacetic acid ( $\text{ClCH}_2\text{CO}_2\text{H}$ ) have been suggested as alternative chemical treatments to TEMPO mediated oxidation [117]. The authors used unbleached TMP reject pulp after hammer milling and fractionation. The treated pulp was then homogenized for four passes. The final product made dense continuous films with smooth surfaces. According to the authors, this is an indication that there are highly individualized fibrils. However, this was contradicted by the SEM images, which showed a heterogeneous fibre distribution with many coarse fibres remaining.

The authors [117] also suggested that, carboxymethylation can increase both the strong acid content and the weak acid content more than 8-fold and is significantly better than sulphonation. This suggests that carboxymethylation will better aid the fibrillation than sulphonation. Weak acids formed were attributed to be in the lignin regions rather than in the cellulose. This is deduced by the substantial yellowing of pulp during carboxymethylation, which suggests that chromophores were formed in lignin during the reaction. Both sulphonation and carboxymethylation resulted in 90-95% yield, which is significantly bigger than the yields from TEMPO mediated oxidation.

Periodate-chlorite oxidation is another technique that may be used, but so far, this has only been used with kraft pulp. There are no reports of it being successfully used to generate MFC from TMP fibres. Periodate-chlorite oxidation adds more carboxyl group groups on the cellulose chain. It also opens the glucose ring and oxidize the secondary OH groups bound to 2<sup>nd</sup> and 3<sup>rd</sup> carbon atoms in the glucose ring into aldehyde groups and subsequently into carboxyl groups [135].

According to the research undertaken so far, it is evident that mechanical treatment alone cannot produce good microfibrillated cellulose from TMP fibres. Chemical treatment will enhance fibrillation, but an effective chemical treatment for TMP fibres is still not available. Carboxymethylation and periodate-chlorite oxidation seem to be the best possible candidate when we consider the yield, yet TEMPO mediated oxidation can result in better quality nanocellulose. Both carboxymethylation and periodate-chlorite need more chemical, reaction steps and time, compared to TEMPO, which is the most popular chemical treatment on kraft pulp.

### 1.2.5. Extractives

Extractives, or known also as phytochemicals, is the term for a class of chemicals, which naturally occur in plants and mainly consist of secondary metabolites comprising volatile organic compounds, pigments, phenols, terpenes, fatty acids, resin acids, sterols and triglycerides. Some of these chemicals are responsible for colour and smell and some of them occur as a part of the natural protective mechanism, e.g. resins in certain trees such as mango, cashew, pine etc. These chemicals have gathered significant attention in the last few years as most of the phytochemicals have or are believed to have positive health effects [45, 136-140]. For example, sitosterol, a naturally occurring sterol in pine and many other species, has been shown to have the ability to reduce cholesterol in blood [141]. Also many phytochemicals are significant anti-oxidants [140]. Many phytochemicals are hydrophobic but occur as easily hydrolysable glycosides and can be extracted by using organic solvents. Because of this, phytochemicals are referred to as 'extractives' in pulp and paper industry [75, 142, 143].

#### 1.2.5.1. Extractives in newsprint industry

Phytochemicals are produced as secondary metabolites and they exist in plant cells and resin canals of plant structure [144]. During the TMP refining process, plant cells and resin canals are ruptured. Volatile compounds such as terpenes, aldehydes and alcohols are carried away with the steam from the primary refiner. Also, small quantities of resin acids and fatty acids can be steam distilled during the process and can remain in steam condensate in the heat recovery systems [48]. Most of the other compounds including fatty acids, fatty acid esters, resin acids, sterols and triglycerides are released in to the TMP whitewater streams. These extractives can cause serious issues in newsprint making as they could deposit onto paper and paper machines as 'pitch' which can be detrimental to paper quality [145, 146].

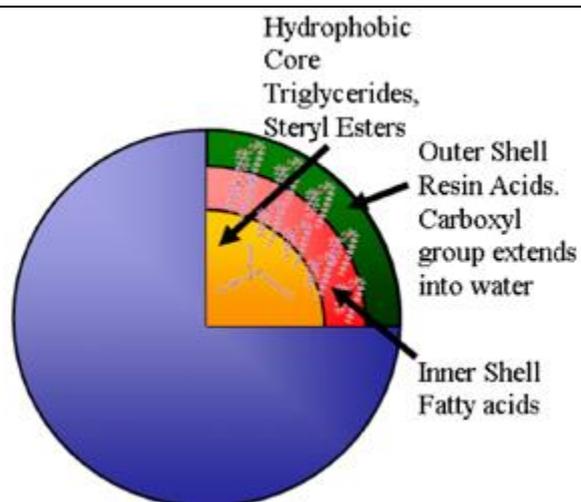
Extractives exist in equilibrium between three different forms in TMP whitewater systems, depending on various factors such as pH, temperature, and fines content [147-152].

#### **a) Soluble**

More hydrophilic compounds such as aldehydes, alcohols can be fully dissolved in water.

#### **b) Colloidal**

Three main classes of extractives: fatty acids, resin acids and triglycerides, can exist as colloidal structures as shown in Figure 1.6.



**Figure 1.6.** Schematic diagram of the colloid structure for wood extractives derived from softwood. Reprinted by permission by Appita, *Appita Journal, Process factors affecting colloid stability and deposit formation in manufacture of newsprint from TMP and recycled fibre*, Desmond Richardson © Appita (2012) [153]

The most hydrophobic group, triglycerides form the central core of the colloid with fatty acids which are less hydrophobic than triglycerides forming the middle layer. The more hydrophilic group of resin acids form the outer layer with their carboxyl groups in contact with water. The size of the colloid depends on composition, pH and temperature [149, 151, 154, 155].

### **Effect of pH**

Resin acids exist in the outer layer of the colloid and can be solubilized at pH values above their colloidal pK<sub>a</sub> values [156, 157]. Depending on the pH, almost 100% of the resin acids could be solubilised [149, 156, 157]. The following table shows the colloidal pK<sub>a</sub> values of some resin acids at 20 °C and 50 °C [156].

**Table 1.2.** Colloidal pK<sub>a</sub> values of some resin acids [156]

Resin acid	Colloidal pK <sub>a</sub> at 20 °C	Colloidal pK <sub>a</sub> at 50 °C
Abietic	7.26	6.18
Dehydroabietic	6.77	6.18
Isopimaric	7.08	6.23
Neoabietic	7.07	6.23

It can be expected that most of the resin acids would become soluble at pH above 8.0. But, this should be investigated individually in each process water stream as solubility

and pKa values can be affected by the presence of electrolytes and other materials. Increasing temperature decreases pKa values of resin acids and increases solubility [156]. Therefore, operating at higher temperature would prove favourable to solubilize resin acids. However, the energy consumption to raise the temperature should be taken into account.

Along with resin acids, fatty acids can also become liberated from the colloids with the increase of pH. The following table shows the colloidal pKa values of the main fatty acids found in process water streams.

**Table 1.3.** Colloidal pKa values of some fatty acids [156]

Fatty acid	Colloidal pKa at 20 °C	Colloidal pKa at 50 °C
Palmitic acid (16:0)	8.34	8.63
Stearic acid (18:0)	9.89	9.28
Oleic acid (18:1)	8.22	8.29
Linoleic acid (18:2)	6.83	6.26

The pKa values of fatty acids are much higher than those of resin acids. However, some fatty acids are expected to be solubilized with higher pH. Therefore, optimum pH ranges should be investigated to reduce the fatty acid concentration in soluble phase.

According to Strand et al, resin acids are completely in the colloidal phase at the pH values below 5.0 [157]. This could be used to move resin acids back into colloidal phase possibly after removing colloids containing triglycerides and some of the fatty acids at higher pH levels.

### **Effect of electrolytes**

When salts are introduced to whitewater, salt cations will start interacting with water more and more. This reduces the interactions of water molecules with the outer layer of the extractive colloid. This causes extractives colloids to aggregate and deposit as pitch [158]. This causes the residual turbidity to go down as more and more colloids are removed from suspension via deposition. Strand et al 2011 suggested that CaCl<sub>2</sub> caused colloids to be destabilised at lower concentrations than NaCl, while LiCl<sub>3</sub> caused the same at even lower concentrations. This can be explained by the increased interactions of water molecules (hydration) with Ca<sup>2+</sup> and Li<sup>3+</sup> than Na<sup>+</sup> [154, 159].

### c) Fibre-bound

Both colloids and free hydrophobic compounds, especially triglycerides and resin acids (at pH below  $pK_a$ ) and will bind to fibres and fines. These extractives are considered stable and contribute to the hydrophobic nature of the TMP fibres [160].

#### 1.2.5.2. Strategies to handle extractives and their implications in newsprint mills

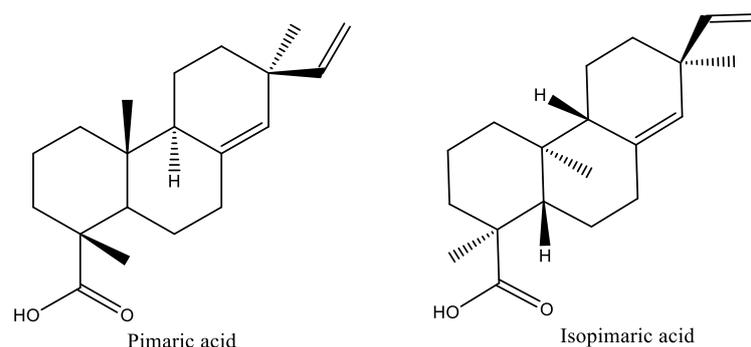
Extractives present in paper machine (PM) whitewater systems can deposit on paper and paper machines due to their hydrophobic nature. This results in either holes or deposits in the paper. This effect is well documented in paper industry and termed as 'pitch' [147, 151, 152, 154]. The common approach to overcome this issue is to stabilise the colloids [149, 151, 154, 155, 158]. Stable colloids tend to remain suspended in water rather than depositing on paper and paper machines and thus reducing the extent of pitch deposition. The presence of extractives in whitewater streams can limit the extent of system closure and therefore increase the consumption of fresh water.

The other methods used are adsorption of extractives on clay and filler materials such as bentonite [147, 161] and wet oxidation to degrade extractives [162-165]. In addition, extractives can be removed by either dissolved air flotation or froth flotation and they are becoming increasingly popular and could achieve increased system closure [145, 154, 163, 166-171]. However, none of these techniques has been used in a biorefinery approach that could overcome pitch deposition and at the same time produce value added chemicals to generate added income to overcome the costs of added operation or generate profits.

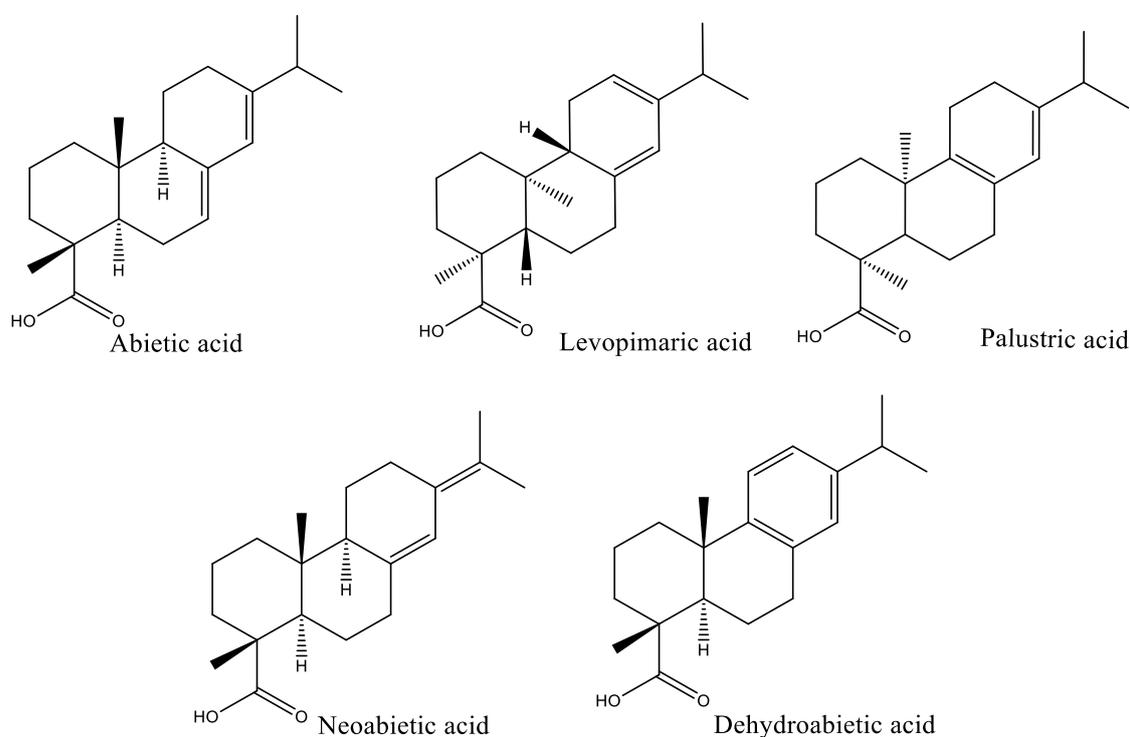
#### 1.2.5.3. Resin acids

Resin acids are naturally occurring non-volatile components of oleoresin and canal resin of pine and spruce species. They are diterpene acids with an empirical formula  $C_{19}H_{29}COOH$ . They are yellowish in colour, and sticky. There are seven major naturally occurring resin acids in plants. They can be classified into pimaric and abietic classes [33]. See Figures 1.7 and 1.8. Abietic, neoabietic, levopimaric and palustric acid exist in equilibrium with each other in the presence of mineral acid or at temperatures beyond  $100\text{ }^{\circ}\text{C}$ . Continuous acid treatment or prolonged heating will shift the equilibrium towards abietic acid. For this reason, kraft resin soaps contain mainly sodium salts of abietic acid, not other resin acids of abietic type [33]. Resin acid mixtures are oxidized through contact with air due to the presence of the conjugated double bond system. This causes a sharp decline of levopimaric acid in wood chips even after a few hours of exposure to air [33]. Some of the acids can get dehydrated into dehydroabietic acid under certain conditions.

This is thought to be the reason for the presence of high dehydroabietic acid content in tall oil [33].



**Figure 1.7.** Pimaric type acids



**Figure 1.8.** Abietic type acids

The current production of resin acids come from the production of tall oil in kraft and Sulphate pulping mills and oleoresin tapping in the pine chemicals industry. They are used in bleaching, cleaning and as an ingredient in varnishes and the rubber industry. Historically rosins (resin acid mixtures) have been used in caulking ships, thus the pine chemical industry was known as the naval stores industry [73, 172, 173].

Most of the resin acids are antioxidants and toxic to aquatic life forms, especially dehydroabietic acid [174, 175]. Therefore, they need to be treated and degraded before being released to natural waterways.

Although it is rare to find refined and separated individual resin acids, the possible applications as an extract or a mixture would be as antioxidants, fungicides, pesticides, and natural adhesives [176, 177].

The novel and proposed applications of refined resin acids include as anti-cancer agents, components of novel rosin based biodegradable toner and ink [178], as neurological regulators [179], drugs for disorders of the nervous system, anti-inflammatory agents, antibacterial agents, antifungal agents, and in treatment of urinary bladder overactivity, stroke treatment and in problems with the hyperactivity of (vascular) smooth muscle cells [178, 180].

The current market price for purified resin acids varies significantly with the purity and quantity required. The approximate market prices for high purity refined resin acids are tabulated below in Table 1.4.

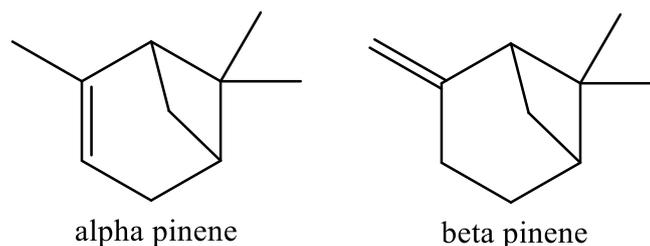
**Table 1.4.** *Economic values of resin acids*

<b>Compound</b>	<b>Price range in USD per g</b>	<b>Source</b>
<b>Pimaric acid</b>	145-1000	[181]
<b>Isopimaric acid</b>	20,000	[181, 182]
<b>Abietic acid</b>	1.2 - 50	[181, 182]
<b>Levopimaric acid</b>	Small number of vendors available, but no direct price available	NA
<b>Palustric acid</b>	Small number of vendors available, but no direct price available	NA
<b>Neoabietic acid</b>	5000	[182]
<b>Dehydroabietic acid</b>	33.6 – 100	[181, 183]

#### 1.2.5.4. Terpenes

Terpenes are naturally synthesized chemicals in plants, built up from isoprene subunits. Terpenes cause plants to smell pleasantly, to taste spicy or show unique pharmacological activities. The biological and ecological importance of terpenes is not fully understood yet, but volatile terpenes are thought to be used by plants to attract certain insects for pollination purposes or repel certain insects and animals who feed on the plant. Also, terpenes play a part as signal compounds and growth regulators (phytohormones) of

plants [184]. The main volatile terpenes found in *Pinus radiata* are  $\alpha$ -pinene and  $\beta$ -pinene. Their structures are shown below in Figure 1.9.



**Figure 1.9.**  $\alpha$ -pinene and  $\beta$ -pinene

Pinenes are highly volatile clear colourless liquids with a turpentine odour and are less dense than water and insoluble in water. Vapours are denser than air. They are industrially used as solvents, lubricants, intermediates for the synthesis of monoterpeneoid fragrances such as camphor, air care products, cleaning and furnishing care products, laundry and dishwashing products, personal care products, as well as plastic and rubber products [184-186].

Current industrial production is from the distillation of turpentine oil (58-65%  $\alpha$ -pinene and 30%  $\beta$ -pinene) from the pine chemical industry [185, 186]. More recently pinenes from turpentine oil have been used to make biopolymers using both biological and catalytic pathways [187-190]. The current world market price range of  $\alpha$ -pinene is USD 2000 – 10000 per MT, depending on the purity required and is around USD 3000-11000 per MT for  $\beta$ -pinene [191].

It is also worth mentioning that both alpha and beta pinenes are flammable, toxic and are skin, eye and respiratory irritants [185, 186].

#### 1.2.5.4.1 Sources of Terpenes

The most common and maybe the only source of terpenes is the turpentine produced in various forest product industries. Turpentine can be classified as follows.

1. **Gum turpentine**, which is steam distilled from the resinous exudate of wounded pine trees
2. **Crude sulphate turpentine (CST)**, which is condensed from the vapours produced during the alkaline digestion of pine wood chips for paper-making
3. **Wood turpentine**, which is obtained by the solvent extraction and steam distillation of waste wood (usually branches and stumps)
4. **TMP turpentine**, which can be recovered from various steam and effluent streams prior to pulping in a thermomechanical pulping (TMP) mill

TMP turpentine is the relatively new entrant to the turpentine market. During presteaming, preheating and mechanical refining of wood chips in a TMP mill, terpenes are released into steam and aqueous streams [48, 192-199]. However, according to Sueiro & Gill 1995, the low concentration of turpentine in the pressate water from the plug screw feeders made removal by decantation unfeasible [192]. Therefore, some downstream processing is needed before separating turpentine through decantation.

### *1.2.5.4.2. Terpene Recovery from TMP Mills*

In kraft pulp mills, terpenes are recovered as 'turpentine' after passing the turpentine condensate through a decanter in which the terpenes are recovered from the top layer. Turpentine is a valuable by-product of kraft/Sulfate pulping mills. However, there has not been many instances where turpentine has been recovered from TMP mills. Only a handful of researchers have investigated the levels of terpenes in process water streams of TMP mills, much less the means to recover terpenes from them.

McDonald et al 1998 analyse the terpene composition in aqueous effluents in a MDF plant (high temperature thermomechanical pulping mill) using radiata pine as wood [193]. The pressate from plug screw feeder after the presteamer (80 °C) and the pressate from plug screw feeder after the preheater (at two different temperatures 155 °C and 167 °C) were collected. The incoming effluents were filtered using a Terylene cloth to remove any chips or fibre bundles. The samples were steam distilled and extracted using a Likens-Nickerson Micro Steam Distillation Unit with dichloromethane as the solvent. The authors found out that  $\alpha$ -pinene,  $\beta$ -pinene and  $\alpha$ -terpineol are the main components in the effluent from the presteamer, with more  $\beta$ -pinene present than  $\alpha$ -pinene. The pressate from plug screw feeder after the presteamer was the best source for terpenes with a total turpentine concentration of ~ 0.8 g/L.

In 2005, Suckling et al studied the volatile organic compounds (VOC) emissions from a TMP pilot plant using radiata pine as raw material [48]. They found that the plug screw pressate contained comparatively higher concentrations of terpenes while the steam condensate from the primary refiner did not contain significant levels of terpenes. Their results again confirm that the best source for terpene recovery in TMP mill are the pressate effluents before primary refining, and the most abundant terpene in radiata pine is  $\beta$ -pinene. Weston et al 2006 has conducted a similar study to Suckling et al 2005 using the same pilot plant setup, and report similar findings [194].

### 1.2.5.4.2.1. Existing Technology to Recover Terpenes from TMP Mills

Ryham et al 1990 and Rauscher et al 2003 both describes a system which separates turpentine from a vent vapour stream from the preheater prior to pulping [196, 198]. This vapour is separated into a turpentine rich vapour and turpentine lean condensate using an evaporator condenser-reboiler. Turpentine rich vapour is condensed using a cooling liquid to produce two phases, turpentine and water. The turpentine phase is then separated using a decanter.

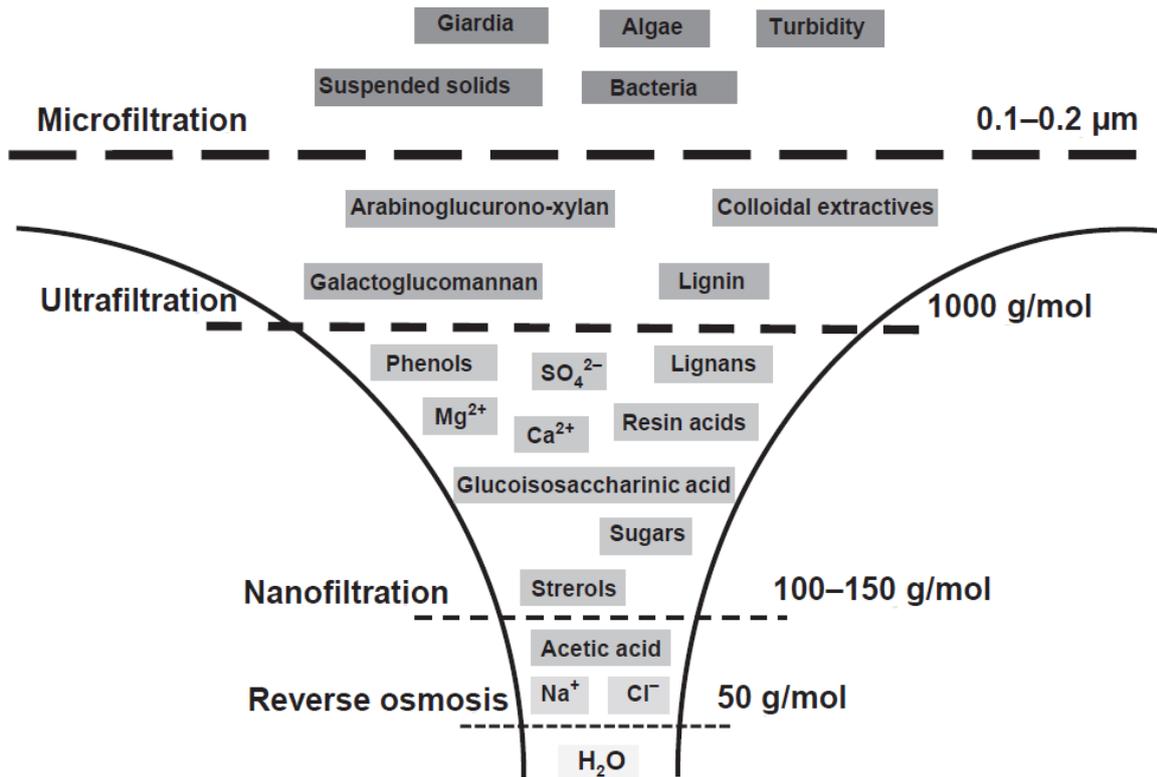
Reynolds et al used the liquid effluent from plug screw feeder to recover turpentine [199]. They used a flash drum to flash the effluent after removing fibers. The resulting steam is condensed into a decanter where turpentine is removed as a separate phase. They also claim that this could be used to recover turpentine and other oleoresin compounds in various condensate streams in a TMP mill.

Lindmark-Henriksson et al 2003 used TMP turpentine produced in the Ortviken Mill, Sweden, for the work in her thesis [197]. She mentions that this turpentine is collected via decantation after condensation of the primary refiner steam. The mill might have been using one of the commercial systems combined heat and turpentine recovery system for TMP plants supplied by Andritz[196].

### 1.2.5.5. Phytochemical Recovery Using Membrane Filtration

Membrane filtration is an effective technique used to remove contaminants from process water streams. The first reported application of membrane technology in pulp and paper industry is an installation of reverse osmosis plant to treat the white water system of a board machine in 1974 [200]. Currently, various membrane technologies such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and membrane bioreactors (MBR) have been implemented in mill scale and many researchers are investigating the ways to improve the efficiency of such technologies in pulp and paper mill applications. One of the advantages of using membrane filtration is that they do not take up large footprint in the mill because of their compact designs [200-202].

The Figure 1.10 from Manttari et al 2015 gives a basic outline of the size ranges of different filtration technologies and the substances in pulp and paper process waters streams which can be recovered using each filtration technique [201].



**Figure 1.10.** Separation scheme for pressure-driven membrane processes. Reprinted by permission from Elsevier: Elsevier Books, [Advances in Membrane Technologies for Water Treatment](#), Membrane technologies for water treatment and reuse in the pulp and paper industries, M. Mänttari © Elsevier (2015) [201]

#### 1.2.5.5.1. Microfiltration

Microfiltration membranes have pore size in the range of 0.1 – 10 microns according to Adnan et al 2010 [203]. However, some other researchers use a wider range of 0.05 – 10 microns [204]. The basic principle of microfiltration is retention by size. The typical materials used in microfiltration are polyvinylidene fluoride (PVDF), polypropylene, polyethylene, polysulfone, polyether sulfone, Teflon, and ceramic materials [204].

In the pulp and paper industry, MF can be used in areas such as deinking effluent, white water treatment, paper machine filtrate, paper mill effluent, kraft spent liquor, coating effluent and bleaching effluent [203]. However, microfiltration is not fully suitable for pulp and paper applications. Fouling by pore plugging is quite frequent in MF membranes, because the pulp and paper mill effluents usually contain particles of similar sizes as the pores in the membranes. Because of this reason, in many cases, fluxes in ultrafiltration are significantly better than fluxes obtained with microfiltration [204]. However,

microfiltration is a good pretreatment for other membrane operations such as reverse osmosis.

Cortinas et al used microfiltration to remove pitch and colloidal suspended matters from a black liquor [205]. Also, Teflon MF membranes have been used to remove terpene oils from an evaporator condensate and achieved around 90% removal [206]. Persson et al used microfiltration to remove colloidal extractives from a thermomechanical pulp mill process water stream [207]. They used 0.2-micron ceramic membrane and the process water stream was at pH 4.3. The possibility of using MF for removal of extractives solely depend on the size distribution of colloids, which is dependent on many factors mainly pH, extractive content and extractive composition. The authors, however, does not mention any significant irreversible fouling problems and any fouling occurred was easily recoverable after back flushing. Although, there is no clear mention of the cleaning frequency or long term irreversible fouling.

### *1.2.5.5.2. Ultrafiltration*

Ultrafiltration membranes have pore sizes in between 0.005 micron to 0.1 micron, and this corresponds to 10-1000 kDa molecular weight cut off (MWCO) [203]. Ultrafiltration is the most widely used membrane in the pulp and paper industry with applications including removal of suspended solids, colour, extractives, turbidity, chemical oxygen demand (COD) and adsorbable organic halogens (AOX), and recovery of raw materials such as coating pigments [204].

Borregard Industries of Norway uses ultrafiltration to concentrate and purify lignosulfonates from a sulphite pulp mill. Purified lignosulfonates are further processed into vanillin and the mill remains the world's largest supplier of artificial vanillin [204]. They have used a tubular filter with polysulfone membrane of 20 kg/mol MWCO. Another sulphite mill belonging to Domsjö Fabriker AB, Sweden use ultrafiltration to treat the process water from a brown pulp wash. The concentrate stream has lignin residues and resins, and it is sent to resin recovery. The permeate is re-used in the cooking process and also as sealing water [204].

Another important application of UF is separation of lignin from black liquor. Both polymeric and ceramic membranes have been used for this purpose [204]. Wallberg et al used tubular ceramic membranes with 15 kg/mol MWCO to concentrate lignin from kraft black liquor [84, 208]. The recovered lignin residues can polymerised into higher molar masses for new products. Low value application of this recovered lignin would be burning the concentrate in boiler for energy production [204].

One of the most valuable applications of ultrafiltration in paper industry is the recovery of coating pigments. Zero effluents from the coating plants, recycling of the concentrated coating colour and reuse of permeate are the main advantages when effluent from coating machines is treated by ultrafiltration. According to Manttari et al 2008, several paper mills are already using this technique and the typical payback is 1-2 years because of the high value of coating pigments [204].

The other applications of ultrafiltration in pulp and paper industry are treatment of thermomechanical (TMP) and chemi-thermomechanical (CTMP) pulp mill effluent [209-211], as internal kidneys in paper mills [212-216], recovery of organic acids from black liquor [217] recovery of hemicelluloses from TMP process water [93, 207], and polishing of evaporator condensate in kraft pulp mills [218].

Ultrafiltration is also widely used to purify process water at the origin, rather than treating a combined stream of all the process water streams [201]. By keeping specific water streams unmixed, the membrane processes could be focused on the most relevant streams and then only smaller volumes would need to be treated (as in the treatment of coating wastewaters). Therefore, membranes are studied widely as internal kidneys to purify process water for reuse. However, one recycle paper mill (Linpac, South Carolina, USA) uses ultrafiltration to treat the subnatant (authors mention it as overflow) of a dissolved air flotation (DAF) unit which treats mill wide process water [201].

### *1.2.5.5.3. Nanofiltration*

Nanofiltration is increasingly becoming popular in pulp and paper industry especially with the advent of new high shear filter modules such as cross rotational (CR) filters and very high shear enhanced processing (VSEP) filters. The pore size for NF is from 0.001 - 0.01 microns and it can be used to remove polyvalent cations, organic matter and to demineralise ground water [203]. Nanofiltration membranes are also classified according to their NaCl rejection percentages. Nanofiltration can be used to treat black liquor, paper coating effluent, paper mill effluent, whitewater, and paperboard mill effluent in pulp and paper mills [203]. Nanofiltration needs pretreatment to remove coarse materials and foulants, otherwise severe fouling and flux drop can occur.

Nanofiltration has been studied to treat process water from pulp and paper mills [212, 213, 215, 216, 219], recover organic acids from kraft black liquor [217], and separate of lignin from a TMP process water stream [207].

### *1.2.5.5.5. Reverse Osmosis*

Reverse osmosis is a common filtration technique used to produce drinking water and pure water for industrial applications. RO membranes can separate particles less than 0.001 micron ( $10^{-9}$  m) in size or 0.05 - 10 kD for molecular weight cut off (MWCO). A wide range of membrane materials can be used for RO, and cellulose acetate, polyamide and aryl-alkyl polyether urea are the most common membrane materials [203]. Similar to NF, RO also needs the water stream to be pretreated before operation.

According to Manttari et al 2010, several mills use RO to treat their raw water supply, and treat the mill effluent after passing through a membrane bioreactor and other biological treatments [202]. According to another review done by the same author, a mill in Canada successfully implemented an RO plant to detoxify the evaporator condensate from a kraft pulp mill, and they were able to achieve almost 99% recovery of water. Pizzichini et al used RO to treat mill effluent after biological treatment and MF filtration, and they were able to reuse 80% of the water in the mill [220]. RO can be used to treat contaminated wastewater from other sources such as urban areas to produce raw water in water stressed area. Ordóñez et al used RO to purify municipal wastewater after MF and UF as pretreatment [221].

### *1.2.5.5.6. Membrane filtration for separation of terpenes from process water streams*

Microfiltration and ultrafiltration could possibly be applied to separate oily substances like terpenes from steam condensate. Minami and other used microfiltration to remove oily substances from a kraft mill evaporator condensate and reported about 90% removal [206]. They used 0.2-micron Teflon membrane as oily substances were found to degrade the usual polysulfone membranes and deform polyethylene supports. Teflon could be used because of its resistance to harsh chemicals. In a similar study, Sun et al used RO to isolate manool from a kraft pulp evaporator condensate [222]. This shows that it is possible to use membrane filtration to recover terpenes and other extractives from steam condensate.

Plug screw pressate and steam condensate could be processed via membrane filtration to separate terpenes at a higher concentration. This would reduce the volume of water to be processed in already available equipment, such as an Andritz Reboiler - Condenser, which could save the energy consumption.

## **1.2.6. Gaps in Knowledge**

The literature review reveals major gaps in existing knowledge. The most important and highest-level gap in knowledge is the lack of research into implementing biorefinery

concepts in TMP mills and newsprint mills. The contrast is significant when we compare the work undertaken regarding chemical pulping mills and research work must be initiated to close this gap and generate new knowledge. The following gaps in knowledge was identified during the literature review.

### 1.2.6.1. MFC Production from TMP Fibres/TMP Whitewater Fines

- There is a significant lack of research in producing MFC or MFC like material from TMP fibres/fines compared to the research being undertaken with chemical pulp. The gap is visible in both mechanical fibrillation techniques and chemical treatment and it is critical to find optimum methods to produce MFC or MFC-like material from TMP pulp.
- There has been no recent research into upgrading the quality of TMP whitewater fines after the research done in the early 2000s.

### 1.2.6.2. Phytochemicals in process water streams

- There is ample research into extracting phytochemicals from wood, bark and even fibres, however there is a lack of research into recovering valuable extractives in TMP process water streams. In addition, there is a need for new biorefinery approaches to simultaneously produce value added chemicals and solve pitch deposition, which is a major issue in newsprint mills.
- Membrane filtration has been widely used to remove extractives from TMP process water systems. However, there has not been any research on how to utilize membrane filtration to recover valuable compounds such as resin acids from process water.
- The literature review reveals a serious lack of research into capturing volatiles in TMP steam recovery systems, other than through heat recovery. New research could provide ways to economically capture volatile terpenes, which could be converted into whole range of new products such as fragrances, and biopolymers, apart from direct applications.

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## **Chapter 2**

### **Identifying Opportunities for Value-Addition in a Thermomechanical Pulping Mill**

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# Chapter 2 – Identifying Opportunities for Value-Addition in a Thermomechanical Pulping Mill

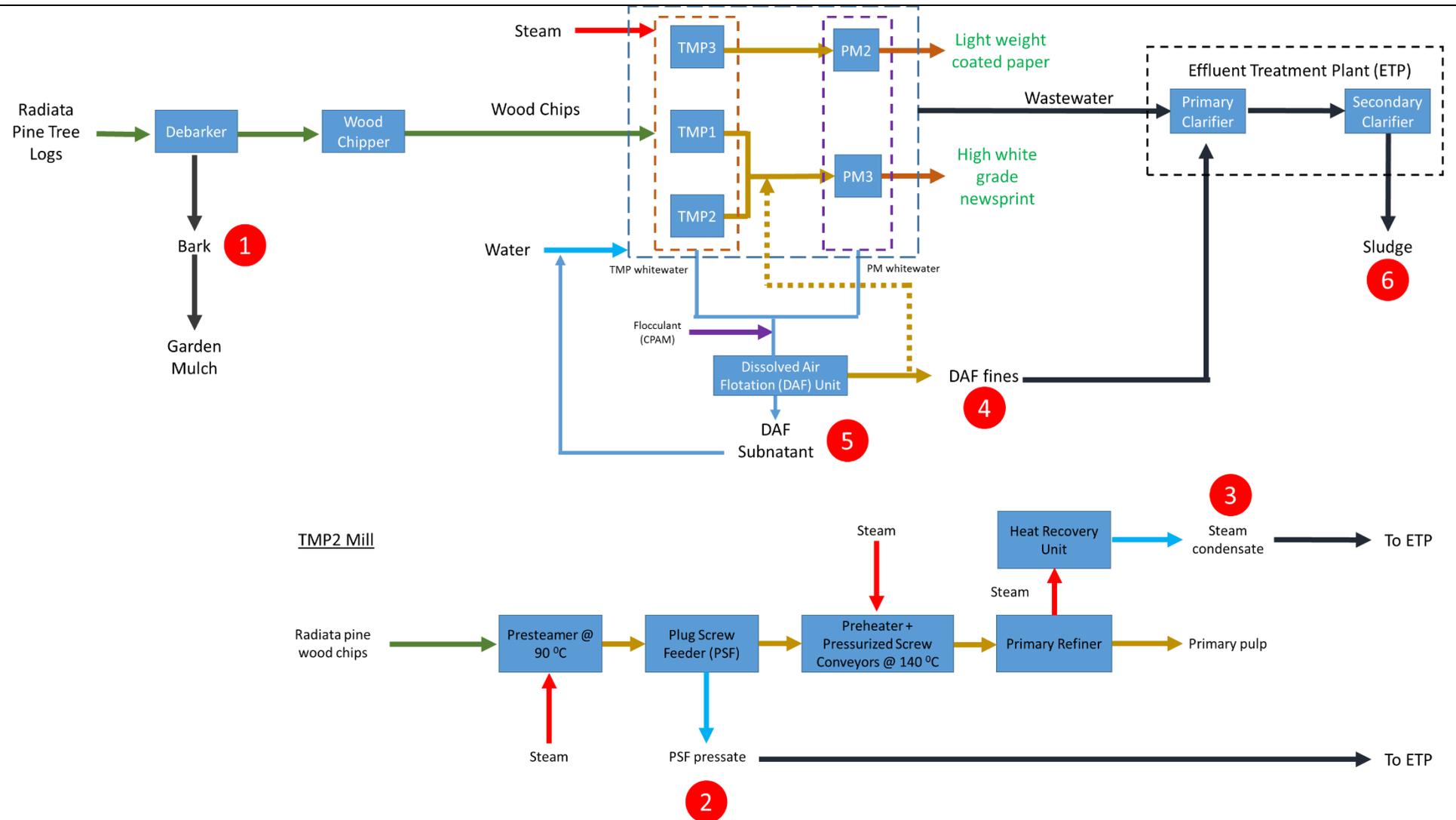
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# Chapter 2 – Identifying Opportunities for Value-Addition in a Thermomechanical Pulping Mill

## 2.1. Norske Skog – Boyer Facility

Norske Skog – Australasia consists of three pulp and paper mill facilities, two in Australia and one in New Zealand. Their primary products are newsprint and lightweight-coated paper. As of 2016, Norske Skog – Australasia owns 17.3% of the Australian pulp, paper and paperboard market [1]. Norske Skog – Boyer mill uses Tasmanian grown Radiata pine (*Pinus radiata sp.*) wood and consists of 3 thermomechanical pulping (TMP) mills and 2 paper machines. Their annual production is 250,000 MT of softwood TMP pulp that is then converted into 145,000 MT of newsprint and 135,000 MT of lightweight-coated paper for magazines. Figure 2.1 shows a simplified process diagram of the facility. They are the sole manufacturer of newsprint and light-weight coated paper in Australasia. Therefore, they are uniquely exposed to the declining market for newsprint.

## Chapter 2



**Figure 2.1.** Simplified Process Flow Diagram of Norske Skog – Boyer Facility: Processes Leading up to TMP2 Mill is shown in the Inset

## 2.2. Biorefinery Opportunities at Norske Skog – Boyer

Radiata pine wood chips is the raw material and high-white grade newsprint and light-weight coated paper are the primary products of the Norske Skog – Boyer Facility. We could come up with numerous biorefinery ideas from wood chips and TMP pulp. Some biorefinery ideas based on wood chips are gasification/pyrolysis to produce energy and value added chemicals, extraction of phytochemicals, and extraction of hemicellulose. TMP pulp could be used extract hemicellulose and phytochemicals, and produce microfibrillated cellulose. However, implementation of any biorefinery idea is constrained by number of parameters such as economies, direction and strategy of the pulp mill and impact on the current production.

In this project, it was decided that any of the proposed biorefinery ideas should not affect the current production levels. This implied that we could not use either the raw material, pine chips or the primary product, unbleached/bleached TMP pulp for a future biorefinery. This restricted and motivated us to analyse the waste streams at Norske Skog – Boyer Facility.

### 2.2.1. Waste Streams at Norske Skog – Boyer Mill

The following waste streams were identified during the initial analysis of the mill. The number in the parentheses refers to the corresponding number circled in Figure 2.1.

#### 2.2.1.1. Bark (1)

Pine wood logs are debarked in a Roller Debarker in which logs are rolled against the inner metal surface of the debarker and against each other to remove the bark from the heartwood. At the moment, the bark is being handled by a different company and is being sold as high quality garden mulch. Furthermore, extracting value from the bark requires processing the bark in unit operations such as gasification will be capital intensive. Therefore, bark was excluded from the consideration for biorefinery development.

#### 2.2.1.2. Plug screw pressate & Primary Refiner Steam Condensate (2 & 3)

TMP pulping typically involves pre-steaming and pre-heating of wood chips prior to primary refining. This is usually done at 80 – 90 °C. Pre-steamed/pre-heated chips are then transported to the primary refiner by the means of a plug screw press. Plug screw press usually generates an aqueous pressate. As discussed in the literature review, plug screw pressate contains volatile organic compounds such as terpenes. See section 1.2.5.4. At Norske Skog – Boyer, this plug screw pressate is only present in #2 TMP mill that is referred to as TMP2 or TMP2 mill hereafter. The plug screw pressate is ejected at

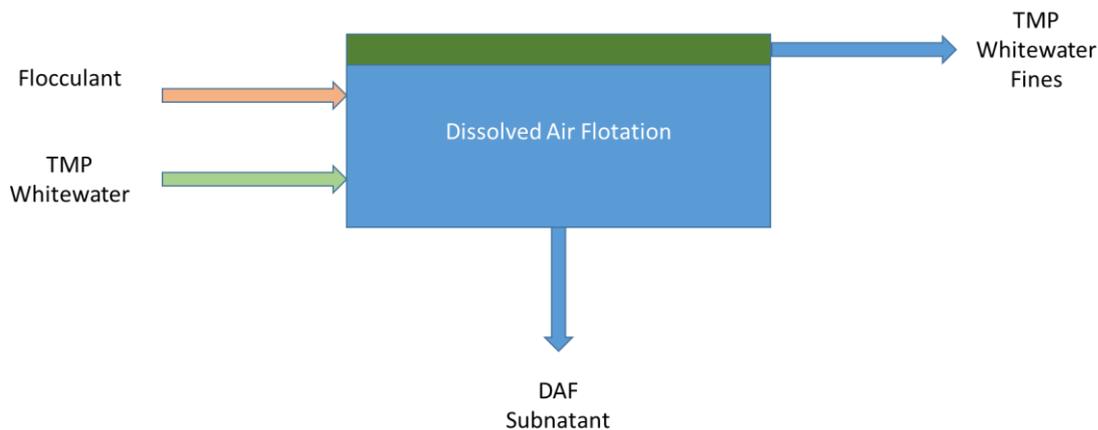
80 °C at 6 L/s flow rate. This plug screw pressate was selected as an ideal candidate for recovering volatile organics.

Pre-steamed/pre-heated wood chips are then fibrillated in the primary refiner. This is usually done at 130 – 150 °C temperatures and higher pressures. Pressurized steam is used to increase the temperature. Steam is then released from the top of the refiner and it carries volatile compounds. See section 1.2.5.4. This steam is sometimes condensed using a heat exchanger to recover energy. At Norske Skog – Boyer, only TMP2 mill has a heat recovery system to capture the primary refiner steam condensate. This primary refiner was also selected as another candidate for recovering volatile organics.

At the start of this project, the composition of these streams were unknown. However, the literature suggest that there could be a significant amount of terpenes in these streams

### 2.2.1.3. Floats and Subnatant from Dissolved Air Flotation Unit (4 & 5)

TMP whitewater in this mill is clarified using a dissolved air flotation (DAF) unit. The fines in whitewater are floated to the top and removed by the means of a scraper. These floats or fines are referred to as TMP whitewater fines hereafter.



**Figure 2.2.** Dissolved Air Flotation Unit of Norske Skog – Boyer Facility

The collected whitewater fines are considered as waste in the process. Although, a fraction is returned back to the papermaking occasionally, it is not preferred as these fines cause poor quality in newsprint. The majority is transferred into the outgoing effluent and processed in the effluent treatment facility, thus limiting the usefulness of the operation for fibre recovery. The current effluent flow to the effluent treatment primary clarifier is around 20 ML per day and around 35 – 40 tonnes of solids is removed from the effluent each day, of which approximately one quarter is whitewater fines that is not recovered by

the DAF treatment of TMP process water. There is therefore potential for an additional 10 tonnes per day of fibre to be recovered if a suitable use could be found for it.

### ***Whitewater Fines***

Fine fibrous materials, generally known in the industry, as 'fines', which are small enough to go through the meshes during thickening, end up in the whitewater system, and get recycled in the process. These fines are referred to as whitewater fines and often considered as waste and to have detrimental effects on paper quality [2]. Rundlof et al 2000 hypothesize three reasons for the poor tensile properties of TMP whitewater fines [2].

1. Ageing of fines due to prolonged circulation in the whitewater due to biological degradation and leaching of hemicellulose to water, etc
2. Contamination of surface due to adsorption of hydrophobic extractives. The same authors suggest that the major reason for the low tensile index is the presence of acetone-extractable substances [3].
3. A high percentage of specific types of TMP fines which have poor bonding abilities such as ray cells, ray-parenchyma cell fragments and fines from knots. These fines contain higher than normal lignin percentages which leads to poor bonding.

These whitewater fines are collected through dissolved air flotation at the Boyer Mill [4]. However, only a fraction of the recovered fines is typically directed back into the papermaking process due to their detrimental effects on paper quality. Options for valorisation of these fines include combustion, pyrolysis, gasification, land application, composting and reuse as an alternative building material. However, the high moisture content of more than 90% inhibits the use in thermochemical processes such as combustion, pyrolysis and gasification.

Wood et al. (2000) used hydrogen peroxide bleaching and refining to add value to these fines with an aim to add them back to the paper making process [2, 5]. In their study, they treated fines collected from a TMP mill reject whitewater pressate with alkaline peroxide. The treated fines were then mechanically treated by either refining, grinding or ball milling. The treated whitewater fines were then added to a TMP and Kraft pulp at 9:1 ratio (10% addition). The authors found that while the addition of whitewater fines, which were subjected to mechanical treatment alone, had negative impact on the tensile strength, the addition of whitewater fines, which were subjected to both alkaline peroxide bleaching,

and mechanical treatment improved the tensile strength of hand sheets. Even though, they were successful in this attempt, the literature does not provide any other studies focused on upgrading these fines.

### ***DAF Subnatant***

DAF subnatant still contains considerable amounts of extractives even after cleaning by dissolved air flotation. Norske Skog – Boyer has been investigating how to remove these extractives and how to recover the value added phytochemicals from it. Froth flotation has been studied extensively as a method to concentrate and recover extractives from the DAF subnatant [6, 7].

The collected whitewater fines could be a good source for producing microfibrillated cellulose. Subnatant from this DAF unit still contains considerable amounts of colloidal extractives. Therefore, DAF subnatant was selected as a possible source for extraction of phytochemicals such as resin acids.

#### **2.2.1.4. Sludge from Effluent Treatment Plant (6)**

Wastewater and waste fibres from TMP mills and paper mills are treated in a two-stage effluent treatment plant (ETP) prior to discharge into the Derwent River. The sludge from this ETP contains biomass from the activated sludge process and contains high moisture levels. This sludge is thickened and transported away for land application in farmlands. Other than that, potential value of this sludge is minimal and therefore was not considered for biorefinery development.

The following table, Table 2.1, summarizes the waste streams that were analysed during the initial investigation. This table summarizes the rationale behind selecting the preferred waste streams and the target products from each waste stream.

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**Table 2.1. Summary Analysis of Waste Streams at Norske Skog – Boyer Facility**

Waste Stream	Advantages	Disadvantages	Other Constraints	Selected for Further Investigation	Volume	Target Products
1. Bark	<ol style="list-style-type: none"> <li>1. Valuable source of phytochemicals</li> <li>2. Could be a good source for gasification and other thermal processes</li> </ol>	-	Currently sold as high quality garden mulch	No	NA	-
2. TMP2 Plug Screw Pressate	<ol style="list-style-type: none"> <li>1. Good source of terpenes</li> <li>2. Could improve the closure of water loop</li> <li>3. Recovery of organics could reduce the load to the ETP</li> </ol>	-	NA	Yes	0.5 ML/day	<ol style="list-style-type: none"> <li>1. Terpenes</li> </ol>
3. TMP2 Primary Refiner Steam Condensate	<ol style="list-style-type: none"> <li>1. Good source of terpenes</li> <li>2. Could improve the closure of water loop</li> <li>3. Recovery of organics could reduce the load to the ETP</li> </ol>	-	NA	Yes	0.3 ML/day	<ol style="list-style-type: none"> <li>1. Volatile Organics (terpenes)</li> </ol>
4. DAF Floats	<ol style="list-style-type: none"> <li>1. Currently being treated as waste, directed to ETP</li> <li>2. Could reduce the load to the ETP if upgraded and reused in the paper mill</li> </ol>	-	NA	Yes	10 Tonnes/day	<ol style="list-style-type: none"> <li>1. Upgraded whitewater fines</li> <li>2. Microfibrillated cellulose</li> </ol>
5. DAF Subnatant	<ol style="list-style-type: none"> <li>1. Good source of resin acids</li> <li>2. Could improve the closure of water loop</li> <li>3. Recovery of organics could reduce the load to the ETP</li> </ol>	-	NA	Yes	10 ML/day	<ol style="list-style-type: none"> <li>1. Resin acids</li> </ol>
6. Sludge from ETP	-	<ol style="list-style-type: none"> <li>1. Low value</li> <li>2. High moisture content – less favourable for gasification and thermal processes</li> </ol>	NA	No	NA	-

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# Chapter 3

## Research Objectives and Thesis Outline

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# Chapter 3 - Research Objectives & Thesis Structure

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# Chapter 3 - Research Objectives & Thesis Structure

## 3.1. Research Objectives

The research objectives were decided based on the gaps in the knowledge identified in Chapter 1 and biorefinery ideas identified in Chapter 2. The primary aim of this research is to investigate the biorefinery concepts, which can be implemented around a TMP mill. It was also decided that only the waste streams should be for this purpose. Therefore, this research only focuses on utilizing TMP whitewater fines and process water streams such as the subnatant from the DAF unit, plug screw pressate and primary refiner steam condensate. The specific aims related to each sub-project are listed below.

### 3.1.1. Upgrading/MFC Production from TMP Whitewater Fines

A1 – Investigate the feasibility of upgrading whitewater fines back to the desired quality of TMP newsprint

A2 – Investigate the feasibility of producing MFC or MFC like material from TMP whitewater fines via mechanical fibrillation techniques

A3 – Investigate the feasibility of producing MFC or MFC like material using the existing refining machinery in a TMP mill

A4 – Study the potential for enhancement of strength properties by using MFC as a paper additive in newsprint

### 3.1.2. Extraction of Phytochemicals from TMP Process Water Streams

B1 – Characterize both qualitatively and quantitatively, the composition of phytochemicals, resin acids and terpenes, in TMP process water streams; whitewater system, plug screw pressate and steam condensate.

B2 – Evaluate the potential of membrane filtration to concentrate, extract and separate resin acids and terpenes from the identified process water streams.

## 3.2. Thesis Structure

The experimental chapters are indicated in *Italic*.

**Chapter 1** – Introduction & Literature Review – Biorefinery Opportunities in a Thermomechanical Pulping Mill

**Chapter 2** – Identifying Opportunities for Value-Addition in a Thermomechanical Pulping Mill

**Chapter 3** – Research Objectives and Thesis Outline

**Chapter 4** – *Homogenizing Fines to Microfibrillated Cellulose – Reducing Energy Consumption at Higher Consistencies*

**Chapter 5** – *Development of Cellulose Nanofibre Quality with Mechanical Energy: Effect of Starting Chemical Composition*

**Chapter 6** – *Upgrading Waste Whitewater Fines from a Pinus Radiata Thermomechanical Pulping Mill*

**Chapter 7** – *Upgrading Thermomechanical Pulping Whitewater Fines through Chemical Treatment*

**Chapter 8** – *Recovery of Resin Acids and Terpenes from Thermomechanical Pulping Process Water by Ultrafiltration*

**Chapter 9** – Conclusions & Recommendations

### 3.3. Thesis Outline

#### 3.3.1. Chapter 1 – Introduction & Literature Review – Biorefinery Opportunities in a Thermomechanical Pulping Mill

This chapter reviews the need for implementing biorefineries and current biorefinery concepts in pulp and paper industry, especially in the thermomechanical pulping mills. Pulp and paper industry in general, except for packaging industry, has been experiencing severe economic hardships because of the declining demand for several grades of paper especially newsprint. Integrated biorefineries can be a solution to produce value added products and can allow the industry to expand into new markets. Recently, there has been an increasing number of research in biorefinery ideas in pulp and paper industry. However, there is minimum research on biorefinery ideas in thermomechanical pulping mills. This chapter also discusses the recent developments in production of microfibrillated cellulose and recovery of phytochemicals from process water streams. Finally, this chapter identifies the gaps in current research in this field and introduces how this project has attempted to fill those gaps.

### 3.3.2. Chapter 2 – Identifying Opportunities for Value-Addition in a Thermomechanical Pulp Mill

This chapter gives a brief description of the Norske Skog – Boyer facility that is the focal point in this study. This chapter also lays out the decision-making behind the proposed biorefinery ideas.

### 3.3.3. Chapter 3 – Research Objectives and Thesis Outline

This is the current chapter and it describes the research objectives and outlines the thesis for ease of understanding.

### 3.3.4. Chapter 4 – Homogenizing Fines to Microfibrillated Cellulose – Reducing Energy Consumption at Higher Consistencies

Homogenization is one of the main mechanisms to produce cellulose nanofibres. Mechanical processing cellulose-containing fibres into cellulose nanofibres with homogenization typically requires a two-stage treatment. An initial mechanical treatment, such as refining, is used to flexibilise the fibres and start the breakdown process, after which the fibres can be homogenized. Without the initial mechanical treatment, the homogenizer is extremely prone to clogging. In the work in this paper, we investigated whether fines fractions, where the fibres are already partially broken down, could be used as feedstock for cellulose nanofibre production without mechanical pre-treatment.

Three different fines-rich sources were identified in a newsprint mill: a) fines separated from a refined bleached softwood Kraft using screening, b) fines separated from TMP pulp process using screening, c) fibrous material from TMP process white-water recovered by processing with Dissolved Air Flotation, with ~80% fines, as measured by screening.

All three of the fibre sources could be processed directly in a homogenizer at 0.25 wt. % with no issues of clogging and without any other pre-treatment. The effect of homogenization was quantified with aspect ratio measurement, fibre diameter distribution measured from SEM and the drainage time to form the sheets as well as the density and porosity of the sheets formed from the homogenized samples. The different measures were not internally consistent with each other, but overall the effect of the homogenization was most significant for the Kraft fines, followed by the TMP white water fines.

The operating range of the homogenizer was investigated with the TMP white water fines. Despite this having the largest fibres of all the three samples, the homogenizer was still able to operate effectively up to the highest solids concentration tested of 1%. From the

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measured pressure drop and flow rate, the theoretical energy consumption was estimated to be reduced by ~37.5% when comparing the highest and lowest solids concentrations.

***Manuscript has been submitted to Cellulose Journal.***

### 3.3.5. Chapter 5 – Development of Cellulose Nanofibre Quality with Mechanical Energy: Effect of Starting Chemical Composition

Energy efficient production of nanocellulose fibres is key to establishing this highly promoted material in an industrial scale. In this work, we attempt to explain how the mechanical energy input together with the chemical composition of the raw materials affect the quality of nanofibres. Bleached eucalyptus Kraft (BEK) pulp, a commercially available microfibrillated nanocellulose from cotton, and whitewater fines were used to produce cellulose nanofibres. BEK was the most responsive to mechanical fibrillation due to low crystallinity and it produced high aspect ratio nanofibres, while TMP whitewater fines were the most difficult to process and resulted in low aspect ratio nanofibres. Nanofibres were then added to TMP newsprint to evaluate the effect on tensile strength. Nanofibers produced from BEK were able to increase the tensile strength the most, while nanofibres from whitewater fines had the least effect. The results showed that a high aspect ratio and a surface chemical composition favouring more hydrogen bonds i.e. pure cellulose are the key criteria when selecting nanofibre for strength improvement in paper. However, MFC produced from TMP whitewater fines had the least increase in drainage time, which could be advantageous in paper mills.

***This work has been published and presented in the Sixteenth Fundamental Research Symposium of the Pulp and Paper Fundamental Research Society, September 2017, Oxford, United Kingdom, as “Development of cellulose nanofibre quality with mechanical energy: effect of starting chemical composition”.***

### 3.3.6. Chapter 6 – Upgrading Waste Whitewater Fines from a Pinus Radiata Thermomechanical Pulping Mill

Homogenization, however, is a significantly energy intensive and expensive process to produce MFC. It also requires new capital investment. However, existing refiners can be used to produce MFC in a more energy efficient manner, reducing the amount of capital investment needed. Both PFI refining and lab scale disc refining was found to be more energy efficient compared to homogenization to increase tensile strength while reducing the fibril diameter. Refining was also found to ease the subsequent homogenization process. MFC produced this way exhibited hydrophobic properties. This could be advantageous in some applications such as composites with non-polar matrices.

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***This work has been published in the Nordic Pulp & Paper Journal as “Upgrading waste whitewater fines from a pinus radiata thermomechanical pulping mill”.***

### 3.3.7. Chapter 7 – Upgrading Thermomechanical Pulping Whitewater Fines through Chemical Treatment

Whitewater fines collected as the floats of the DAF unit are rarely used within the papermaking process at Norske Skog Boyer, because of their detrimental effect on sheet strength. In Chapter 6, we investigated the effect of mechanical treating the fines to upgrade them to the required strength. Treatment with 3000 kwh/t of refining energy increased the sheet strength by ~45% from 28 Nm/g to 40.5, which is higher than the strength of the sheets made from the main TMP pulp. In this chapter, the use of two chemical treatments to upgrade the fines to the required sheet strength is investigated.

The first treatment was washing in ethanol. This removed 10% of the mass of the fines ethanol soluble extractives and increased the tensile index of the sheets made, from 28 Nm/g to 34.5 Nm/g. The second treatment was caustic washing/treatment. This was carried out at four different temperatures and four different caustic strength levels. Fibres, which were treated at room temperature and 0.5 M caustic strength, showed the best improvement. The standard hand sheets made out of these fibres showed a tensile index of 48.8 Nm/g, which is ~ 74% increase from the untreated whitewater fines. The weight of extractives recovered from the caustic liquor after centrifugation was 5.5%. Treated whitewater fines could then be added to the thermomechanical pulp to improve the strength. However, further experiments and studies are needed to further optimize the properties.

### 3.3.8. Chapter 8 – Recovery of Resin Acids and Terpenes from Thermomechanical Pulping Process Water by Ultrafiltration

Resin acids and terpenes are important constituents of wood extractives in pulp paper industry, and have many value added applications as pharmaceuticals, anti-oxidants and starting material for fragrances and polymers. Resin acids and terpenes come out the wood during the primary processing in thermomechanical pulping. Recovering these chemicals from thermomechanical pulping process water system could be a way to implement biorefining. In this chapter, the potential of recovering resin acids from whitewater and terpenes from plug screw pressate using ultrafiltration is reported. Two-stage ultrafiltration is proposed; membrane filtration of thermomechanical pulp mill whitewater at pH 9.5 through a 100-kDa regenerated cellulose membrane, and membrane filtration of permeate from Stage 1 at pH 4.5 through a 30-kDa membrane regenerated cellulose. The proposed process can recover 64% of resin acids present in

the original whitewater stream with 77% enrichment of resin acids. Terpenes could completely isolated and concentrated in the retentate by using ultrafiltration. The concentrated retentate could be an efficient feed to subsequent unit operations to separate terpenes.

### 3.3.9. Chapter 9 – Conclusions & Recommendations

This chapter summarizes the conclusions of the several studies undertaken in this project and proposes steps and areas of interest for future research.

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# Chapter 4

Homogenizing Fines to Microfibrillated  
Cellulose – Reducing Energy Consumption at  
Higher Consistencies

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# Preface

Homogenization is the most widely used mechanical treatment method to produce microfibrillated cellulose. However, it is an energy intensive process and often limited by the consistency of the suspension. Whole pulp such as unrefined bleached hardwood and softwood pulp must be refined prior to processing in homogenizer. This is done to shorten and flexibilise the long coarse fibres. Otherwise, the long fibres can clog the homogenizer causing operational downtime and/or equipment damage. Nevertheless, homogenization is typically done at low consistencies such as 0.25 wt% to avoid clogging, even with pre-refining. In this Chapter, we investigate the possibility of reducing the energy consumption during homogenization by utilizing various fines available in a thermomechanical pulping mill. Three different fines were used: Kraft fines, TMP Fines and TMP whitewater fines. Homogenization was tried at different consistencies from 0.25 wt% to 1.0 wt%. Energy consumption was measured using an inline power meter connected to the homogenizer.

This work addresses the objectives A1 and A2.

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# Chapter 4 – Homogenizing Fines to Microfibrillated Cellulose – Reducing Energy Consumption at Higher Consistencies

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# Chapter 4 – Homogenizing fines to microfibrillated cellulose – reducing energy consumption at higher consistencies

Thilina Gunawardhana<sup>1</sup>, Paul Banham<sup>2</sup>, Desmond E. Richardson<sup>2</sup>, Antonio F. Patti<sup>3</sup>, Warren Batchelor<sup>1</sup>

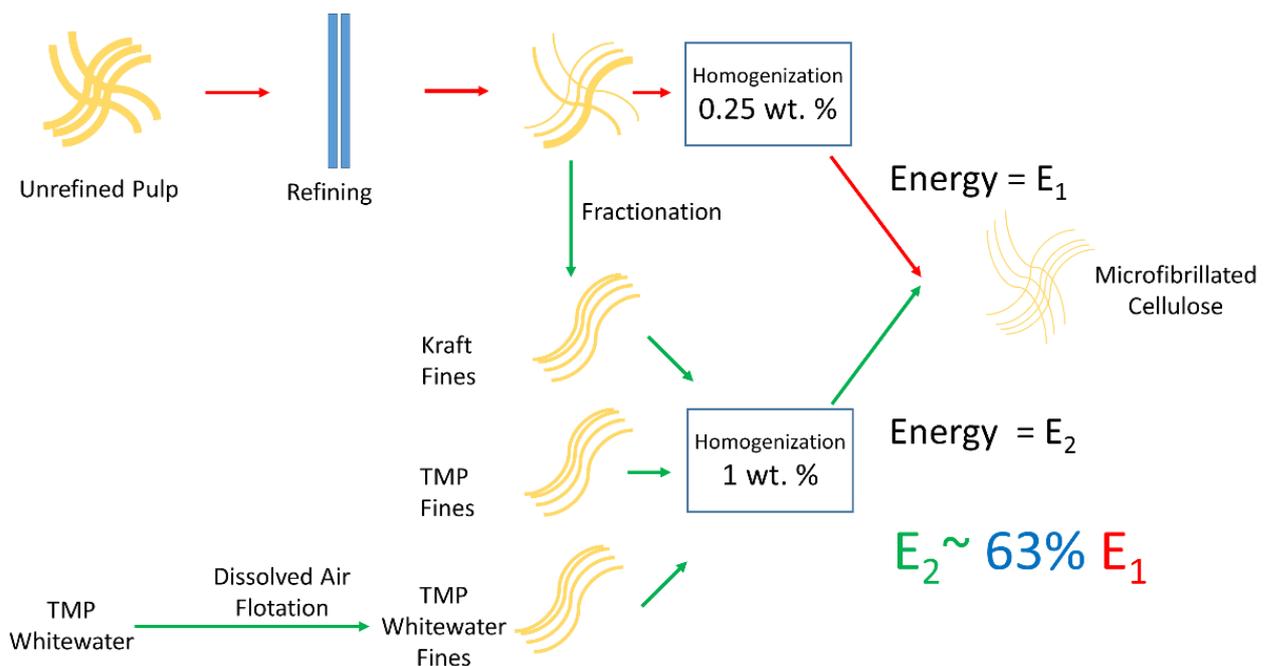
<sup>1</sup>Bioresource Processing Institute of Australia (BioPRIA), Department of Chemical Engineering, Monash University, Clayton VIC 3800, Australia

<sup>2</sup>Norske Skog Paper Mills (Australia), Boyer, TAS 7140, Australia

<sup>3</sup>School of Chemistry, Monash University, Clayton VIC 3800, Australia

Corresponding Author: [warren.batchelor@monash.edu](mailto:warren.batchelor@monash.edu)

## 4.1. Graphical Abstract



## 4.2. Highlights

- Three different fines sources; (a) & (b) fines separated using screening from a refined bleached softwood Kraft and softwood thermomechanical pulp, respectively, c) fibres from thermomechanical pulping whitewater recovered via dissolved air flotation, with ~80% fines, were evaluated for potential for microfibrillated cellulose production.
- Fines could be homogenized at a higher consistency than refined whole pulp without operational difficulties in the homogenizer.

- We estimate that a ~ 37.5% reduction in specific energy consumption is possible by increasing the consistency from 0.25 wt. % to 1.0 wt. % and fines provide excellent means of achieving this.
- The effect of homogenization was most significant in Kraft fines, followed by TMP whitewater fines.
- Kraft fines are an ideal source for producing microfibrillated cellulose matching commercially available products.

### 4.3. Abstract

Homogenization is one of the main mechanisms to produce cellulose nanofibers. An initial mechanical treatment is essential to flexibilise the fibres and start the breakdown process prior to homogenization. Otherwise, the homogenizer is extremely prone to clogging. In this work, we investigated whether fines fractions, where the fibres are already partially broken down, could be used as feedstock for nanofibre production without mechanical pre-treatment.

Three different fines-rich sources were identified in a newsprint mill: a) & b) fines separated using screening from a refined bleached softwood Kraft and softwood thermomechanical pulp, respectively, c) fibres from thermomechanical pulping whitewater recovered via dissolved air flotation, with ~80% fines.

All three fibre sources could be processed directly in a homogenizer at 0.25 wt. % without any pre-treatment and with no issues of clogging. The effect of homogenization was quantified with measurement of aspect ratio and fibre diameter and drainage time, density and porosity of the sheets formed. The different measures were not internally consistent with each other, but overall the effect of the homogenization was most significant for the Kraft fines, followed by the whitewater fines.

The operating range of the homogenizer was investigated with the whitewater fines. Despite this having the largest fibres of all the three samples, the homogenizer was still able to operate effectively up to the highest solids concentration tested of 1%. From the measured pressure drop and flow rate, the theoretical energy consumption was estimated to be reduced by ~37.5% when comparing the highest and lowest solids concentrations.

### 4.4. Keywords

Microfibrillated cellulose; nanocellulose; fines; homogenization; energy; high consistency

## 4.5. Introduction

Microfibrillated cellulose (MFC) is a widely investigated naturally occurring material as a novel, recyclable and renewable polymer [1]. MFC. It is often referred to as nanocellulose, and has been touted as a high strength polymer with many novel applications [2]. Almost any source of cellulose, which is the most abundant, natural or synthetic polymer on earth, can be used to produce MFC [3]. These qualities increase the potential value of MFC even further.

MFC can be defined as the product of separation of fibrils in the secondary cell walls of cellulosic fibres [4]. MFC is generally classified as a nanomaterial with a very high aspect ratio (length to width, L/D). On average, MFC has a width range of 10-100 nm and length range of 0.5 – 50  $\mu\text{m}$  [1]. The different terminologies used in the field of cellulose nanomaterials arises from the different size ranges of different materials, as shown in Table 4.1. In this paper, we use the term microfibrillated cellulose or MFC hereafter.

**Table 4.1.** *Relative size of different cellulose nano materials [1]*

<b>Particle type/terminology</b>	<b>Length (<math>\mu\text{m}</math>)</b>	<b>Width (nm)</b>
<b>Wood fibre</b>	> 1000	~ 30000
<b>Microcrystalline cellulose (MCC)</b>	10-50	10-50
<b>Microfibrillated cellulose (MFC)</b>	0.5-50	10-100
<b>Nanofibrillated cellulose (NFC)</b>	0.5-2	4-20
<b>Cellulose nanocrystals (CNC)</b>	0.05-0.5	3-5
<b>Bacterial cellulose (BC)</b>	>1	30-50

MFC has a relatively large surface area that provides a basis for higher tensile strength via increasing the number of bonds. This results in higher tensile strength in MFC than normal fibres, depending on the quality and the source of MFC. For example, one of the commercial MFCs available in the marketplace, Daicel MFC Celish Grade, has a tensile index around 85 Nm/g [5]. This particular MFC is believed to be produced by microgrinding/homogenization of bleached cotton fibres [6]. The nanoscale diameters of the fibres result in a tight pore structure, which results in decreased air permeability. This makes MFC a suitable material for improving barrier properties [7]. MFC also shows increased hydrophilicity, due to the increased amount of exposed hydroxyl groups.

TEMPO oxidized nanocellulose typically have diameters less than 10 nm and sheets made of them exhibit high optical transparency and high tensile strength [4]. This provides access to a range of applications such as transparent structures for electronic applications and novel packaging [4]. The pulp and paper industry benefits the most by producing this value added material. At the same time, MFC has applications in the pulp and paper industry itself, as a strength additive and a coating agent [8, 9].

A range of materials has been investigated for MFC production, including chemical and thermomechanical pulps (TMP) from wood, agricultural residues, such as corn straw and rice straw, native grasses such as spinifex and alternative materials such as bacterial cellulose [3]. However, MFC derived from chemical pulp, mainly Kraft pulps, remains the most sought-after material [1]. Microfibrils and/or nanofibrils produced from TMP pulp are often referred to as “nanolignocellulose (NLC)” or “lignocellulosic nanofibrils (LCNF)” due to the presence of lignin in the pulp [10, 11].

Several techniques have been used to produce MFC. Extended refining can be used to produce MFC and has been tried out in a semi-commercial process [12]. Co-grinding with fillers such as bentonite or calcium carbonate can be used for in-situ generation of microfibrils (IMERYS) [13, 14]. However, homogenization remains the most widely used and preferred technique [15-17].

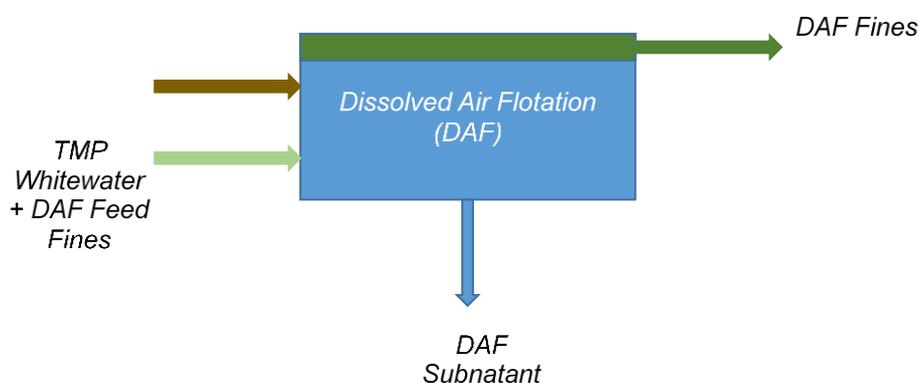
During homogenization, a fibre suspension is forced through a narrow passage under very high pressure (500 – 1000 bar). The sudden drop in pressure when passing through the narrow passage makes the fibres fibrillate into microfibrils. By design, homogenization requires very dilute suspensions in the range of 0.25 – 2 wt. % consistency. This makes homogenization a significantly energy intensive process [17]. In addition, mechanical pre-treatment is necessary prior to homogenization of wood fibres due to their length and coarse nature [18]. Long and coarse fibres can cause clogging in the narrow passages in homogenizers and can cause excessive downtime [18]. This is even more critical when homogenizing softwood pulp compared to hardwood pulp, because softwood has longer fibres than hardwood. At the laboratory scale, PFI refining and Valley beating are used to reduce the fibre length and make fibres more flexible [18]. Hammer milling and ball milling may be used as well [10, 11]. Chemical pre-treatment such as TEMPO mediated oxidation is used as an effective treatment prior to homogenization [19]. However, it produces a different type of nanocellulose with distinctively different properties from conventional MFC.

The main objective of mechanical pre-treatment is to reduce the fibre length to avoid clogging. Indirectly, we are processing whole pulps and generating fines by refining, which requires additional energy consumption. However, pulp mills, especially thermomechanical pulping mills where the operating principle is based on refining, have a variety of fines material already in the system. TMP whole pulp typically contains between 30-40% fines, which can be fractionated to recover the fines [20]. TMP process water also contains fines, which are often referred to as “whitewater fines” [21]. These fines are released into the process water system at various stages of pulp thickening and paper making. Usually TMP mills buy Kraft pulp and refine the fibre prior to adding it as a strength enhancer in some grades of paper. This generates fines that may be recovered via fractionation.

In this paper, we show that these fines can be homogenized directly without any pre-treatment, and can be an effective source for MFC production.

#### 4.6. Materials

Norske Skog – Boyer mill processes Radiata pine (*Pinus radiata*) wood in 3 thermomechanical pulping (TMP) mills and 2 paper machines. TMP whitewater in this mill is clarified using a dissolved air flotation (DAF) unit [22]. See Figure 4.1. The whitewater fines are floated to the top and removed by a scraper. These floats or fines were collected at ~ 5% consistency and thickened using a laboratory vacuum filtration unit with a 20-mesh screen. The fines content of these DAF fines was calculated as ~80% after fractionating using a Somerville Fractionator. 10g (dry weight) of the DAF fines were washed with 2 litres of 96% ethanol (Ajax Finechem (AJA1046-2.5LPL)) in a 2 litre Schott glass bottle for 18 hours on a magnetic stirrer. Filtrate was collected through a Whatman Grade 541 filter paper and concentrated using a Heidolph Rotary Evaporator. The extractive content measured was 9.9 wt. % dry basis.



**Figure 4.1.** Dissolved air flotation (DAF) in Norske Skog – Boyer

A whole TMP pulp from the same mill was fractionated using a Somerville Fractionator, through a 200-mesh screen to recover the fines. The filtrate was then thickened using a Whatman Grade 541 filter paper on a laboratory vacuum filtration unit. These fines are referred to as “TMP fines” hereafter. The percentage of fines in TMP whole pulp was calculated as 33 wt. %. The energy input to TMP is approximately 2600 kWh/Tonne. Once dried, bleached Radiata Pine Kraft pulp which had been refined in a Metso RF-2 Optifiner, was fractionated using a Somerville Fractionator and a 200-mesh screen to recover “Kraft Fines” using a similar method to that of the “TMP fines”. Refined Kraft pulp contained 10 wt. % fines. The energy consumption in the Metso RF-2 Optifiner was estimated to be 55 kWh/tonne. Altogether, three different types of fines were used in this research; DAF fines, TMP fines and Kraft fines.

## 4.7. Methodology

### 4.7.1. Fibre length analysis

Fibre dimensions were analysed using a Metso FiberLab by using dilute suspensions (~0.05 wt. %) of each pulp sample before homogenization. Image analysis in the software can only analyse larger fibres, and the detection of finer material of less than 0.02 mm is minimal.

#### 4.7.1. Nanofibre Production

Suspensions with 0.25 – 1.0 wt. % were made from each pulp and homogenized using a high pressure homogenizer (GEA Niro Soavi), for 5 passes at 1000 bar. Specific energy consumption of the homogenizer was estimated by calculating the pump work. The efficiency in the drive motor and energy losses were not taken into consideration. The pump work ( $W$ ) is calculated as below.

$$W = \frac{P - P_{atm}}{\rho}$$

Where,  $P$  is the homogenizer pressure,  $P_{atm}$  is the atmospheric pressure and  $\rho$  is the density of the suspension. The density of the 0.25 wt. % suspension was assumed to be the same as of water, which is 1000 kgm<sup>-3</sup>.

#### 4.7.2. Nanofibre Characterization

Aspect ratio (length/diameter) after each treatment stage was evaluated by estimating the gel point of the fibre suspension through sedimentation experiments described in Varanasi et al. 2013 [6]. In this method, a series of dilute suspensions, often from 0.01 –

0.1 wt% suspensions of MFC are prepared and poured equal volumes to a series of measuring cylinders, and the initial height of the suspension is recorded. The suspensions were allowed to settle > 48 hours and final sediment heights were measured. The ratio of final sediment height to initial suspension height is plotted against the consistency of the suspension, and a quadratic fit is found. The linear coefficient of this quadratic equation gives the gel point consistency which is then used to estimate the average aspect ratio of the fibres using a set of empirical equations as given in Varanasi et al. The skeletal density of dry lignocellulosic fibres was measured using a Micrometrics AccuPyc 1330 Pycnometer as  $1375 \text{ kgm}^{-3}$ . Sugiyama et. al 1991 reported the skeletal density as  $1582 \text{ kgm}^{-3}$  [23]. Therefore, when calculating the aspect ratio, it was assumed that the hydrated densities of the DAF fines, and TMP fines were  $1333 \text{ kgm}^{-3}$  and the hydrated density of Kraft fines was assumed as  $1500 \text{ kgm}^{-3}$ . The respective equation according to effective medium theory (EMT) was used and the aspect ratio was calculated using the following equation,

$$A = B \times C_c^{-0.58}$$

where  $A$  is the aspect ratio of the fibres, and  $C_c$  is the solid concentration corresponding to the gel-point.  $B$  is the factor corresponding to the density; for DAF fines, and TMP fines, the factor is 2.98, while for Kraft fines it is 3.19 [6]. The value is lower for the DAF fines and TMP fines as lignin has a lower density as shown above.

Scanning electron microscopy (SEM) images of the different nanofibre suspensions were taken using an FEI Nova NanoSEM to measure the fibre width distribution. SEM samples were prepared by evaporating a droplet from a very dilute (~0.001 wt. %) suspension onto a silicon chip mounted on a carbon tab. Once dried, samples were coated with a 2 nm layer of Iridium. Images were acquired at different voltages (3 – 10 kV) and different magnifications (5000 – 100,000X). Fibre diameters were analysed using ImageJ software by taking measurements from images. All the fibres in each selected image were measured and more than 100 fibres were measured for each sample.

#### 4.7.3. Sheet making

The consistency of the suspension was adjusted to 0.2 wt. % and 60 gsm sheets were made by using 600 g of the suspension. No retention aid was added and all the sheets were made on Whatman Grade 541 filter papers using a standard semi-automatic British Hand Sheet Machine. Drainage time (seconds) was measured from the start of the “Drain” cycle in the hand sheet maker until the sheet was fully drained, which was visually

estimated from when the water disappeared from the whole surface of the sheet. Sheets were air dried under restraint in a conditioned testing room (23 °C and 50% RH), and stored there until further use.

#### 4.7.4. Sheet testing

The oven dry weight (g) of the sheets was measured after drying them at 105°C for 4 hours. Sheets were weighed using a balance with 0.001g sensitivity. Thickness (µm) was measured using an L&W Micrometer 51. Twenty (20) measurements were taken from each sheet. Air permeance (µm/Pa.S) was measured using an L&W Air Permeance Tester. Tensile testing was measured using 15 mm wide strips and a 100 mm test span with 10 mm/min extension rate, using an Instron 5566 Tensile Tester. Force (N) and elongation at break (mm) were recorded. The strength results were expressed as the tensile index; calculated by dividing the maximum tensile strength (at break) by the width of the strip (15 mm) and by grammage of the paper sheet (g/m<sup>2</sup>).

## 4.8. Results and discussion

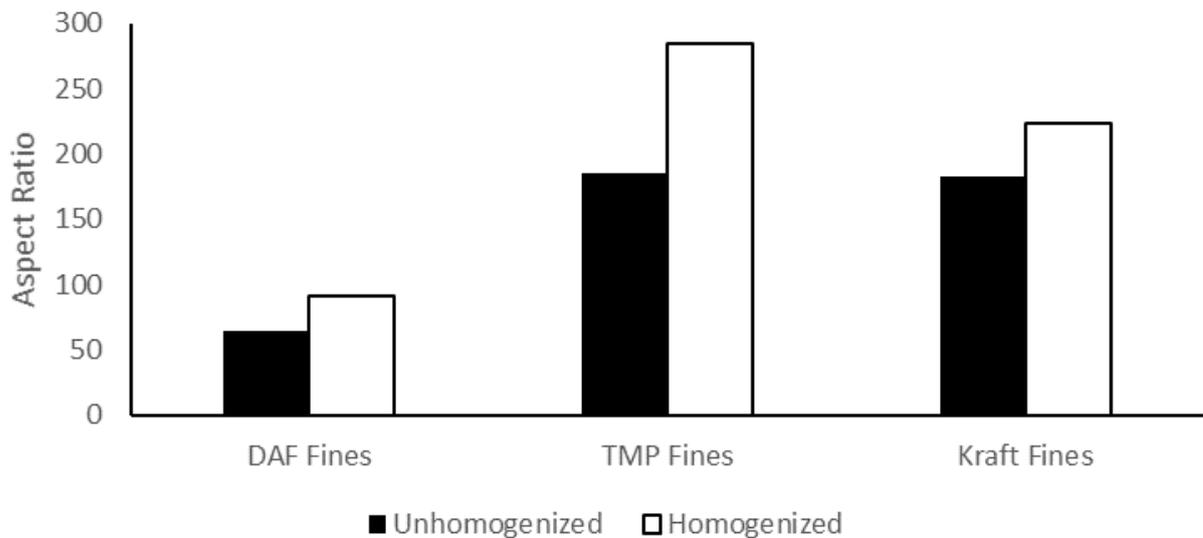
### 4.8.1. Fibre characterisation

FiberLab measures the dimensions by capturing images of individual fibres and analysing those images. The resolutions of these images only allows accurate analysis of width and cell wall thickness of fibres greater than 0.2 mm in length, while fine particles of less than 0.2 mm length are often not detected. However, FiberLab data, Table 4.2, provides useful information of the starting fibres. The Bauer-McNett screening showed that the DAF Fines sample had 80% by weight of fines. The FiberLab data shows that the remaining 20% of the sample that was not fines has dominated the fibre length measurement. The TMP Fines and Kraft Fines had similar dimensions, reflecting their selection through Somerville screening.

**Table 4.2.** *FiberLab measurements of fines*

<b>Fibre Dimension</b>	<b>DAF</b>	<b>TMP Fines</b>	<b>Kraft Fines</b>
<b>Fibre Length – Arithmetic Average( mm)</b>	0.57	0.17	0.15
<b>Fibre Length – Length Weighted Average( mm)</b>	1.23	0.27	0.26
<b>Fibre Length – Mass Weighted Average( mm)</b>	1.94	0.62	0.71
<b>Fibre Width (µm)</b>	30.7	22.1	21.8
<b>Cell Wall Thickness (µm)</b>	8.8	5.0	4.0

DAF Fines originally had a short aspect ratio of 65. Homogenization of DAF fines increased the aspect ratio to 91. See Figure 4.2. Both TMP Fines and Kraft Fines had much higher aspect ratios of around 180. However, TMP fines developed further than Kraft Fines, resulting in an aspect ratio of 285 while Kraft Fines reached only 224. This could be due to the once dried nature of Kraft pulp used. Hornification of fibres may have hindered the fibrillation.



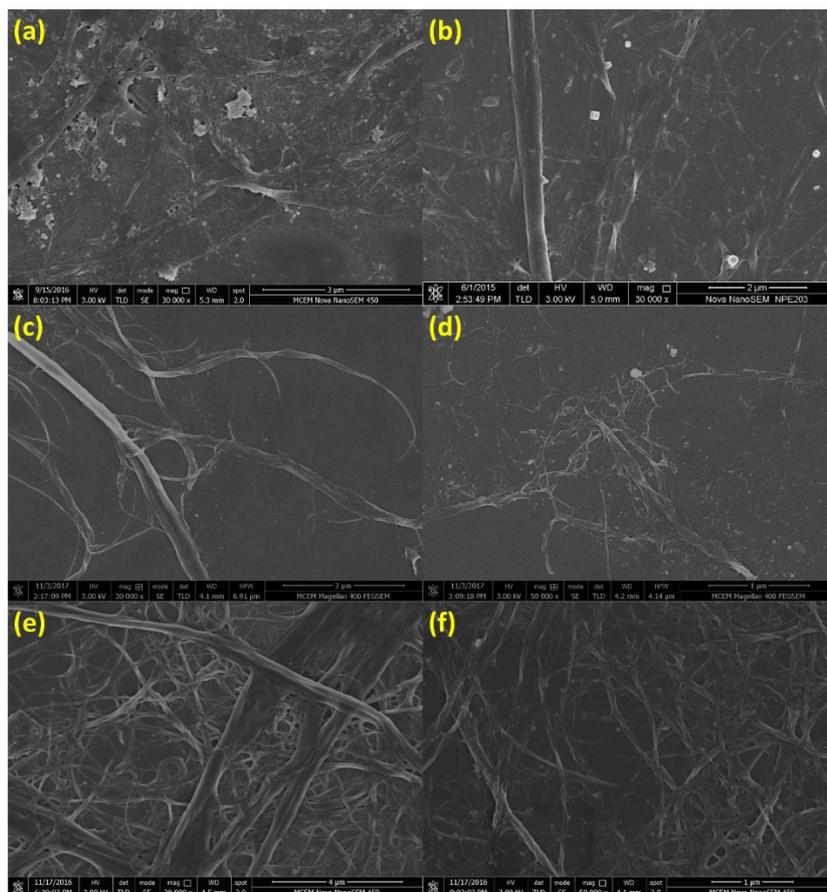
**Figure 4.2.** *Development of Aspect Ratio with Homogenization*

Figure 4.3 shows some selected scanning electron micrographs of fibres before and after homogenization. The median diameters calculated after image analysis are shown in Figure 4.4. As inset (a) shows, DAF fines had coarse fibres and particles. The rectangular shaped particles can be identified as ray parenchyma cells and their fragments. They are not usually classified as fibres, thus the term ‘particle’ is used. There are also a fair number of fines and fibrillar materials too. Prior to homogenization, DAF fines had a median diameter of 321 nm. Homogenization decreased the median diameter significantly to 80 nm. This was attributed to the development of microfibrils as shown in inset (b). Two types of microfibrils were identified. Non-individualized microfibrils that were incompletely separated from the larger fibres and individualized microfibrils that were completely isolated.

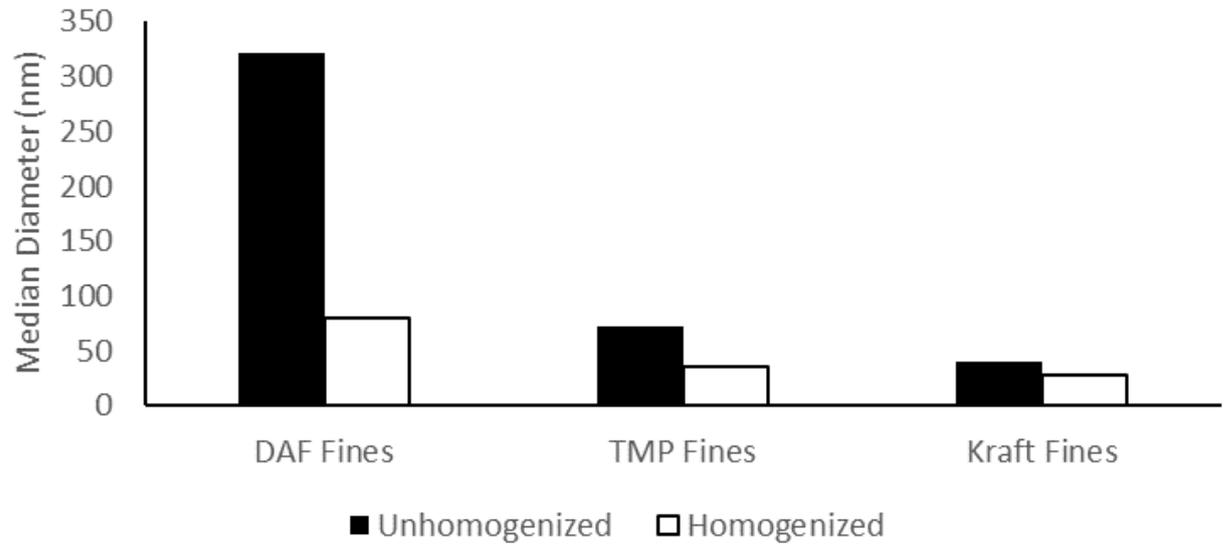
TMP Fines, however, had different fibre morphologies. Fewer numbers of rectangular and coarser particles, the ray parenchyma cells and their fragments, were observed in the TMP Fines. Whitewater fines accumulate ray parenchyma cells and their fragments as they are recirculated and concentrated in the papermaking process. However, TMP fines

that were recovered by fractionating fresh TMP whole pulp did not have as great an accumulation of ray parenchyma cells or their fragments. TMP fibres were observed as lean and longer fines. Therefore, they had a higher aspect ratio that was significantly higher than both DAF fines. The starting median diameter of TMP fines was calculated as 72 nm while homogenization for five (5) passes reduced it to 36 nm. Behaviour of Kraft fines was similar to TMP fines. However, they had a lower starting median diameter of 40 nm, which was reduced to 28 nm after homogenisation.

The median diameters calculated through SEM images did not align with the diameters calculated through fibre length analysis. The fibre length analyser can only detect the larger fibres as mentioned earlier. The resolutions of images acquired during this process only allows analysis of length, width and cell wall thickness of fibres greater than 0.2 mm in length and fine particles of less than 0.02 mm length are often disregarded. However, we can identify much smaller nano scale fibres through SEM analysis. Thus, the median diameter calculated through SEM analysis is much lower than that through instrumental fibre length analysis and is more accurate.

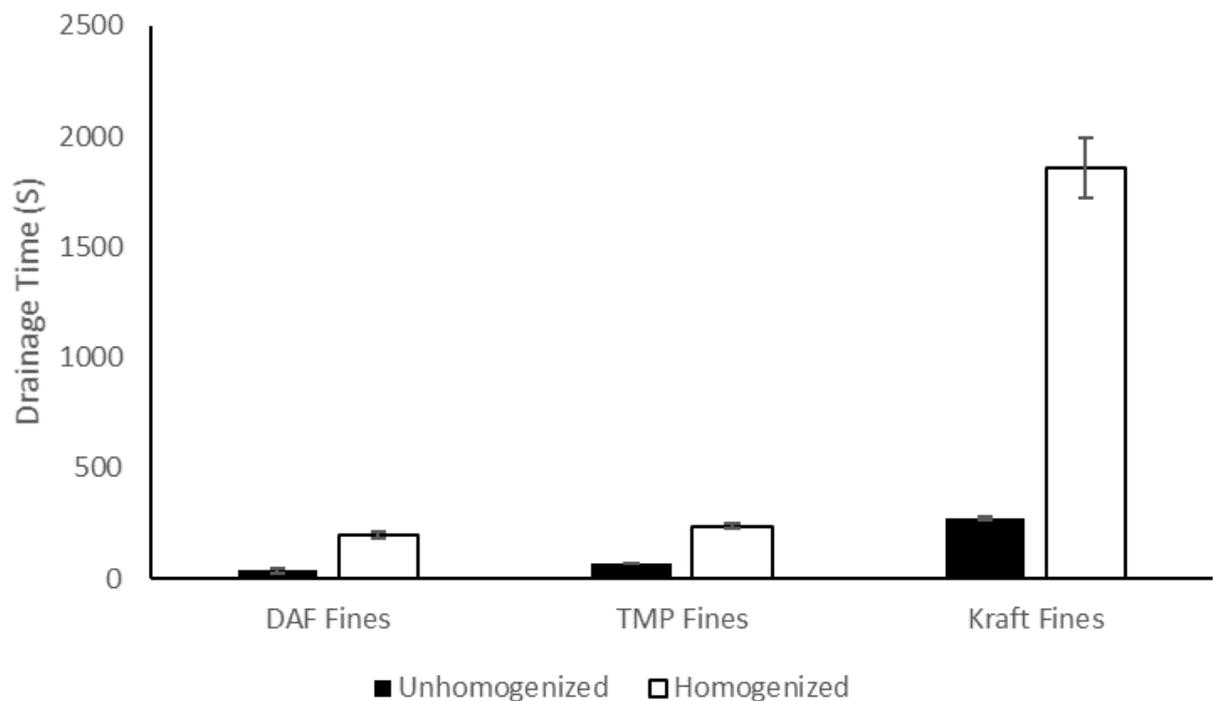


**Figure 4.3.** Microfibril development with homogenization – Scanning Electron Micrographs: (a) & (b) DAF fines unhomogenized and homogenized, (c) & (d) TMP fines unhomogenized and homogenized, (e) & (f) Kraft fines unhomogenized and homogenized



**Figure 4.4.** Change in median diameter with homogenization

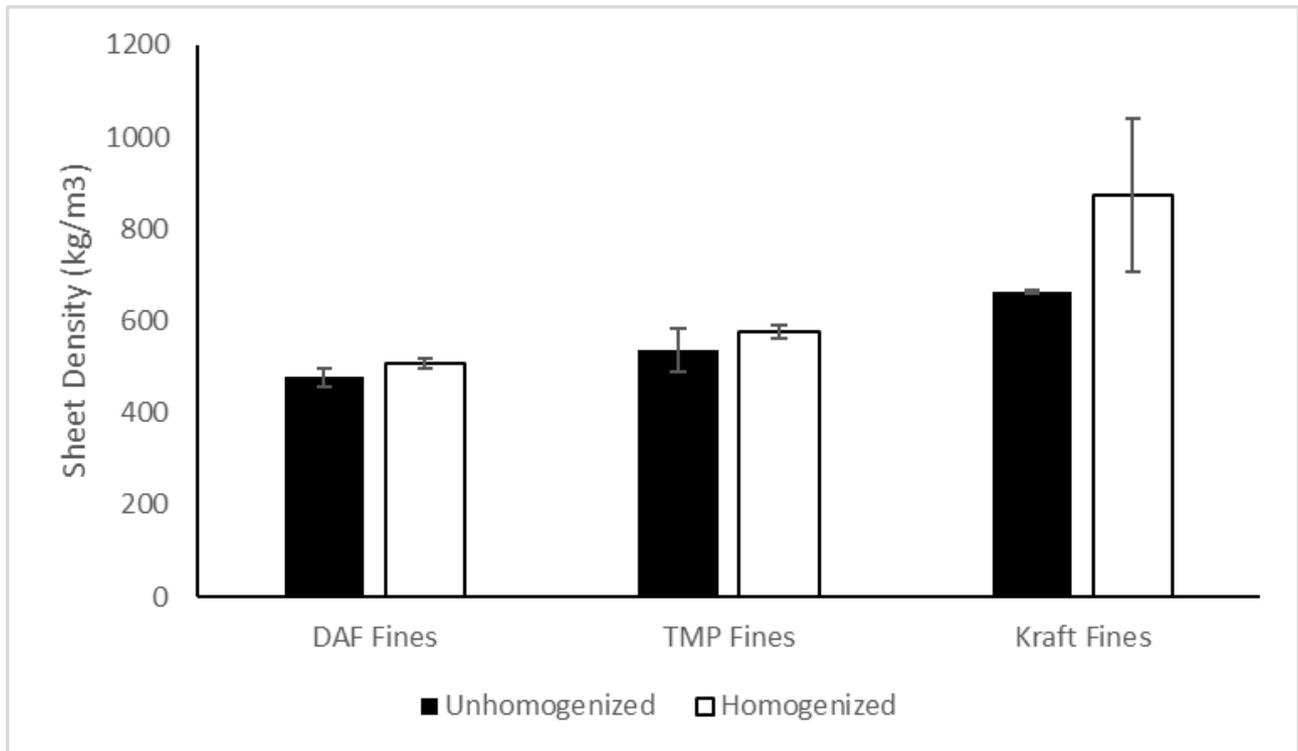
#### 4.8.2. Sheet properties



**Figure 4.5.** Effect of Homogenization on Drainage Time

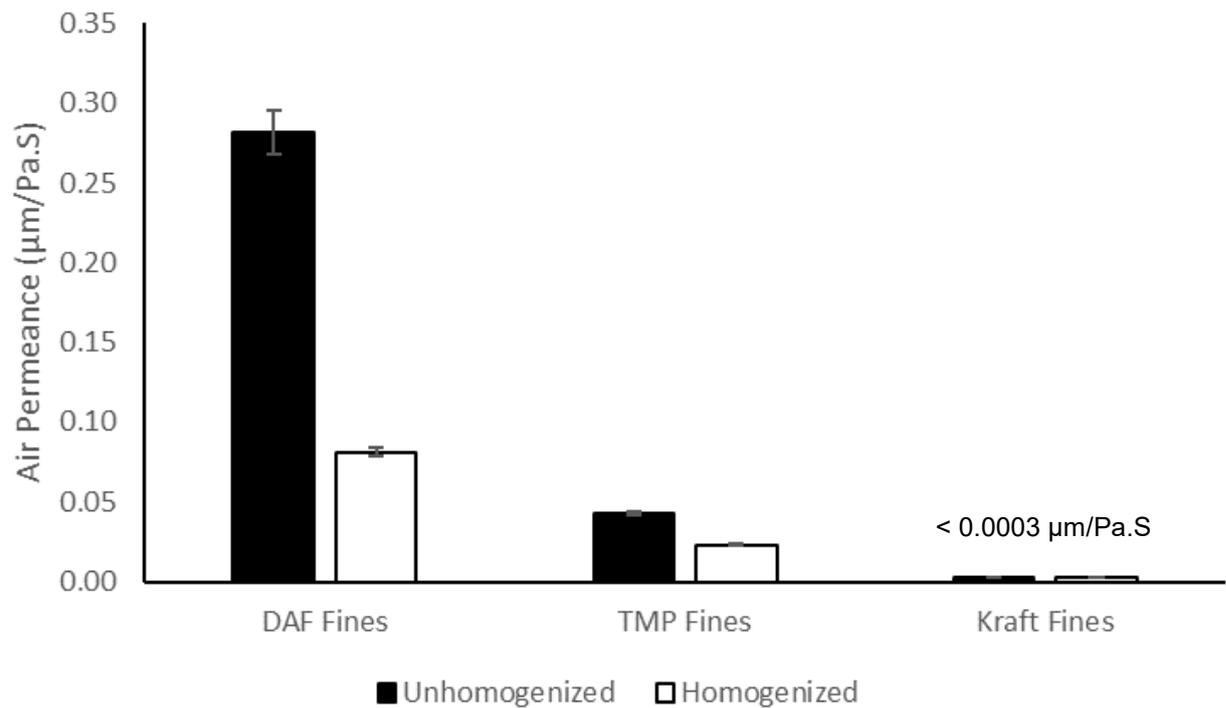
DAF Fines, and TMP Fines, all had significantly lower drainage times than Kraft Fines. See Figure 4.5. This was attributed to their larger fibre diameters and surface chemical composition due to lignin and extractives on their surfaces, which made them hydrophobic. They would release water more readily than Kraft Fines that have a hydrophilic surface. Homogenization of DAF Fines and TMP Fines increased the drainage time significantly, due to the creation of microfibrils. However, the drainage time of Kraft Fines increased even more significantly, taking almost 31 minutes to drain a hand sheet.

This was attributed to the lower diameters of MFC produced by Kraft Fines and increased amount of hydrophilic surface area.



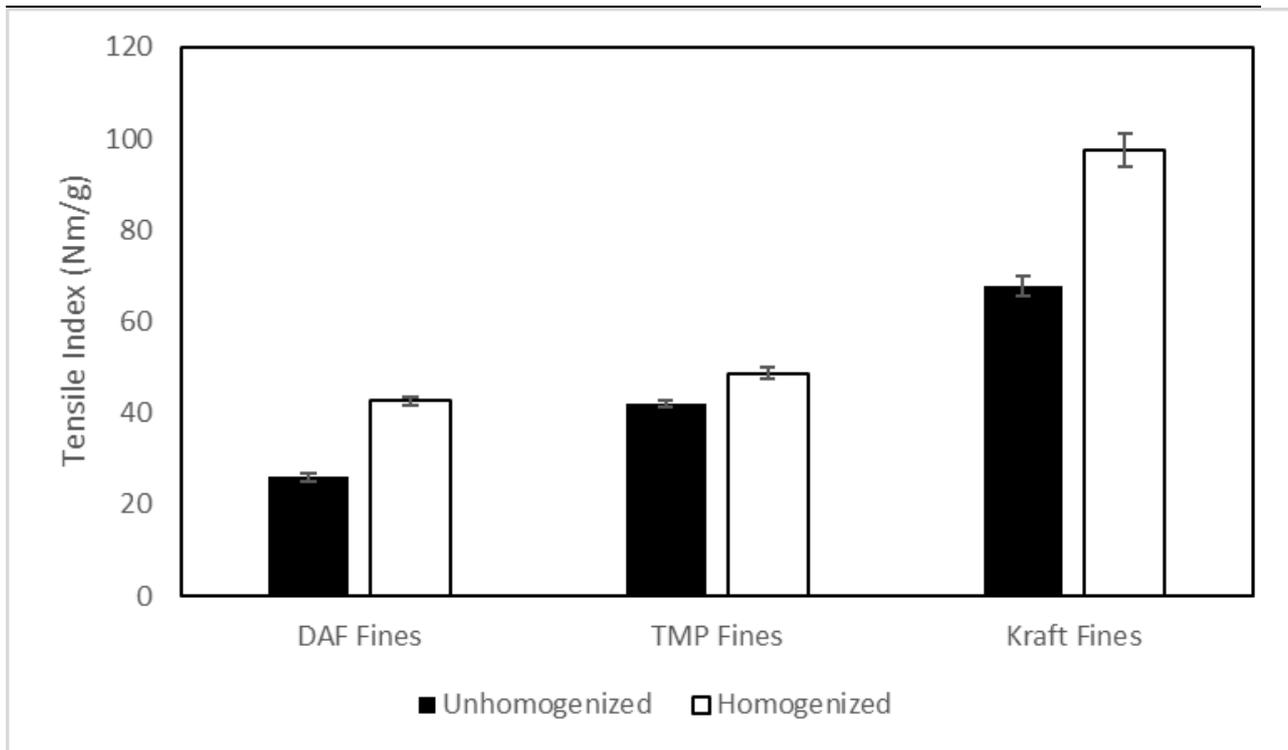
**Figure 4.6.** Effect of homogenization on Sheet Density

Sheet density is expected to increase after any fibrillation technique and lead to an increase in tensile strength. This was observed in all fibre types. See Figure 4.6. However, the response in all the fibres other than Kraft fines was not significant. Homogenization of Kraft fines increased sheet density significantly. The reason for the wider error bar is due to some sheets shrinking during the drying process. This shrinking makes it difficult to measure the thickness accurately, which reflects in the calculated sheet density. Sheets made from Kraft fines showed intensified shrinking while drying. Sheets made from other homogenized fibres also showed relatively smaller levels of shrinking.



**Figure 4.7.** Effect of homogenization on air permeance of hand sheets

As the fibre diameters decrease, the pores become smaller, increasing the barrier properties of hand sheets made. DAF fines had the highest air permeance, which after homogenization remained significantly higher than other fibre types. See Figure 4.7. TMP fines had lower air permeance values. Sheets made from Kraft fines showed the lowest air permeance both before and after homogenization, both values being lower than the lower measurement limit of the L&W Air Permeance Tester, (0.0003  $\mu\text{m}/\text{Pa.S}$ ). The SEM images suggested that both TMP fines and Kraft fines had similar median diameters after homogenization. However, the SEM images showed that TMP fines still contained some larger fibres. This could have resulted in a pore size distribution with some relatively large pores leading to increased air permeance. By contrast, Kraft fines seemed to be more homogenous thus reducing the air permeance. Another advantage Kraft fines have is their superior bonding ability compared to TMP fines. The surface of TMP fines are have a high loading of lignin and hydrophobic extractives, which inhibit hydrogen bonding between fibres. However, Kraft fines do not have such inhibition. This would make the fibres bond more tightly, thus creating a tighter pore structure.



**Figure 4.8.** Development of tensile strength with homogenization

Whitewater fines have a low tensile strength [21]. One of the main reasons is the presence of non-fibrillar particles such as ray parenchyma cells and their fragments. They inhibit fibre – fibre bonding, thus decrease the tensile strength. Whitewater fines are also contaminated with hydrophobic extractives which also reduce hydrogen bonding [24]. DAF fines however, are further contaminated by additional hydrophobic extractives, which are bound onto the fibres during dissolved air flotation, with 10% by weight of the samples extractable in ethanol. TMP Fines however started at a higher tensile strength of 42.1 Nm/g and developed to 48.6 Nm/g after homogenization. See Figure 4.8. This was probably due to the absence of non-fibrillar particles in TMP fines, less surface extractives content and higher aspect ratio as shown in Figure 4.2. Kraft fines however had superior tensile strength (67.9 Nm/g) before homogenization which increased to almost 100 Nm/g after homogenization. This was attributed to the almost pure cellulose surface facilitating more hydrogen bonding and higher aspect ratio in MFC produced from Kraft fines.

This research indicates that the use of fines is more efficient than whole pulp when homogenization is used to produce MFC, as it is not required to pre-treat these fines in the PFI mill. None of the fines caused any operational issues during homogenization. The DAF Fines were passed through the homogenizer at even increased solid consistencies of 0.7 wt. % and 1 wt. %. Even at those higher consistencies, the homogenizer did not

clog or experience any operational difficulties. This is proof that fines are far more suitable starting materials for MFC production, compared to whole pulps.

However, there was a huge contrast in development of fibre properties. Kraft fines were developed most by homogenization, their tensile strength increasing from 67.9 Nm/g to 97.4 Nm/g, while their median diameter reduced from 40 nm to 28 nm. The tensile strength compared well against commercially available MFC, Daicel MFC Celish Grade, which has a tensile strength of 75-80 Nm/g and a median diameter of 75 nm. This suggests that Kraft fines are an adequate substitute for commercially available MFC without the need for additional energy input. It is noteworthy that, although commercial MFC has undergone additional mechanical treatment, it is only 10 to 18% higher in tensile strength than Kraft fines.

With respect to fines from a TMP mill, DAF fines seemed to be the most suitable option if the mill is considering producing MFC. From our results, the TMP fines should show better starting tensile strength and develop more efficiently than DAF fines. MFC made from TMP fines will also have lower median diameter compared to DAF fines. However, generating sufficient quantities of TMP fines for MFC production might prove tricky, as fractionating fines out of TMP whole pulp requires diluting the pulp suspension, which means the use of large quantities of water, and requires significant amount of time and energy. Technologies to produce a suitable fines stream from highly refined pulp will be discussed further in this paper. Removing TMP fines from whole pulp would prove unwise as fines contribute to most of the tensile strength in TMP whole pulp, and would prove undesirable for the pulp quality. However, DAF fines would not pose such drawbacks. Collecting whitewater fines is much easier than fractionating TMP fines as they can be efficiently collected using a dissolved air flotation unit. This has been effectively used in TMP mills such as Norske Skog – Boyer, for clarifying their whitewater systems. At the same time, these recovered fines are often considered as waste, owing to their poor quality, and sent to an effluent treatment processes. Therefore, using the DAF fines for MFC production, will be economically positive

Homogenization alone cannot add sufficient strength to DAF fines. It has been shown that refining is a better alternative and when DAF fines are refined prior to homogenization, the strength of DAF fines can be more than doubled while producing a better quality of MFC with median diameters from 14 nm to 19 nm [25]. Simple delignification of these fines could also increase the properties of these fines significantly by removing lignin and extractives from the fibres.

The use of waste fines is not strictly restricted to TMP mills. Just as TMP whitewater fines, Kraft pulp and paper mills have their own waste whitewater streams. Fines, which pass through papermaking forming fabrics, enter process water streams, which are clarified to remove solids (fibres and fillers). Kraft paper mills usually have two such waste fines streams for bleached and unbleached paper, otherwise known as whitepaper clarifier fines and brown paper clarifier fines. It should prove worthwhile to also investigate these fines for MFC production.

### 4.8.4. Separation of fines from refined pulp

Separation of fines from refined pulp has not been easy and economically feasible in the industrial scale. Various fibre fractionators such as Somerville and Bauer-McNett could be used on a lab scale. Fractionators separate fines from larger fibres via a fine mesh that would only allow fines to go through while retaining larger fibres. However, their use is limited to quantification of fines content in refined pulp for fibre quality analysis. Usually, one must dilute the pulp suspension well below 0.5% or even less before fractionating the fines. Otherwise, it would not be possible to separate all the fines efficiently from the longer fibres. This obviously requires large volumes of water and energy to pump water and operate the machinery. Therefore, on a larger scale, it would be unwise to separate fines through fractionation via meshes. However, some other technologies could be used to selectively separate fines from lightly refined pulp.

Dissolved air flotation could be one such technology that could possibly be optimized to selectively float fines away from larger and coarser fibres [22]. This could be achieved by manipulating the size of the air bubbles and the rate of aeration, and warrants further research.

Hydrocyclones, sometimes called 'centrifugal cleaners', could also be another alternative where fines could be taken away from the larger fibres based on the ratio of their centripetal force to fluid resistance [26]. Denser and coarser particles have a higher ratio while light and fine particles have a lower ratio. Therefore, larger fibres would end up at the bottom and can be collected from the underflow or rejects. Overflow or accepts would contain the lighter and finer fibres.

More recently, Madani et al introduced a novel technique to separate fines from coarser fibres. They successfully applied this to separate fines from a semi-bleached Kraft pulp [27] and fractionated a MFC suspension to remove longer fibres [28]. In this method, fibres were separated according to their yield stress under centrifugal force. Fractionation

of fibres according to their coarse or fine nature could be done by carefully selecting the centrifugal force applied on a dilute suspension. Yield stress is defined as the minimum stress needed to move a particle away from a stable suspension or make that particular suspension unstable. If the applied centrifugal force is greater than the yield stress of the particle, it will move away from the suspension towards the direction applied by the centrifugal force. Larger and coarser fibres would have a lower yield stress while smaller and finer fibres would have a higher yield stress. The larger and coarser fibres can be moved away from the suspension by carefully selecting a centrifugal force i.e. rotational speed. Smaller and finer fibres would then remain in suspension, which can be separated out.

### 4.8.5. Homogenization at higher consistencies

DAF fines were homogenized at both 0.25 wt.% and 1.0 wt. %. Higher viscosity of the 1.0 wt. % suspension reduced the flow rate and it took 7.5 minutes to process 500 mL of the suspension while 0.25 wt.% suspension only took 3 minutes. Energy consumption was estimated by calculating the pump work [29] and dividing by the mass flow rate to estimate the energy consumption per unit mass. The results showed that the specific energy consumption can be decreased by increasing the solid consistency. However, the effect is dampened by the increasing viscosity. Although, there is still a reduction in energy with the specific energy consumption estimated to be reduced by 37.5% when the consistency is increased from 0.25 wt. % to 1.0 wt. %.

## 4.9. Conclusions

There are various streams of fines in a newsprint production process, which could be used for MFC production by homogenization. It was possible to homogenize fines for 5 passes at 1000 bar without facing any operational issues. The use of fines was efficient compared to the use of whole pulp which requires mechanical pre-treatment prior to homogenization. TMP whitewater fines recovered using a dissolved air flotation unit (DAF) increased their tensile strength from 26.0 Nm/g to 42.6 Nm/g after homogenization, while the median diameter was reduced from 321 nm to 80 nm. TMP fines were able to produce better quality MFC with a tensile strength of 48.6 Nm/g and a median diameter of 36 nm. However, Kraft fines were superior to any TMP fines due to their chemical composition and lack of surface contamination. Homogenization of Kraft fines produced a MFC with tensile strength of 97.4 Nm/g and median diameter of 28 nm. Further research is necessary to find energy efficient fractionation and separation of fines. It was estimated

that an energy reduction of ~37.5% is possible by increasing the solid consistency from 0.25 wt. % to 1.0 wt. %.

## 4.10. Acknowledgments

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## **Chapter 5**

**Development of Cellulose Nanofibre Quality  
with Mechanical Energy: Effect of Starting  
Material**

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## Preface

Cellulose nanofibres could be developed from various raw materials with the addition of mechanical energy. However, different raw materials respond to the mechanical energy addition on different levels, depending on their chemical compositions. In this Chapter, we studied three different raw materials: Bleached Eucalyptus kraft pulp, commercially available microfibrillated cellulose made of cotton, and whitewater fines from a Radiata Pine thermomechanical pulping mill, respond to the addition of mechanical energy via refining and/or homogenization. Nanofibre quality was assessed by scanning electron microscopy and sedimentation experiment to estimate aspect ratio. Nanofibres were then added to Radiata Pine newsprint furnish at 1:9 ratio. Sheet properties were assessed and the effect of different nanofibre addition was evaluated.

This Chapter addressed objectives A2 and A4.

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# Chapter 5 – Development of Cellulose Nanofibre Quality with Mechanical Energy: Effect of Starting Material

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# Chapter 5 – Development of Cellulose Nanofibre Quality with Mechanical Energy: Effect of Starting Material

Thilina Gunawardhana<sup>1</sup>, Praveena Raj<sup>1</sup>, Swambabu Varanasi<sup>1</sup>, Gil Garnier<sup>1</sup>, Antonio Patti<sup>2</sup>, Warren Batchelor<sup>1\*</sup>

<sup>1</sup>BioResource Processing Research Institute of Australia (BioPRIA), Department of Chemical Engineering, Monash University, Clayton 3800, VIC, Australia.

<sup>2</sup>School of Chemistry, Monash University, Clayton 3800, VIC, Australia

\*Corresponding author: warren.batchelor@monash.edu

## 5.1. Abstract

Energy efficient production of nanocellulose fibres is key to establishing this highly-promoted material in an industrial scale. In this work, we attempt to explain how the mechanical energy input the chemical composition of the raw materials affect the quality of nanofibres. Bleached eucalyptus Kraft (BEK) pulp, a commercially available microfibrillated nanocellulose from cotton, and whitewater fines collected from a radiata pine thermomechanical pulping (TMP) mill were used to produce cellulose nanofibres. BEK was the most responsive to mechanical fibrillation due to low crystallinity and it produced high aspect ratio nanofibres, while TMP whitewater fines were the most difficult to process and resulted in low aspect ratio nanofibres. Nanofibres were then added to TMP newsprint to evaluate the effect on tensile strength. Nanofibers produced from BEK were able to increase the tensile strength the most, while nanofibres from TMP whitewater fines had the least effect. The results showed that a high aspect ratio and a surface chemical composition favouring more hydrogen bonds i.e. pure cellulose, are the key criteria when selecting nanofibre for strength improvement in paper.

## 5.2. Introduction

Nanocellulose have been widely promoted as an environmentally friendly material to replace fossil fuel derived polymers such as polythene. Some of the highly-promoted characteristics of nanocellulose include high specific surface area, high strength, high thermal coefficient, low toxicity and biodegradability, transparency and excellent barrier properties [1-4].

Many different processes can be used to produce nanocellulose and they are being extensively reviewed in literature [2, 3, 5, 6]. Typically, they are produced by subjecting fibres to high shear forces for extensive fibrillation. Turbak et al. 1983 and Herrick et al. 1983 suggested the name “microfibrillated cellulose” [7-9]. The dimensions of various nanocellulose materials are defined as follows; microfibrillated cellulose (MFC) have a diameter of 10-100 nm, with a length of more than 1  $\mu\text{m}$ . Nanofibrillated cellulose (NFC), also known as nanocellulose (NC), have a diameter of 4–20 nm, with a length of more than 1  $\mu\text{m}$  [10]. Both MFC and NFC typically have high aspect ratios; length/diameter.

Different mechanical treatment processes are used to produce nanocellulose. Most popular method is to subject various plant materials to high pressure homogenization [7, 9, 11]. Other processes such as microfluidization [12, 13] and micro-grinding [12], and cryocrushing [14].

A variety of raw materials can be used to produce nanocellulose. The most widely used is wood which is readily available as pulp from papermaking process. Bleached Kraft pulp is the most common material to produce nanocellulose [11, 15-17]. Other chemical pulps such as bleached sulphite pulp is used as well [18]. Agricultural products such as cotton [19] and by-products such as rice straw and wheat straw [20] are also used. Most of the raw materials used contain only cellulose either because of a chemical treatment; Kraft and sulphite pulps, or by nature; cotton. Thermomechanical pulp containing cellulose, hemicellulose, and lignin along with other phytochemicals, have been used sparingly in nanocellulose production [11, 21, 22]. Lignin is thought to hinder the fibrillation process and requiring more energy input [11]. Chemical pretreatment or oxidation is used to reduce the energy consumption in nanofibre production. TEMPO mediated oxidation remains the most popular method while carboxymethylation [21], periodate oxidation [23], sulphonation [21, 24] and enzymatic hydrolysis using endoglucanase [25] are also used. Chemically treated fibres can be fibrillated more efficiently using the earlier mentioned mechanical processes.

As discussed earlier, many different mechanical processes in combination with chemical treatment, and many raw materials can be used to produce nanocellulose. This makes it even more critical to properly characterize nanocellulose. As with any other nanomaterial, the dimensions of nanocellulose; the length and the diameter, are the most critical piece of information. Different electron microscopic techniques such as scanning electron microscopy and transmission electron microscopy (TEM) can be used to measure the diameter via image analysis [26-29]. Popular image analysis software such as ImageJ

can be used for this purpose. Length of the nanocellulose, however, can't be measured by using electron microscopy as it is almost impossible to find and separate the ends of each individual fibre and sometimes it is impossible to see the entire length of the fibre unless a low magnification is used, in which identification of nanoscale diameters is not possible.

An indirect way to calculate the length of nanofibres is to first estimate the aspect ratio. Aspect ratio can be used to calculate the length by multiplying by the diameter. Typical technique to estimate the aspect ratio is to find the gel point of the fibre suspension. Gel point is defined as the lowest solids content at which a fibre suspension forms a continuously connected network and is related to the fibre aspect ratio via a series of equation proposed by Martinez et al. 2001 [30]. Later, this method was adapted by Zhang et al 2012 for nanofibre suspensions [29].

In this work, we used different raw materials to produce nanocellulose via high pressure homogenization. Then we characterized those nanofibre suspensions via electron microscopy, and gel point to assess the effect of chemical composition of the raw materials on nanofibre production. Then, we attempted to relate the aspect ratio and the chemical composition, to strength enhancing ability of these nanofibres in newsprint.

### 5.3. Materials

Three distinct types of lignocellulose feedstock were used for nanofibre production. The first is never-dried bleached eucalypt Kraft pulp (BEK) which was supplied from the Australian Paper Maryvale, Victoria. Secondly, commercial microfibrillated cellulose (MFC) was supplied from DAICEL Chemical Industries Limited (grade Celish KY-100S). Whitewater fines from a radiata pine thermomechanical pulp (TMP) mill were collected from Norske Skog Paper Mills (Australia) at Boyer, Tasmania, using a dissolved air flotation unit to separate the fines from the suspension. The extractive content measured by sample loss after three successive extractions each in ethanol and hexane was 11.9%. Bleached TMP pulp from radiata pine with 160 CSF freeness, collected never-dried from the same mill, was used as the base pulp for nanofibre addition. All pulp was stored at 4°C until used.

### 5.4. Methodology

#### 5.4.1. Nanofibre production

Fibres were treated with different levels to evaluate the effect of energy input. Table 5.1 summarizes the different homogenization conditions used. BEK fibres were refined for

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10000 revs in a PFI mill prior to homogenization to avoid plugging. No such treatment was necessary for both commercial MFC and TMP whitewater fines. All samples were homogenised at 0.3 wt%.

**Table 5.1.** Different homogenization conditions for nanofibre production for quality testing

Fibre type	Nanofibre Characterisation		Nanofibre addition into TMP furnish	
	Homogenizer pressure (bar)	Number of passes	Homogenizer pressure (bar)	Number of passes
Bleached Eucalyptus Kraft (BEK) Pulp	500	1	1000	5
	1000	1		
	1000	3		
	1000	5		
Commercial MFC	500	1	1000	5
	1000	1		
	1000	5		
TMP whitewater fines	1000	5	1000	5
	1000	10		
	1000	15		
	1000	20		

Specific energy consumption coefficients derived by Kerekes et al. 2005 [31] were used to estimate the energy consumption in the PFI mill. The coefficient for bleached Eucalyptus Kraft pulp is 0.15 kWh/Tonne-rev.

Specific energy consumption of the homogenizer was estimated theoretical by calculating the pump work. The efficiency in the drive motor and energy losses were not taken into consideration. The pump work is calculated as below.

$$W = \frac{P - P_{atm}}{\rho} \quad (1)$$

Where, P is the homogenizer pressure,  $P_{atm}$  is the atmospheric pressure and  $\rho$  is the density of the suspension. The suspensions used for homogenization are very dilute at

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0.25 wt%. Therefore, the density of the suspension was assumed to be the same as of water which is 1000 kg/m<sup>3</sup>.

#### 5.4.2. Nanofibre characterisation

Aspect ratio (length/diameter) after each treatment stage was evaluated by estimating the gel point of the fibre suspension through sedimentation experiment [32, 33]. In this method, a series of dilute suspensions, often from 0.01 – 0.1 wt% suspensions of MFC are prepared and poured equal volumes to a series of measuring cylinders, and the initial height of the suspension is recorded. The suspensions were allowed to settle > 48 hours and final sediment heights were measured. The ratio of final sediment height to initial suspension height is plotted against the consistency of the suspension, and a quadratic fit is found. The linear coefficient of this quadratic equation gives the gel point consistency which is then used to estimate the average aspect ratio of the fibres using a set of empirical equations as given in Varanasi et al. Scanning electron microscopy (SEM) images of the different nanofibre suspensions were taken using an FEI Nova NanoSEM to analyse the development of nanofibres. SEM samples were prepared by evaporating a droplet for a very dilute (~0.001 wt. %) suspension on a silicon chip mounted on carbon tab. Once dried, samples were coated with 2 nm layer of Iridium. Images were acquired at different voltages (3 – 10 kV) and different magnifications (5000 – 100000X). Fibre diameters were analysed using ImageJ software by taking measurements from images with more than 30000X magnification. All the fibres in each selected image was measured and more than 100 fibres were measured altogether, for each sample.

Both sides of the composite sheets were also analysed under the SEM to evaluate the incorporation of nanofibres into the TMP furnish. SEM samples were prepared by cutting small rectangular pieces of each sheet and sticking it on a carbon tab mounted on a SEM sample stub. Samples were coated with 2 nm layer of Iridium prior to observation under 3 kV and 5000 – 10000X magnifications.

#### 5.4.3. Sheet Making

Nanofibres were mixed with bleached radiata pine TMP pulp in the ratio of 1:9 (10% addition of nanofibres) and mixed for 1 hour prior to sheet making. A 10% addition rate was selected in order to maximize the sensitivity of the effects and to enable effective means of comparing each nanofibre type to each other. The consistency of the final suspension was adjusted to 0.2 wt. % and 60 gsm sheets were made by taking 600 g of the suspension. No retention aid was added, and all the sheets were made on Whatman Grade 541 filter paper using a standard automatic British Hand Sheet Maker. Drainage

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time (seconds) was measured from the start of the “Drain” cycle in the hand sheet maker until the sheet is fully drained. This was done by visual inspection and the sheet was considered to be ‘fully drained’ when the water is disappeared from whole surface of the sheet. Sheets were air dried under restraint in a conditioned testing room (25 °C and 50% RH), and stored there until further use. Sheets from just unhomogenized TMP whitewater fines were also made for comparison.

### 5.4.4. Sheet Testing

Oven dry weight (g) was measured by measuring the total weight of sheets after drying them at 105 °C for 4 hours. Sheets were measured with balance with 0.001g sensitivity.

Thickness ( $\mu\text{m}$ ) was measured using an L&W Micrometer 51. 20 measurements were taken from each sheet. Air permeability ( $\mu\text{m}/\text{Pa}\cdot\text{S}$ ) was measured using an L&W Air Permeance Tester. 10 measurements were taken from each sheet to capture the whole surface the sheet. Tensile testing was done on 15 mm wide strips and a 100 mm test span with 10 mm/min extension rate, using an Instron 5566 Tensile Tester. Force (N) and elongation at break (mm) were recorded.

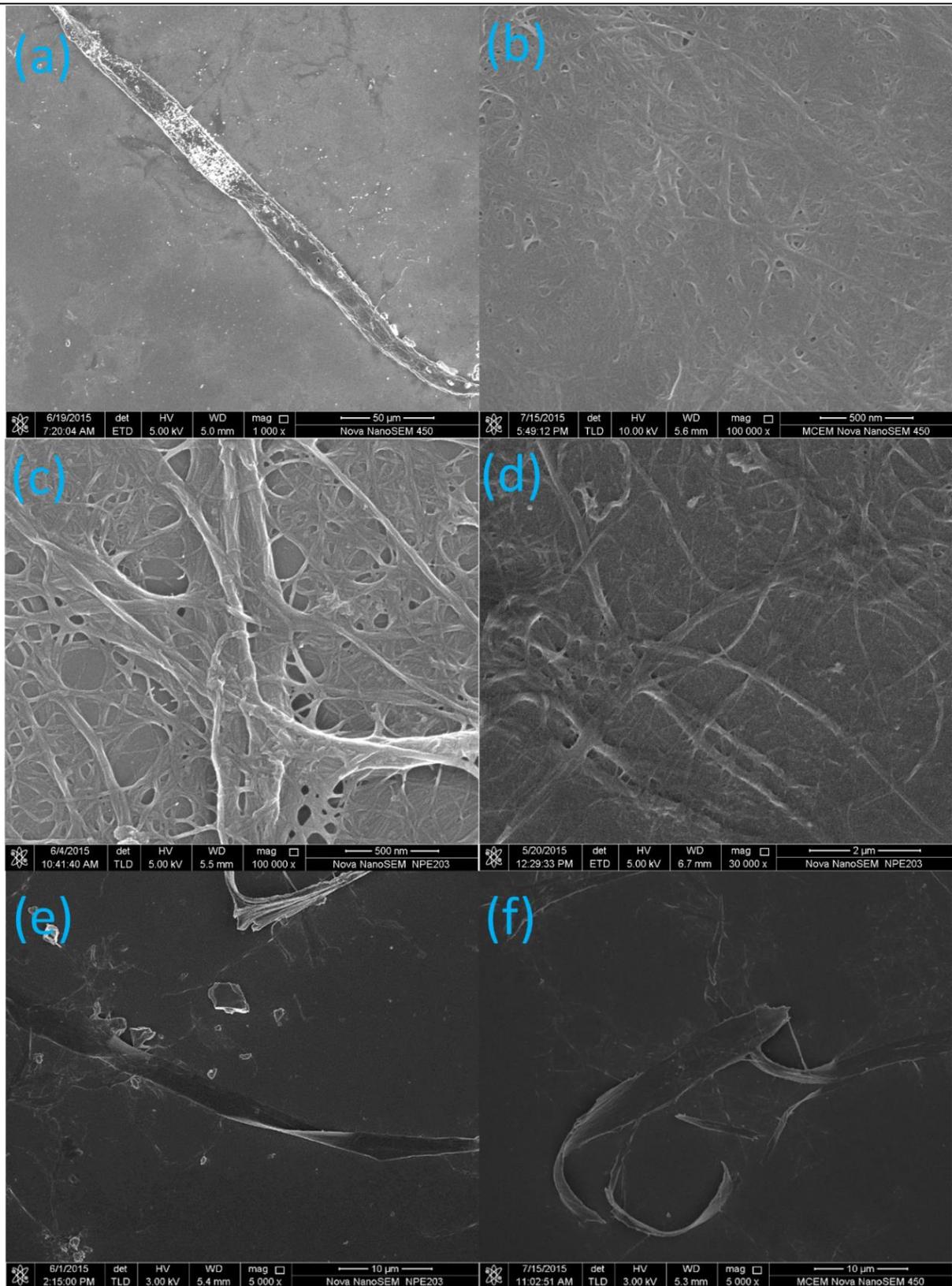
## 5.5. Results

### 5.5.1. Nanofibre and fibre characterisation

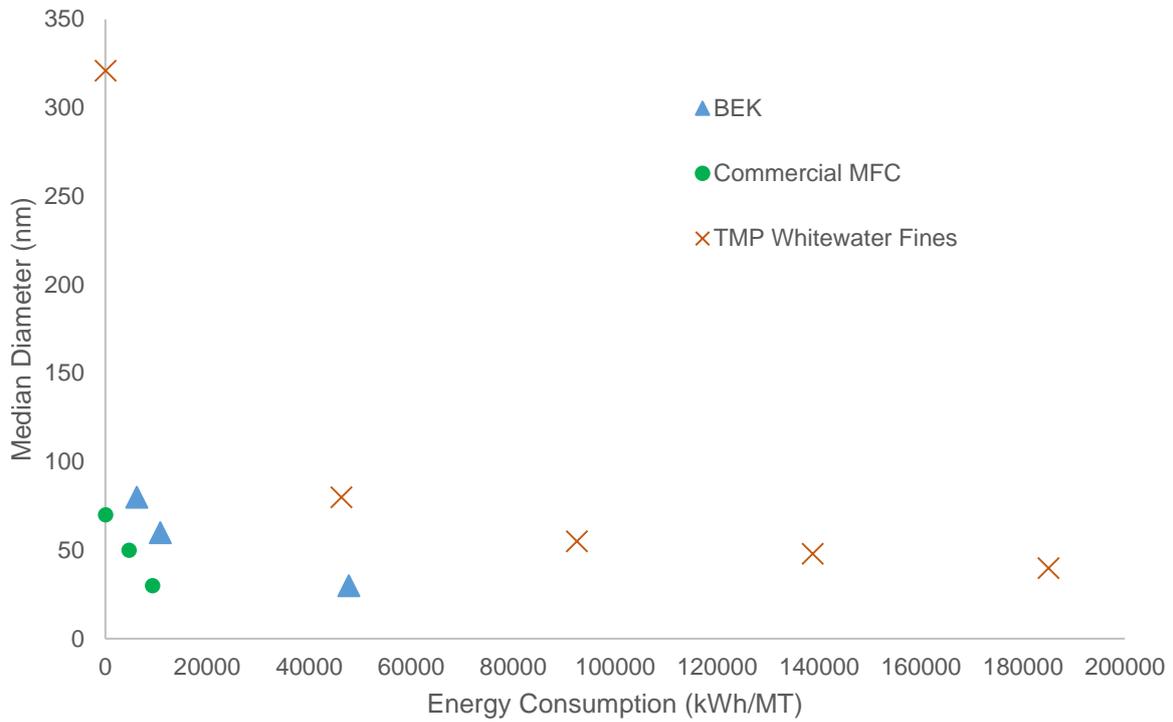
The initial diameter of the BEK fibres of over 10  $\mu\text{m}$  is not shown. However, with the continued addition of energy, the fibre diameter reduces rapidly. When BEK is PFI refined, and homogenized for 1 pass at 500 bar, the median diameter reduces to 80 nm. This further reduces to 30 nm when BEK is homogenized to 5 passes at 1000 bar (Figure 5.1). Overall, BEK responds to mechanical treatment quite efficiently.

The commercial MFC has a relatively low median diameter of 70 nm. The median diameter reduces steadily with energy input. A single pass at 500 bar through the homogenizer results in a median diameter of 50 nm, while treating at 1000 bar reduces the diameter to 30 nm.

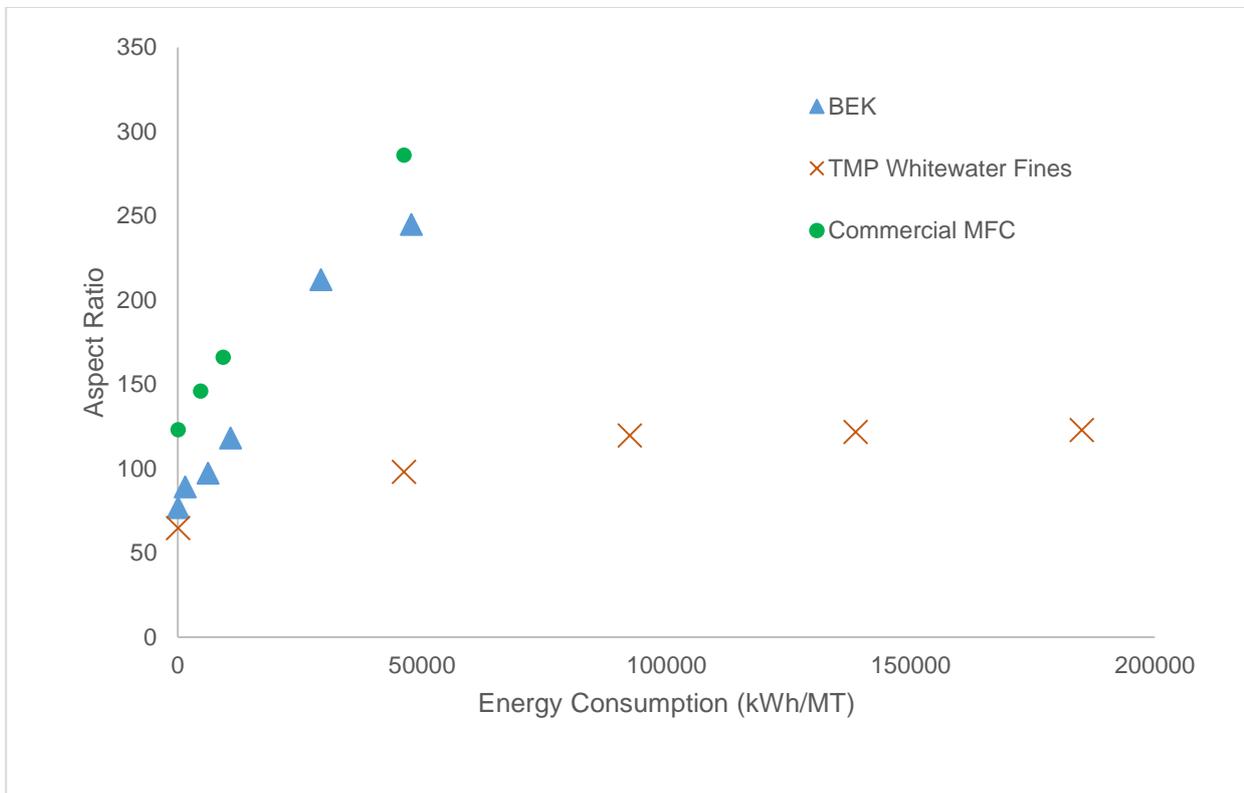
TMP whitewater fines were the most difficult to process. The median diameter was reduced from 321 nm to 80 nm after 5 passes through the homogenizer, but only decreased slowly with further processing. Even after 20 passes through the homogenizer, the median diameter was only reduced to 40 nm. The SEM image (Figure 5.2) of TMP whitewater fines after 20 passes shows that there were still larger fibres that had not been broken down.



**Figure 5.1.** SEM images of various fibres at different treatment levels; (a) BEK after PFI refining, (b) BEK after PFI and 5 passes through the homogenizer at 1000 bar, (c) Commercial MFC before homogenization, (d) Commercial MFC after homogenization for 1 pass at 1000 bar, (e) TMP whitewater fines before homogenization, (d) TMP whitewater fines after homogenization for 20 passes at 1000 bar



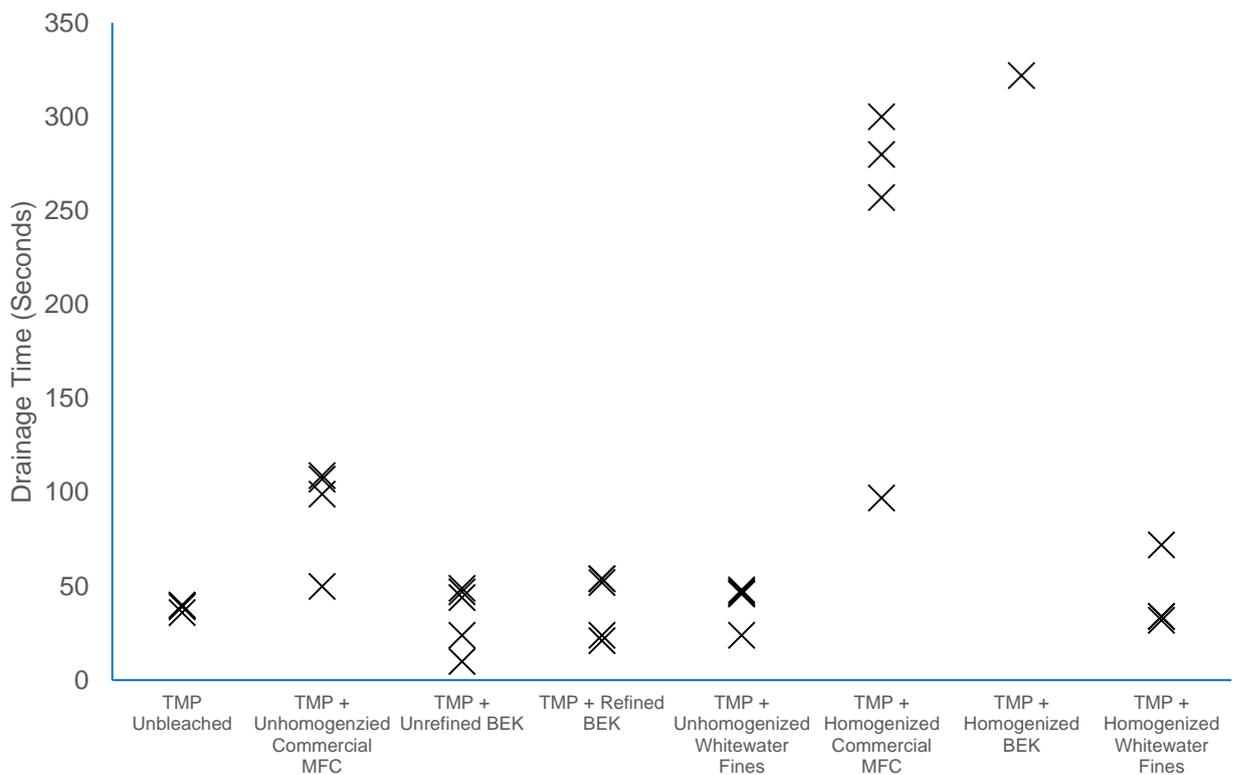
**Figure 5.2.** Change in median diameter with energy input. BEK starting diameter of 10,000 nm (10  $\mu$ m) is not shown



**Figure 5.3.** Aspect ratio of different nanofibres

Aspect ratio is evaluated using the gel point experiment. The gel point is the lowest solids content at which a fibre suspension forms a continuously connected network and is related to the fibre aspect ratio [32, 33]. The aspect ratio of all three feedstocks initially increased with increasing homogenisation energy, showing that the fibre delamination dominated over fibre shortening. The rate of increase of the aspect ratio was also inversely related to the rate of decrease of fibre diameter. The BEK fibres were the easiest to separate due to its high cellulose content and higher fraction of amorphous cellulose. Both the commercial MFC and the TMP fines were difficult to process, but for different reasons. In the case of the commercial MFC, the strongly bonded crystalline cellulose structure was difficult to separate, while for the TMP fines, the high residual lignin content made the fibres highly resistant to breakdown.

### 5.5.2. Sheet making



**Figure 5.4.** Drainage time of composite handsheets

The drainage time of the composite papers showed significant variance between sheets, for reasons, which are currently unclear. The use of the filter papers allowed for close to 100% retention, as the basis weight of all the sheets was very close to 60 gsm.

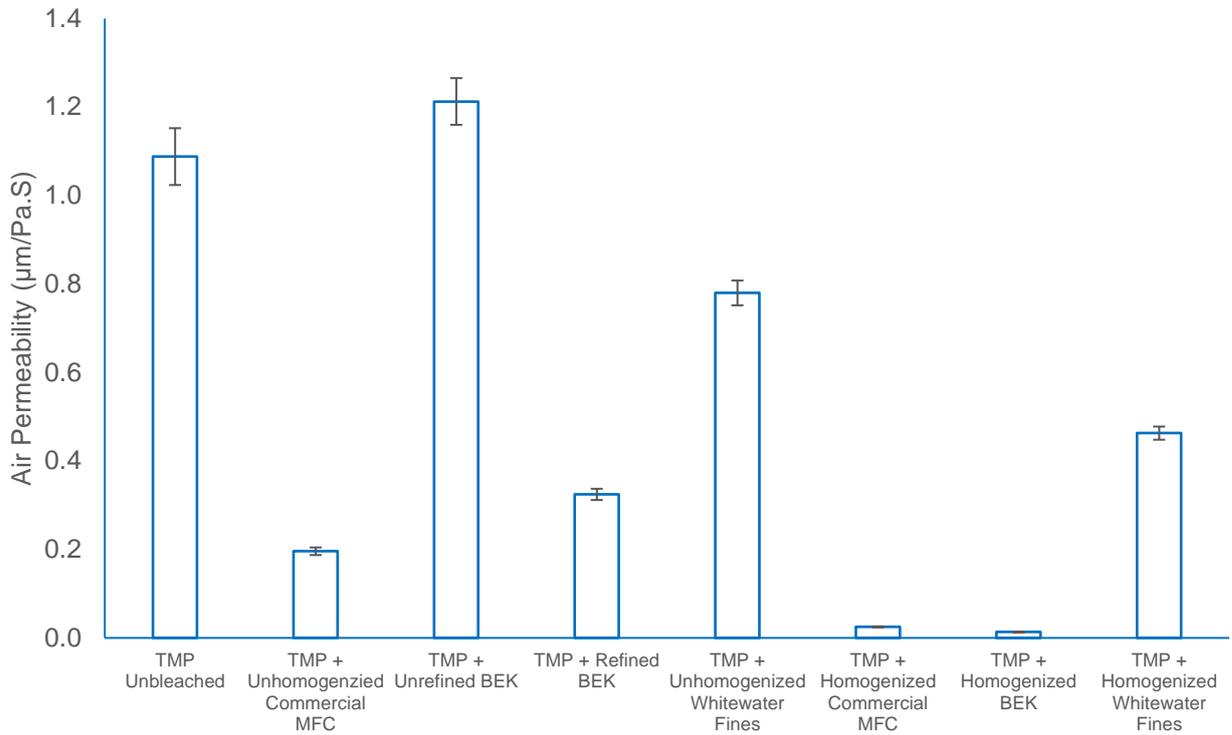
However, there is a strong pattern across the different types of composite papers. Addition of unhomogenized commercial MFC to TMP furnish almost doubles the drainage time. This is due to two reasons; tight pore structure with the addition of finer material and

more hydrophilic nature of commercial MFC, both increasing the drainage time. Addition of homogenized commercial MFC increases the drainage time by almost 6-fold. This is still due to the above-mentioned reasons. However, the effects are multiplied because of the even finer material and increased surface area. The addition of refined and unrefined BEK did not increase the drainage time. The unrefined BEK fibres contain large fibres and the number of fines is negligible. Therefore, the addition of unrefined BEK fibres would have been expected to have reduced the drainage time. In contrast, refined fibres do contain significant number of fines. However, the number of fines would be significantly lower than that TMP pulp, which usually contain 30-40% of fines by weight. Therefore, it was not expected the addition of refined BEK would not have increased the drainage time, and this reflected in results as well. However, homogenization of refined BEK increases the drainage time quite significantly. Some of the sheets made showed extremely high drainage times, more than 20 minutes, for yet unknown reason. Only the fastest is shown here. The increase in drainage time is due to the presence of hydrophilic nanofibres with high specific surface area. The addition of both unhomogenized and homogenized TMP whitewater fines does not change the drainage time significantly, although it would have been expected that the reduction in fibre diameter after homogenisation should have further increased the drainage time. Overall, the results show that the only TMP derived nanofibre can be added without significantly impacting drainage, under the conditions tested here.

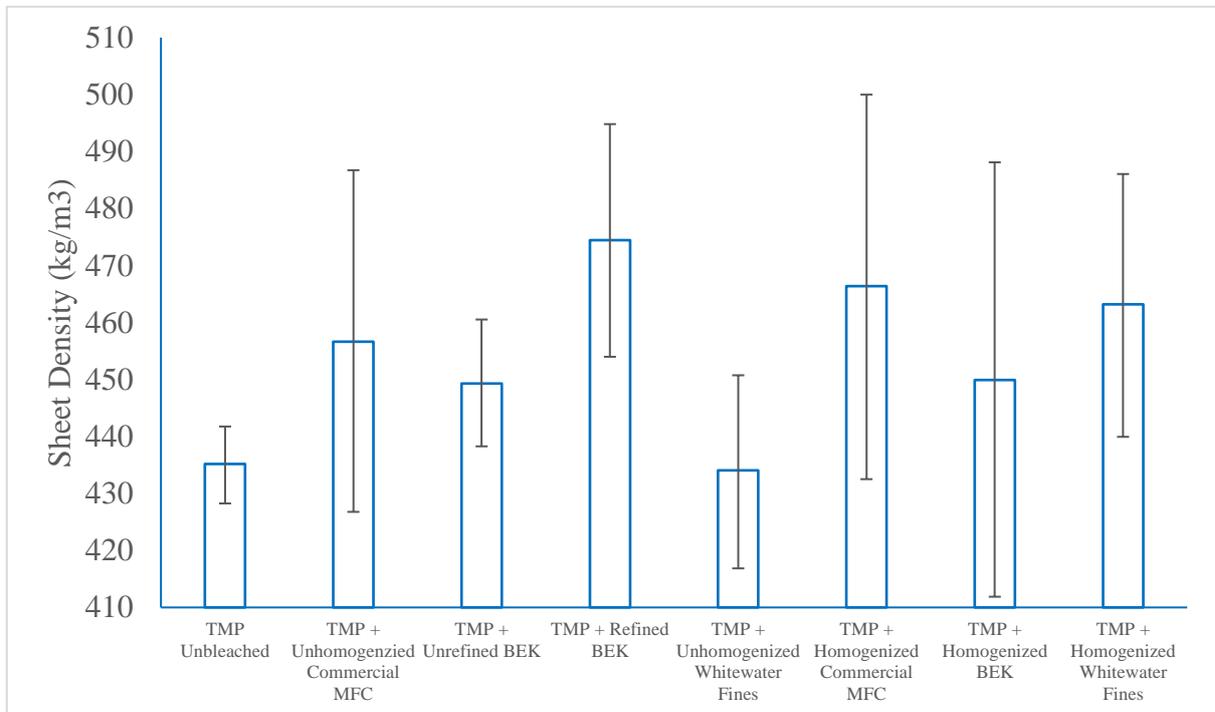
### 5.5.3. Sheet properties

Air permeability data closely correlates with that of drainage time. The addition of unhomogenized MFC reduces the air permeability due to tighter pore structure, and homogenized MFC reduces the air permeability even further. This could be explained by the reduction in pore size after the addition of MFC. The addition of unrefined BEK does increase the air permeability slightly. This could be explained by the increase in pore size due to replacing 10% of the large fibres and fines by 10% of just larger fibres. However, in contradiction to the drainage time data, the addition of refined BEK does decrease the air permeability indicating that pore sizes are getting smaller. As expected, homogenized refined BEK does decrease the air permeability even lower than homogenized MFC. Unhomogenized whitewater fines however, did not reduce the air permeability as compared to both refined BEK and unhomogenized commercial MFC. This is due to the presence of large fibres. Even when homogenized whitewater fines are added into the TMP furnish, air permeability remained significantly higher than both homogenized BEK and commercial MFC. As observed in the SEM images, even with 20 passes through the

homogenizer, large fibres are visible and this leads to large pore size which results in higher air permeability.

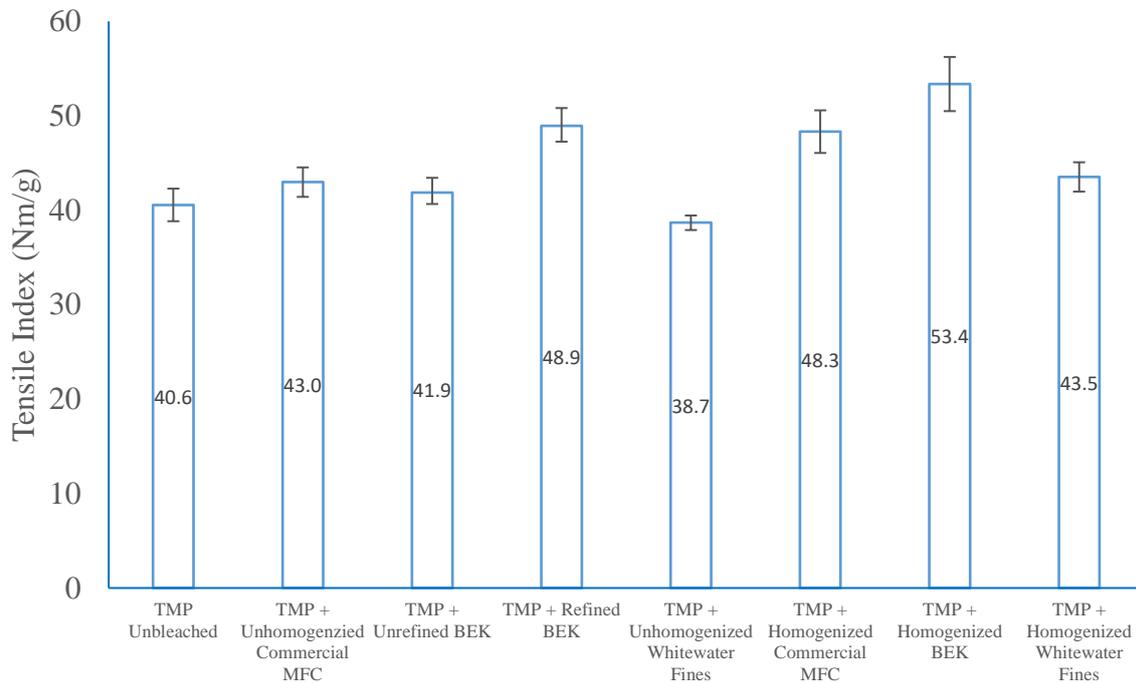


**Figure 5.5.** Air permeability of composite handsheets. The error bars represent the 95% confidence intervals



**Figure 5.6.** Sheet density of composite sheets. The error bars represent the 95% confidence intervals

Sheet density does not vary by much across all the types of composite papers. This is not surprising given that only 10% of the coarse structure of TMP furnish is being substituted.

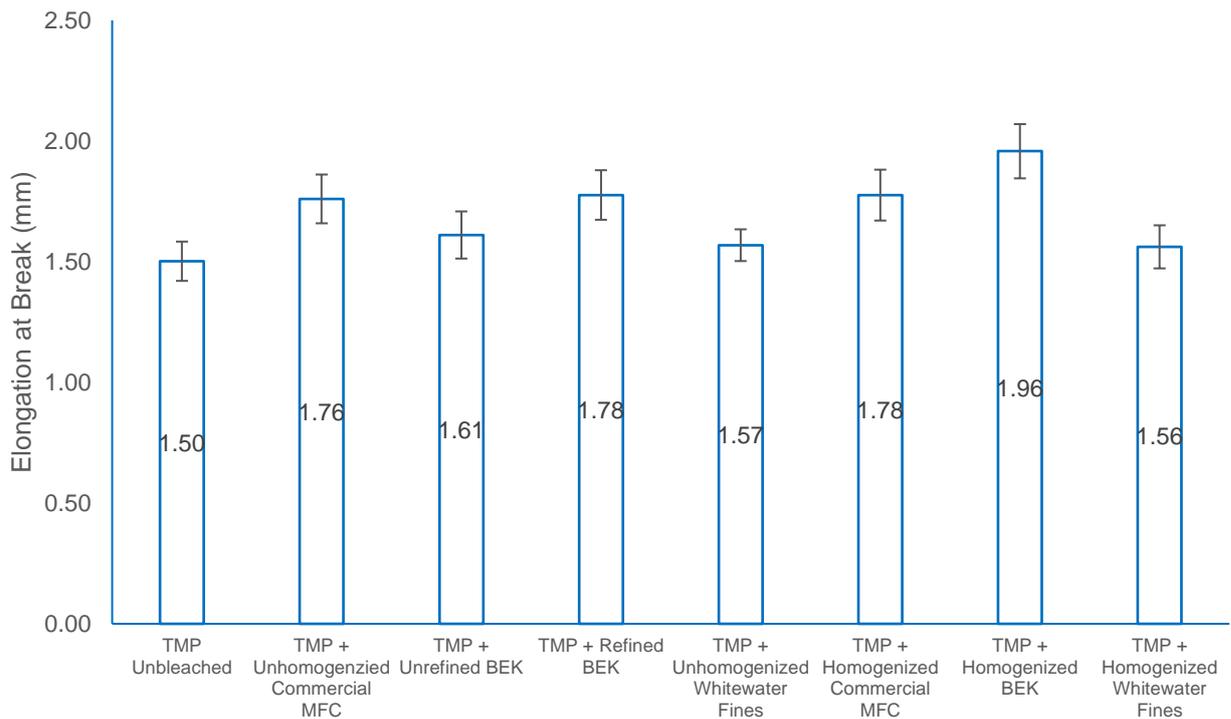


**Figure 5.7.** Tensile indices of composite handsheets. The error bars represent the 95% confidence intervals

Tensile strength results are very interesting. The addition of unhomogenized commercial MFC increased the tensile index of the sheets slightly. Predictably, the addition of homogenized MFC increased the tensile index by 19%. Unrefined BEK does not improve the tensile index much. However, refined BEK increased the tensile index by 20%. This is of the same level as resulted by homogenized MFC. Homogenized refined BEK increased the tensile index up to 53.4 Nm/g, which is ~ 32% gain. Commercial MFC and refined BEK have similar aspect ratios. However, refined BEK develops more efficiently in homogenization with significantly reduced fibre diameter. Therefore, homogenized BEK has much higher specific surface area than homogenized MFC. This increases the relative bonded area between the TMP furnish and the nanofibres resulting in higher increase in tensile index.

Interestingly, the addition of whitewater fines had a negative effect on the tensile index. This is probably due to the nature of TMP whitewater fines. TMP whitewater fines are circulated in the process for many passes. During this process, many hydrophobic extractives are adsorbed on to the surface. Furthermore, the whitewater fines used in this

experiment are collected from float of a dissolved air flotation (DAF) unit. In this process, additional hydrophobic extractives are adsorbed on to the surface and fibres have an extractive content of 11.9 wt. %. Adsorption of extractives hinders the fibre-fibre hydrogen bonding which reflected in tensile index. However, when homogenized TMP whitewater fines are added, tensile index increases and matches to the level achieved by unhomogenized commercial MFC. Increase in aspect ratio and reduced hindrances from hydrophobic extractives via increased surface area are both seem to contributing to the increase in tensile index. However, the aspect ratio does not increase as much as the homogenized BEK. This could be due to both lower aspect ratio in homogenized TMP whitewater fines and the surface chemical composition. This is reflected in the low tensile strength of unhomogenized TMP whitewater fines, which has a tensile index of 25.7 Nm/g. The lignin, and adsorbed hydrophobic extractives on the surface of TMP whitewater fines are reducing the amount of hydrogen bonds between fibres. Therefore, it results in much lower increase in tensile index.



**Figure 5.8.** Elongation at break of composite handsheets. The error bars represent the 95% confidence intervals.

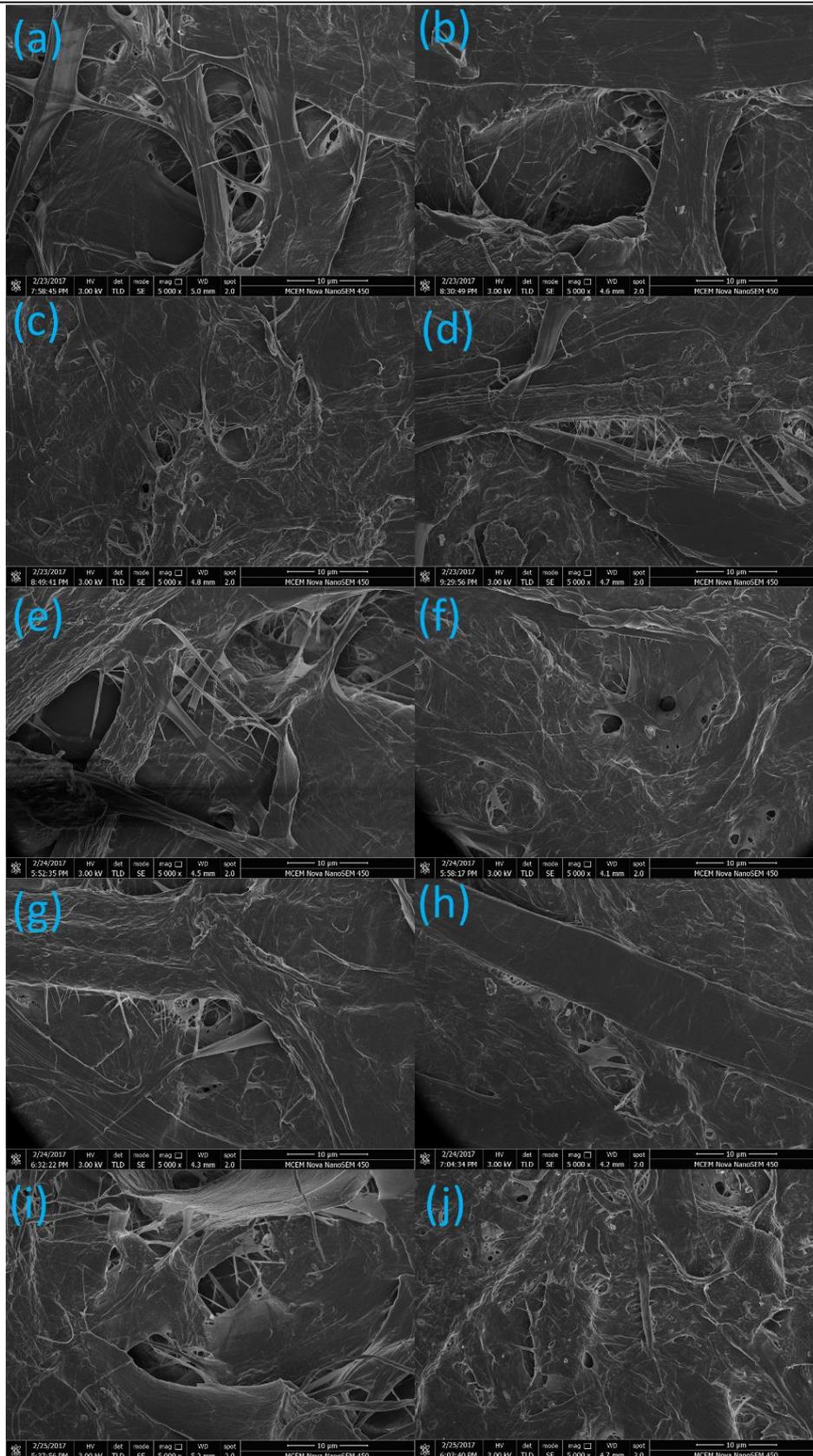
Elongation at break follows a very similar pattern to that of tensile index. This is quite typical behaviour for fibre networks where more strength often is associated with greater stretch at break.

Figures 5.9 and 5.10 show both sides of TMP bleached base handsheets and different composite handsheets. Filter paper side is the bottom of the sheet when the suspension is still draining and the blotting paper side is the top side. Both sides were observed under the SEM to understand how the nanofibres distribute within the handsheet. TMP handsheets show large fibres and large pores in both sides. Some smaller fibres, fines, can be identified as well.

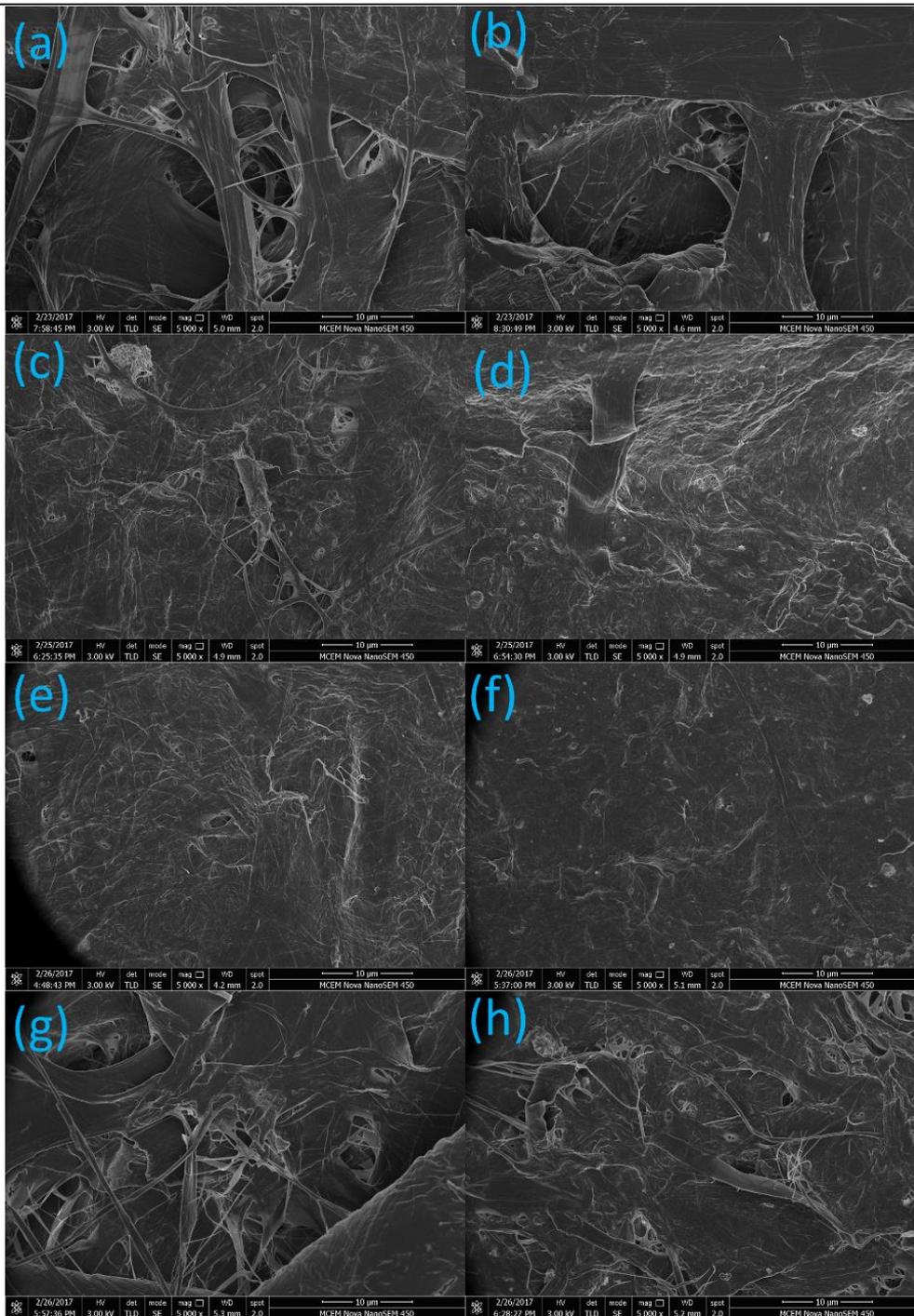
Figures 5.9 (c) and (d) show the handsheets containing unhomogenized MFC. More of the smaller fibres can be identified and some can even be seen acting as bridges between large fibres. These fibre-fibre bonding contribute to the increase in tensile index. It could also be observed that more of the smaller fibres can be identified in the bottom side of the sheet. The smaller fines and MFC are retained on the filter paper and it leads to a smoother surface, which is observable in the SEM photos. This could be observed in other types of handsheets as well. We could identify more nanofibres present in the handsheet (see figure 5.10 (c) and (d)). We can also notice that large pores in the surface are disappearing. This is in line with the observations made in both drainage time and air permeability.

Addition of unrefined BEK does not change the sheet surface due to being made of large fibres. When refined BEK is added, we could see the small fines acting as bridges between larger fibres. This effect is further intensified with homogenized BEK. The SEM photos show sheet surfaces with almost no big pores. Again, these observations justify the results in drainage time and air permeability measurements.

The addition of TMP whitewater fines however, does not produce smoother surfaces as was the case with commercial MFC and BEK. Even with the addition of homogenized whitewater fines, we could see relatively large pores on the blotting paper side and to a lesser extent in the filter paper side. Nevertheless, this is not totally surprising as drainage time and air permeability both suggested that the pore structure in TMP-homogenized whitewater fines composite sheets is not as tight in the sheets containing homogenized MFC and BEK.



**Figure 5.9.** SEM images of the composite sheets before homogenization (L- blotting paper side (BPS), R- filter paper side (FPS)) ; (a) &(b) TMP base sheet, (c) & (d) TMP + Commercial MFC (e) & (f) TMP + BEK Unrefined, (g) & (h) TMP + BEK Refined (i) & (j) TMP + Whitewater Fines



**Figure 5.10.** SEM images of the composite sheets after homogenization (L- blotting paper side (BPS), R- filter paper side (FPS)); (a) & (b) TMP base sheet (c) & (d) TMP + Commercial MFC (e) & (f) TMP + BEK Refined (g) & (h) TMP + Whitewater Fines

## 5.6. Discussion

### 5.6.1. Nanofibre production

Both diameter calculations through SEM images and aspect ratio through gel point experiment give us a detailed narrative of nanofibre production. BEK was the most responsive to mechanical treatment as very large fibres (diameter of 10  $\mu\text{m}$ ) were broken down to nanofibres (diameter of 30 nm) after PFI refining and 5 passes through the homogenizer. Commercial MFC was less efficiently broken down with mechanical energy in comparison to BEK. Both materials have a majority of cellulose. However, commercial MFC has a higher crystallinity index of 78 than BEK which has a crystallinity index of only 66 [33]. The more crystalline commercial MFC makes fibrillation difficult, and explains why BEK breaks down more quickly under homogenisation.

On the other hand, TMP whitewater fines are the least responsive of the three starting materials. Rate of fibrillation is only moderate and further slows down with increased number of passes through the homogenizer. This could be explained by the chemical composition of these fines. Typically, TMP fibres contain high levels of lignin, 30 – 40%. Whitewater fines have higher lignin levels than other TMP fibres due to the enrichment by ray parenchyma cells [34]. The presence of lignin hinders fibrillation. In fact, ray parenchyma cells and cell fractions are resistant to break down by any mechanical fibrillation processes [34]. All these reasons contribute to the observed low response to energy addition.

As a result of the varied levels of fibrillation, nanofibres produced from both BEK and commercial MFC after 5 passes through the homogenizer are relatively high, while whitewater fines yielding nanofibres of low aspect ratio.

### 5.6.2. Addition of nanofibres into TMP furnish

The main objective of this study was to study the effects of nanofibre addition on tensile strength of TMP furnish. The tensile strength is affected by many factors and best described by the modified Page equation (See equation 2) [35].

$$\frac{1}{T} = \frac{9}{8Z} + \frac{3w_f}{\tau_b l_f RBA} \quad (2)$$

Where, T is tensile strength, Z is the zero-span strength of the paper reflecting fibre strength,  $\tau_b$  is fibre-fibre bonding,  $w_f$  is width of the fibres,  $l_f$  is length of the fibres, RBA is relative bonded area which is proportional to sheet density.

Sheet density of the composite papers does not change significantly and vary in between 400 – 500 kgm<sup>-3</sup>. Therefore, we could assume that the effects of the sheet density as negligible. The ratio  $w_f/l_f$  is actually the inverse of the aspect ratio ( $l/d$ ) of the fibres. Therefore, according to the Page equation, the tensile strength of the sheet is directly related to the aspect ratio of the fibres.

TMP unbleached fibres have an aspect ratio of 83 and the sheets have a tensile index of 40.6 Nm/g. The maximum increase in tensile strength is from the addition of homogenized BEK. The increase effected by the addition of homogenized MFC is smaller than that of homogenized BEK. However, statistical analysis show that they are not significantly different. The higher tensile strength effected by the addition of both these fibres can be related to the high aspect ratio. However, the addition of refined BEK also increases the tensile index to the similar level. This might be due to the favourable bonding in TMP & Refined BEK mixture, rather than the aspect ratio of refined BEK.

When whitewater fines are added, the tensile index decreased. As discussed earlier, these whitewater fines have high lignin content and hydrophobic extractives in their surface. This hinders the hydrogen bonds, which leads to decreased fibre-fibre bonding,  $\tau_b$ . According to Page equation, tensile strength is directly proportional to  $\tau_b$ . Also, the whitewater fines have very low aspect ratio of 65 and the tensile index is decreased when these low aspect ratio fibres are added. Homogenization of whitewater fines increases the aspect ratio to 98, which is reflected in recovered and increased tensile index. It is evident that energy addition can improve the quality of these fines which would otherwise be considered as detrimental when added to TMP furnish. It is also worth noticing that drainage time is not affected by the addition of homogenized whitewater fines, this would be definitely advantageous in mill scale paper production.

## 5.7. Conclusion

The results in nanofibre production shows that the chemical composition is key factor determining the efficiency of nanofibre production. Higher lignin content in fibres essentially mean additional energy input is needed to produce nanofibres. The aspect ratio and chemical composition of the nanofibres are the key criteria, which determine an effective nanofibre for strength enhancement in paper.

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## Chapter 6

Upgrading Waste Whitewater Fines from a  
*Pinus Radiata* Thermomechanical Pulping Mill

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## Preface

Whitewater fines from thermomechanical pulping mills are usually considered as a waste material because of their poor quality. These fines could be added back to the newsprint to save material and money, if we could upgrade them back to the desired quality. In this Chapter, we look into the possibility of upgrading whitewater fines using existing refiners in a thermomechanical pulping mill. Whitewater fines were refined using a PFI mill and a lab-scale single-disc refiner prior to analysing fibre and sheet properties. Mechanical energy addition was continued using a homogenizer to evaluate the possibility of producing microfibrillated cellulose from whitewater fines. Scanning electron microscopy was used to analyse the quality of microfibrillated cellulose produced.

This chapter addresses objectives A1, A2 and A3.

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# Chapter 6 – Upgrading Waste Whitewater Fines from a Pinus Radiata Thermomechanical Pulping Mill

Thilina Gunawardhana<sup>1</sup>, Paul Banham<sup>2</sup>, Desmond E. Richardson<sup>2</sup>, Antonio F. Patti<sup>3</sup>, Warren Batchelor<sup>1</sup>

<sup>1</sup>Bioresource Processing Institute of Australia (BioPRIA), Department of Chemical Engineering, Monash University, Clayton VIC 3800, Australia

<sup>2</sup>Norske Skog Paper Mills (Australia), Boyer, TAS 7140, Australia

<sup>3</sup>School of Chemistry, Monash University, Clayton VIC 3800, Australia

Corresponding Author: [warren.batchelor@monash.edu](mailto:warren.batchelor@monash.edu)

## 6.1. Summary

The pulp and paper industry is very efficient in utilizing its wood resource. However, due to the large amounts of resource used, waste from pulp and paper industry is significant in both its quantity and the opportunities it provides. However, fibrous waste has typically only been used for heat recovery, direct land application or separated and sent to landfill. In this study, two options were investigated for utilising fine fibrous waste recovered by Dissolved Air Flotation (DAF) treatment of effluent from a thermomechanical pulping mill. 3000 kWh/t of mechanical treatment of the waste fibres increased the sheet strength from 28 Nm/g to 40.5 Nm/g, which is high enough to reuse these fibres within the mill by recycling them back into the main process stream. Additional high-pressure homogenization is capable of producing hydrophobic nanoscale (10 – 20 nm) fibrils, which could be used in special applications such as bio-nano-composites with non-polar matrices.

## 6.2. Introduction

The pulp and paper industry produces a variety of wastes ranging from solid waste, sludge and waste water [1]. Deinked recycled paper mills produces the majority of the waste and it is often complex in nature due to various inorganics present [2]. Kraft and other chemical pulping processes produce the most waste in the pulping of virgin fibres, as the constituents other than cellulose, are chemically removed or degraded mainly as black liquor, tall oil and turpentine [2]. Both these have been found useful for extraction

of by-products such as lignin and terpenes [3-5]. However, the chemicals used in the pulping process increase the load of the effluent treatment plant [1].

Thermomechanical pulping (TMP) was introduced as a greener alternative to chemical pulping as it is both chemical free and high yield, however, with a higher energy consumption [6]. Fibres are produced by refining of wood chips at high temperature. This process results in a fibre stream which has a similar chemical composition to the starting wood chips as only some of the volatile extractives are separated in the evacuated steam. However, it still produces a significant amount of waste mainly in the form of whitewater from the pulping and papermaking processes, and waste fibre [7]. The majority of TMP whitewater is usually recycled in the system while the remainder is directed to the effluent treatment facility. Membrane filtration has been widely used to filter the wood extractives present and to recover water of good quality back to the process [8]. Waste fibres and organic material present in whitewater are treated by effluent treatment processes, which usually comprise primary treatment to capture solids, including fibre, followed by secondary treatment to remove soluble and colloidal organic material arising from the pulp and papermaking processes.

Fine fibrous materials, generally known in the industry as 'fines', which are small enough to go through the screens during thickening, end up in the whitewater system, and get recycled in the process. These fines are referred to as whitewater fines and often considered as waste and to have detrimental effects on paper quality [9]. These whitewater fines can be collected through dissolved air flotation [10]. However, only a fraction of the recovered fines is typically directed back into the papermaking process due to their detrimental effects on paper quality. Options for valorisation of these fines include combustion, pyrolysis, gasification, land application, composting and reuse as an alternative building material. However, the high moisture content of more than 90% inhibits the use in thermochemical processes such as combustion, pyrolysis and gasification.

Wood et al. (2000) used hydrogen peroxide bleaching and refining to add value to these fines with the aim of adding them back to the paper making process [11]. In their study, they subjected fines collected from a TMP mill reject whitewater pressate, to an alkaline peroxide treatment. The treated fines were then mechanically treated by either refining, grinding or ball milling. The treated whitewater fines were then added to a TMP and Kraft pulp at 9:1 ratio (10% addition). The authors found that while the addition of whitewater fines, which were subjected to mechanical treatment alone, had negative impact on the

tensile strength, the addition of whitewater fines which were subjected to both alkaline peroxide bleaching and mechanical treatment improved the tensile strength of hand sheets. Even though, they were successful in this attempt, the literature does not provide any other studies focused on upgrading these fines.

There has been an increased interest in producing cellulose microfibrils (CMF) from various pulp sources. In this study, whitewater fines were evaluated as a potential source for Cellulose microfibril (CMF) production, with the options of reuse within the process or other applications also considered.

### 6.2.1. Nanofibre Production

Cellulose microfibrils (CMF), often termed as nanocellulose, has attracted a lot of attention as a high strength polymer with many novel applications. Interest has been enhanced by the fact that CMF can be generated from almost any source of cellulose, which is the most abundant, natural or synthetic, polymer on earth. CMF is primarily the end product of the separation of fibrils in the secondary cell walls of cellulose containing fibres, and was first introduced by Turbak and Herrick in 1983, as a non-calorific food additive and rheological additive to paints and formulations [12, 13]. CMF is generally classified as a nanomaterial with a very high aspect ratio (length to width, L/D). CMF has a width range of 10-100 nm and length range of 0.5 – 50  $\mu\text{m}$  [14].

The small diameters and high aspect ratios of CMF leads to increased surface area which in turn results in increased strength. Therefore, CMF sheets inherently have higher tensile strength than sheets from normal fibres, depending on the quality and source of CMF. For example, CMF produced via homogenization of cotton fibres can have a tensile index around 85 Nm/g [15]. The small diameters of CMF mean that they will be closely packed when made into a sheet. This results in decreased air permeability. Also, there is an increased hydrophilicity in CMF because of higher amounts of exposed hydroxyl groups from increased surface area [16]. More importantly, CMF has applications in the pulp and paper industry itself as a strength additive and a coating agent [17].

Different mechanical fibrillation techniques can be used to produce CMF. High pressure homogenization is the most widely used method [18-20]. A fibre suspension is forced through a narrow passage under very high pressure (500 – 1000 bar). The sudden drop in pressure when passing through the narrow passage makes the fibres fibrillate into microfibrils. By design, homogenization requires very dilute suspensions in the range of 0.25 – 2 wt.% consistency. This makes homogenization a significantly energy intensive

process. In addition to the high energy consumption, stiff fibre such as TMP whole pulp and unrefined Kraft pulp are known to give operational issues such as clogging. Often mechanical or chemical pretreatment is used to reduce the clogging in the homogenization process or reduce the energy consumption [21-23].

Pulp refining processes such as PFI refiners and Valley beaters have also been used as mechanical pretreatment prior to homogenization [19]. However, refining alone can only be used to produce relatively coarse CMF. Imerys are using traditional double disc refiners to co-grind fibres with minerals for in situ production of microfibrils [24, 25]. PFI refining has been used to fibrillate TEMPO oxidized fibres effectively [26]. There are very few studies which investigate the effect of extensive refining on the development of microfibrils, i.e. high number of revolutions in the PFI mill or increased number of passes in a traditional double disc or conical refiner. The commercial GL&V process uses refining to produce cellulose nanofibrils (CNF) from chemical pulps [27].

Effective use of refining to generate significant amounts of microfibrils, would reduce the energy consumption significantly as the specific energy consumption is lower than that of high pressure homogenizers simply due to high consistency operation. Also, refining is a much more robust operation compared to homogenization. This could be advantageous in economically implementing CMF production in existing pulp mills.

A range of raw materials from bacterial cellulose to wood pulp has been used by researchers to produce CMF or CNF, using a variety of treatments such as homogenization and microgrinding, with or without pretreatment [18]. The majority of the research into producing CMF has used chemical pulp, mainly Kraft pulp as the feedstock [28]. However, only a few researchers have explored the possibility of using pulp/fibres from TMP to produce CMF or CNF [22, 29]. The major bottleneck preventing the use of TMP is the presence of lignin, which increases the energy required to separate the fibrils to produce CMF. This has led some researchers to use the term “nano-ligno-cellulose” or NLC for CMF like materials produced from TMP [29].

In this work, we have used a PFI refiner and a lab scale Sprout Bauer 12-1CP refiner to treat the whitewater fines from a thermomechanical pulping mill. The primary objective was to investigate the potential for upgrading the fibrous waste to the quality of commercial grade newsprint pulp and reach complete biomass utilization within the mill. The potential for producing microfibrils via the addition of high levels of energy (high pressure homogenization) was also investigated.

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## 6.3. Materials and Methods

### 6.3.1. TMP Whitewater fines

Norske Skog – Boyer mill uses Radiata pine (*Pinus radiata*) wood and consists of 3 thermomechanical pulping (TMP) mills and 2 paper machines. TMP whitewater in this mill is clarified using a dissolved air flotation (DAF) unit. The fines in whitewater are floated to the top and removed by the means of a scraper. These floats or fines are referred to as TMP whitewater fines hereafter.

The collected whitewater fines are considered a process waste. Although, a fraction is returned back to the papermaking, it is not preferred as these fines cause poor quality in the final newsprint product. The majority is transferred into the outgoing effluent and processed in the effluent treatment facility, thus limiting the usefulness of the operation for fibre recovery. The current effluent flow to the effluent treatment primary clarifier is around 20 ML per day and around 35 – 40 tonnes of solids is removed from the effluent each day, of which approximately one quarter is whitewater fines that is not recovered by the DAF treatment of TMP process water. There is therefore potential for an additional 10 tonnes per day of fibre to be recovered if a suitable use could be found for it.

Bleached Radiata pine TMP pulp was also collected from the same facility.

### 6.3.2. Nanofibre Production

The floats from this DAF unit were collected at a solids concentration of 5 wt.% and thickened using lab vacuum filtration with a #20 mesh to a consistency of 17.4 wt.%.

TMP whitewater fines were refined in the PFI mill after adjusting the consistency to 10 wt.%, according to TAPPI Standard T248, for 5,000, 10,000, 15,000, 20,000, 30,000, 40,000 and 50,000 revolutions.

TMP whitewater fines were also refined in a Sprout Bauer 12-1CP lab scale refiner for 3 and 6 passes at 25.4  $\mu\text{m}$  (1/1000 inch) plate gap at atmospheric pressure. The refining was started at ambient temperature. After each pass the pulp was broken up by hand and a sample was taken for consistency analysis. Then, the pulp was fed back into the refiner straight away. The refining was done at the original solid consistency of the collected thickened pulp of 17.4 wt.%.

Suspensions from PFI refined (15000 and 50000 revs refined) fines, and lab refined (3 passes and 6 passes) fines were homogenized in a high-pressure homogenizer (GEA Niro Soavi), for 5 passes at 1000 bar. Whitewater fines were also homogenized without

any refining, for 5 and 10 passes at 1000 bar. In all cases, the suspension consistency was 0.25 wt.%.

Specific energy consumption coefficients derived by Kerekes were used to estimate the energy consumption in the PFI mill [30]. No specific coefficient for TMP fibres or fines from Radiata pine was given. Therefore, the coefficient for unbleached softwood Kraft pulp, 0.20 kWh/Tonne/rev, was used in the calculations in this paper.

Energy consumption during lab refining in the Sprout – Bauer 12-1CP refiner was obtained from the energy meters attached to the equipment. Specific energy consumption was then calculated using the measured consistency values after each pass.

Specific energy consumption of the homogenizer was estimated theoretically by calculating the pump work. The efficiency in the drive motor and energy losses were not taken into consideration. The pump work ( $W$ ) is calculated as shown in Eq. 1.

$$W = \frac{P - P_{\text{atm}}}{\rho} \quad [1]$$

Where,  $P$  is the homogenizer pressure,  $P_{\text{atm}}$  is the atmospheric pressure and  $\rho$  is the density of the suspension. The density of the 0.25 wt.% suspension was assumed to be the same as of water which is  $1000 \text{ kgm}^{-3}$ .

Results are shown for both PFI refining and lab refining against the energy consumption, to directly compare the two refining techniques.

### 6.3.3. Nanofibre Characterization

Aspect ratio (length/diameter) after each treatment stage was evaluated by estimating the gel point of the fibre suspension through sedimentation, as described by Varanasi et al. [31]. In this method, a series of dilute suspensions, often from 0.01 – 0.1 wt% suspensions of MFC are prepared and poured equal volumes to a series of measuring cylinders, and the initial height of the suspension is recorded. The suspensions were allowed to settle > 48 hours and final sediment heights were measured. The ratio of final sediment height to initial suspension height is plotted against the consistency of the suspension, and a quadratic fit is found. The linear coefficient of this quadratic equation gives the gel point consistency which is then used to estimate the average aspect ratio of the fibres using a set of empirical equations as given in Varanasi et al. When calculating the aspect ratio, it was assumed that the density of the fibres was  $1333 \text{ kgm}^{-3}$  and the respective equation according to effective medium theory (EMT) was used. The aspect ratio is calculated using the following equation, Eq. 2, by Varanasi et al. (2013), where  $A$

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is the aspect ratio of the fibres, and  $C_c$  is the solid concentration corresponding to gel-point.

$$A = 2.98C_c^{-0.58} \quad [2]$$

Scanning electron microscopy (SEM) images of the fibres in the different nanofibre suspensions were taken using an FEI Nova NanoSEM to measure the fibre width distribution. SEM samples were prepared by evaporating a droplet from a very dilute (~0.001 wt. %) suspension on a silicon chip mounted on a carbon tab. Once dried, samples were coated with 2 nm layer of Iridium. Images were acquired at different voltages (3 – 10 kV) and different magnifications (5,000 – 100,000X). Fibre diameters were measured from the images using the ImageJ software. All the fibres in each selected image were measured and more than 100 fibres were measured altogether, for each sample.

The water drop contact angle of the sheets made from the fibres were measured using a DataPhysics Optical Contact Angle (OCA) 35 system. A deionised water droplet of 3  $\mu$ L was dropped on to the paper sheet made from fibres and the initial contact angle was measured using image analysis.

#### 6.3.4. Sheet making

The consistency of the suspension was adjusted to 0.2 wt.% and 60 gsm sheets were made by taking 600 g of the suspension. No retention aid was added, and all the sheets were made on Whatman Grade 541 filter paper using a standard automatic British Hand Sheet Maker. Drainage time (seconds) was measured from the start of the “Drain” cycle in the hand sheet maker until the sheet was fully drained, which was visually estimated from when the water disappeared from the whole surface of the sheet. After draining, the sheet was then couched manually by placing two new blotting papers and the couching plate, in that order, on top of the sheet and pressing with a rolling pin according to the TAPPI standard T205. Then, the filter paper was lifted off the mesh, with the sheet, two blotter papers and the couching plate still on top of it. Then, it was placed on a table with the couching plate in the bottom. The filter paper was then carefully removed from the sheet and the bottom most blotting paper was replaced with a new blotting paper. A gloss pressing plate was carefully placed on top the sheet and another blotting paper was put on top of it. It was then pressed at 345 kPa for 5 minutes between two square metal plates, using an automatic sheet press. After the first press, the hand sheet was then transferred onto a new blotting paper along with gloss pressing plate and pressed again for 2 minutes

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at the same pressure. Sheets were then air-dried in a conditioned testing room (25 °C and 50% RH), under restraint and stored there until further use. Approximately, five to six sheets were made for each refining level.

Untreated whitewater fines and whitewater fines which were homogenized for 5 passes were also mixed with bleached Radiata pine TMP pulp in the ratio of 1:9 (10% addition of nanofibres) and mixed for 1 hour prior to sheet making. The rest of the sheet making was carried out according to the method described above.

### 6.3.5. Sheet testing

Oven dry weight (g) was measured by measuring the total sheet weight after drying them at 105°C for 4 hours. Sheets were weighed using a balance with 0.001g sensitivity.

Thickness ( $\mu\text{m}$ ) was measured using an L&W Micrometer 51. Twenty measurements were taken from each sheet. Air permeability ( $\mu\text{m}/\text{Pa}\cdot\text{S}$ ) was measured using an L&W Air Permeance Tester. Tensile testing was done on 15 mm wide strips and a 100-mm test span with 10 mm/min extension rate, using an Instron 5566 Tensile Tester. Approximately 24 strips were measured for each refining and homogenization level. Force (N) and elongation at break (mm) were recorded. The strength results were expressed as tensile index, calculated by dividing the maximum tensile load (at break) by the width of the strip (15 mm) and by grammage of the paper sheet ( $\text{g}/\text{m}^2$ ).

## 6.4. Results and Discussion

### 6.4.1. Nanofibre Characterization

#### 6.4.1.1. Aspect Ratio

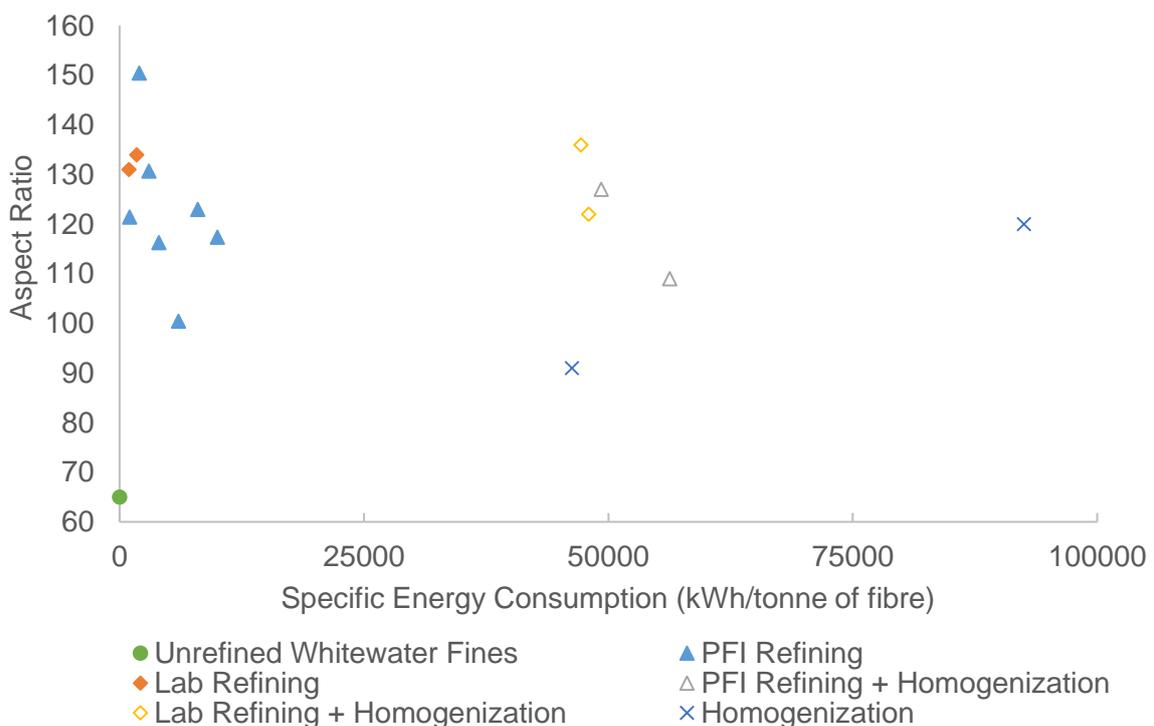
Figure 6.1 shows the aspect ratio of whitewater fines, calculated from gel-point measurements. Whitewater fines had an initial aspect ratio of 65, which increased with PFI refining. It reaches a plateau around 110 - 140, even with subsequent refining. This suggests that fibrillation was dominant initially. However, with further input of energy, cleaving of fibres was more dominant than fibrillation.

Fibrillation during refining is divided into two types. Internal fibrillation is the first effect of refining and P and S1 layers are delaminated due to the cyclic compression forces inside the refiner [32]. External fibrillation on the other hand is secondary and defined as grinding off the fibrils from the fibre surface and is associated with exposing of the S2 layer [32]. External fibrillation is visible in the microscopic images as the fibrils are still attached to the surface of the fibres [33]. As identified in many SEM images of nanofibers, external

fibrillation seems to be the main mechanism of nanofiber development during refining and homogenization. Microfibrils which are attached to the surface of the fibres can also get completely detached, resulting in individualized microfibrils or nanofibers. Fibre cleaving or fibre shortening is often deemed as undesirable effect of refining [34]. Breaking of fibres happens when the strain on a fibre is sufficiently high. It can happen in two distinct ways: cutting of fibres by direct shearing from the refiner bars, and failure when the fibres are pulled from a network of other fibres [35].

We believe that initial refining favours external fibrillation, leading to the production of both non-individualized and individualized microfibrils, thus increasing the aspect ratio initially. However, when fibres are further refined, cleavage of intact fibres and microfibrils dominates, compared to fibrillation, which keeps the aspect ratio in the range of 110-140, even with continued addition of energy. Lab refining showed a similar trend as well.

Direct homogenization of whitewater fines showed that whitewater fines are less receptive to the energy addition by homogenization. Even with the input of more than 90,000 kWh/tonne of energy, the aspect ratio remained at 120. Further homogenization of whitewater fines for 15 and 20 passes at 1000 bar resulted in aspect ratios of 122 and 123 respectively. There is previous evidence of the same phenomena happening during homogenization, even though its mechanism is completely different from refining [36].



**Figure 6.1.** Change in aspect ratio with energy consumption

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#### 6.4.1.2. SEM Images & Fibre Diameter

Figure 6.2 contains some representative SEM images showing the relationship between fibril development and energy input. All the images used for diameter calculations can be found in the supplementary data. SEM images of unrefined whitewater fines show the presence of large fibrillar and non-fibrillar particles (Inset a). Whitewater fines are known to have a mixture of different fibre morphologies. Fines are produced when they are sheared off from the fibre wall. Therefore, the morphology of the fines depends on their origin in the fibre wall. The outer parts of the fibre walls produce flake-like particles, while the inner S1 and S2 layers produce more fibrillar particles of different size and shape. Also, there are other non-fibrillar particles such as ray parenchyma and fragments of ray parenchyma which appear as short and wide rectangular particles [11, 37]. PFI refining generated significant amounts of fibrils and further addition of energy via homogenization increased the number of fibrils, as shown in insets (b) and (c) respectively. Fibrils emanating from the large fibrillar particles can be seen in inset (b), as well as individualized microfibrils. The image in inset (c) shows that homogenization of refined fines generated more individualized nanoscale fibrils than refining alone. Direct homogenization also produced significant amounts of fibrils. Similar observations were made in the laboratory refining as well.

As shown in Table 6.1, PFI refining reduced the fibre diameter of the whitewater fines quite effectively. After 15000 and 50000 revolutions in the PFI mill, the median diameters were 81 nm and 48 nm respectively. Further homogenization of the fibres produced from the above refining levels resulted in median diameters of 19 nm and 14 nm respectively. Laboratory refining seemed to promote better fibrillation, than PFI refining. However, subsequent homogenization of lab refined fibres didn't show the same level of fibrillation observed in PFI refined fibres. Direct homogenization of whitewater fines produced fibres with median diameter of only 55 nm, even with the addition of significantly higher amounts of energy. This suggests that pre-refining of fibres prior to homogenization can assist fibrillation during homogenization. We conclude that coarse nanofibres can be produced with refining alone, while a combination of refining and homogenization could be used to produce very fine nanofibers.

**Table 6.1.** Median diameters of fibres as calculated from SEM images

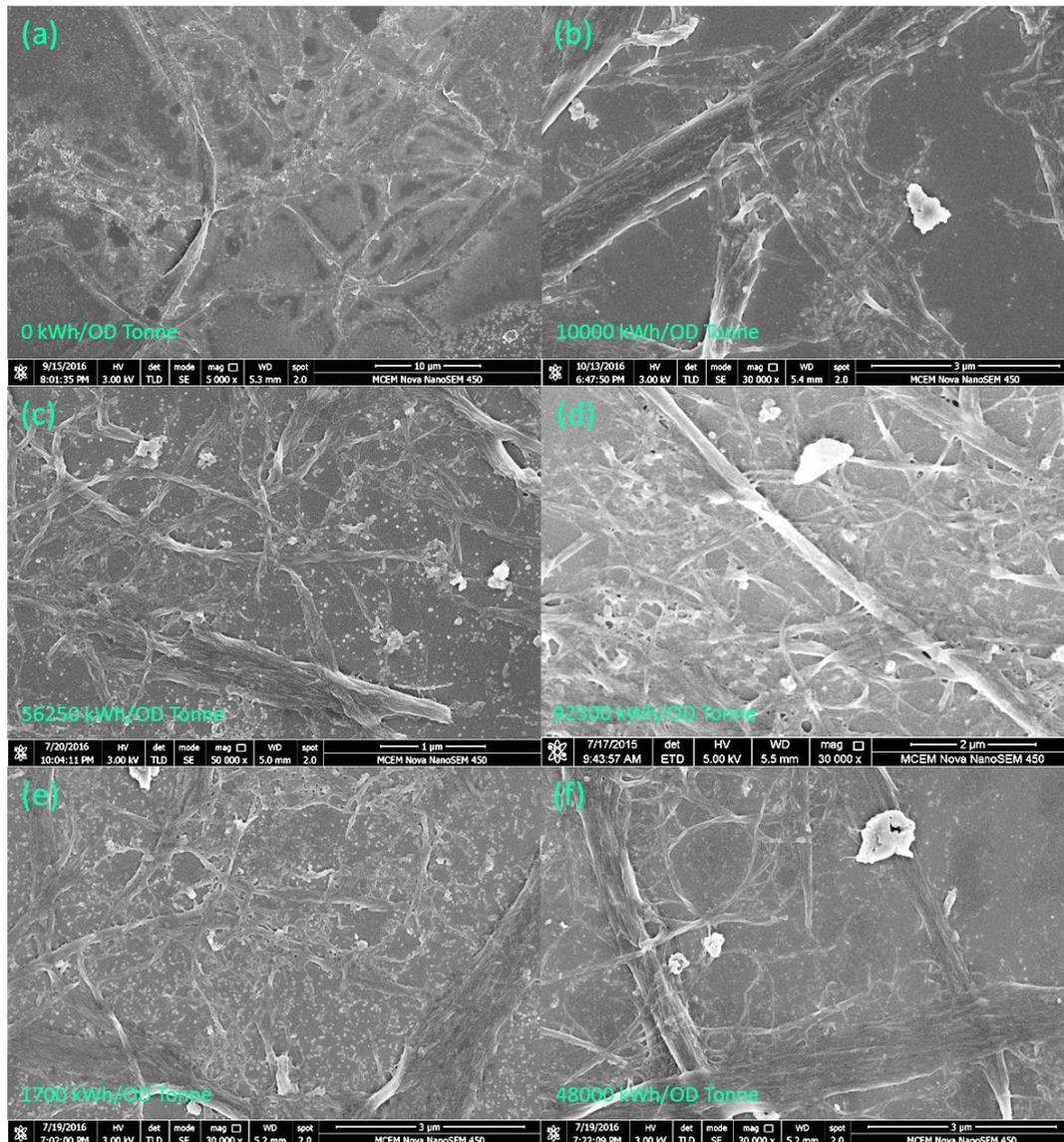
<b>Refining Level</b>	<b>Specific Energy Consumption (kWh/tonne of fibre)</b>	<b>Median Diameter (nm)</b>
Unrefined	0	321
PFI Refining	1000	203
	2000	117
	3000	81
	4000	54
	6000	72
	8000	49
	10000	48
	Lab Refining	933
1726		44
PFI Refining + Homogenization	49250	19
	56250	14
Lab Refining + Homogenization	47183	85
	47976	42
Homogenization	46250	64
	92500	55

## 6.4.2. Sheet Properties

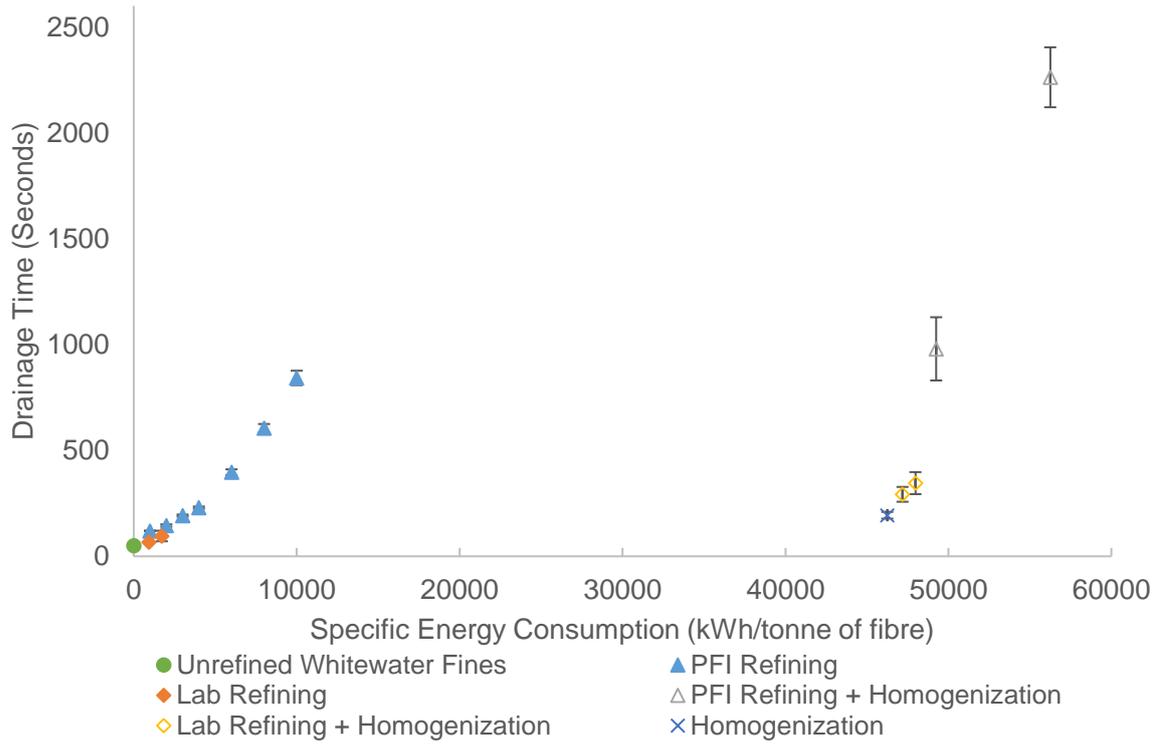
### 6.4.2.1. Drainage Time

Drainage time of sheets made from whitewater fines (Figure 6.3) increased gradually with both PFI and lab refining. However, the addition of energy via homogenization to PFI refined fines did not increase the drainage time at the same rate as in PFI or lab refining. This is not fully consistent with what has been observed before where the drainage time seems to be controlled by fibre diameter [38]. When fibre diameter decreases, drainage time increases. Smaller fibre diameter results in low pore sizes and low porosity. This blocks the water drainage from the sheet. However, as explained before, refining can produce flake-like particles due to peeling off from the outer fibre walls, which might cover up the pores. Thus, drainage time increases rapidly with refining. However, expansive fibrillation action during homogenization might not be able to generate flake-like particles.

Thus, we don't notice see the same rate of increase in drainage time. This could explain the low drainage time observed in whitewater fines homogenized for 5 passes. It had a median diameter of 80 nm, and a low drainage time. On the other hand, whitewater fines which were PFI refined for 15000 revolutions and homogenized for 5 passes had a median fibre diameter of 19 nm, and a considerably higher drainage time. The drainage behaviour of lab refined, and homogenized whitewater fines may also be explained in a similar way.

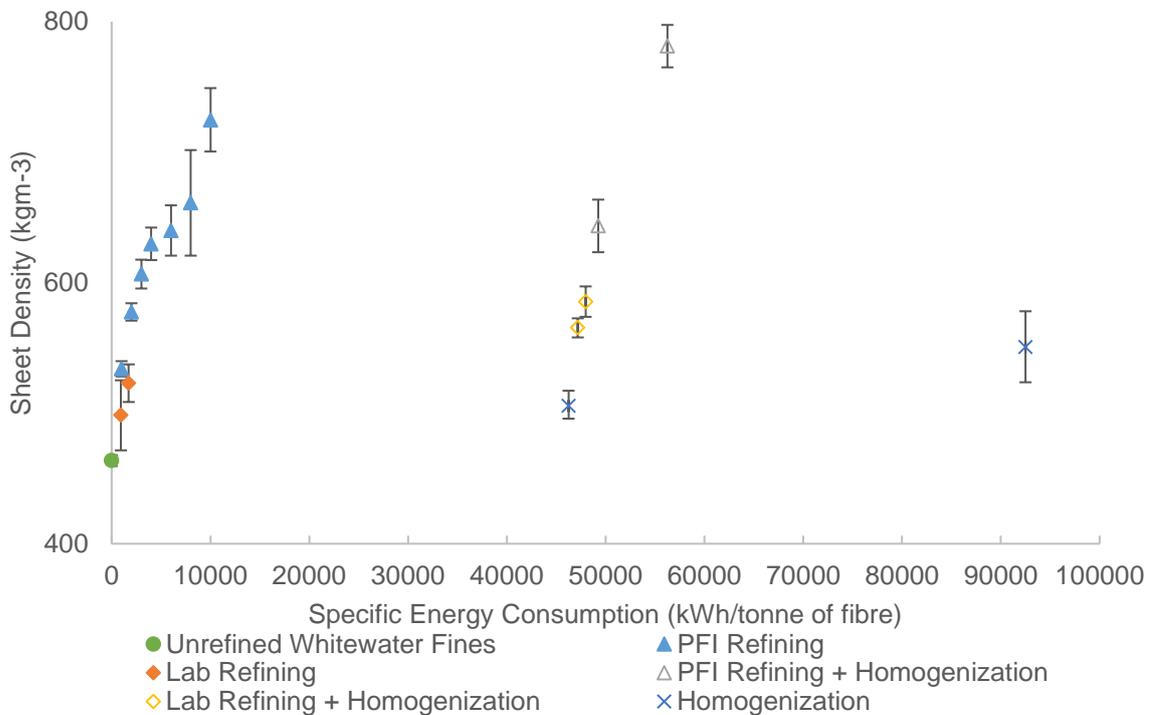


**Figure 6.2.** SEM Images; (a) Whitewater fines – unrefined/unhomogenized, (b) Whitewater fines – PFI refined for 50000 revs, (c) Whitewater fines – PFI refined for 50000 revs and homogenized for 5 passes, (d) Whitewater fines – homogenized for 10 passes, (e) Whitewater fines – lab refined for 6 passes, (f) Whitewater fines - lab refined for 6 passes and homogenised for 5 passes. The specific energy consumption is shown in the bottom left hand corner of each image.



**Figure 6.3.** Effect of energy consumption of drainage of hand sheets. The error bars represent 95% confidence intervals.

#### 6.4.2.2. Sheet Density

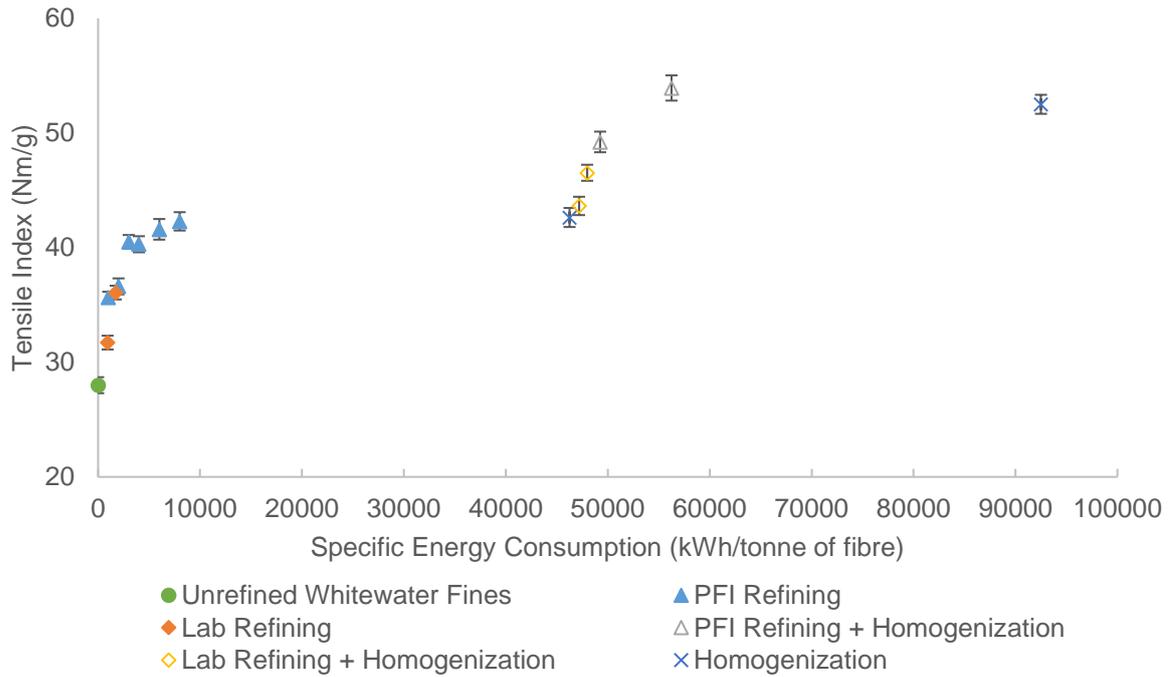


**Figure 6.4.** Effect of energy consumption on sheet density. The error bars represent 95% confidence intervals.

As discussed earlier, reduction in fibre diameter decreased the pore size and porosity. This in turn increased the density of the sheet. As shown in Figure 6.4, PFI refining of whitewater fines increased the bulk density considerably with increased energy input. However, subsequent homogenization of whitewater fines did not increase the sheet density at a similar rate. Lab refining and subsequent homogenization produced hand sheets with lower density, as expected. This was due to the higher median diameter, which resulted in a less dense structure. A similar behaviour was observed in the whitewater fines, which were directly homogenized.

### 6.4.2.3. Tensile Strength

Figure 6.5 shows the tensile strength of sheets made from whitewater fines, calculated as tensile index. Tensile index of untreated whitewater fines, 28 Nm/g, was significantly lower than the tensile index of bleached TMP pulp, (40.6 Nm/g). However, the addition of just 3000 kWh/tonne by PFI refining alone increased the tensile index to 40.5 Nm/g. This was significant as it is comparable to that of bleached TMP pulp. Addition of further 5,000 kWh/tonne (8,000 kWh/tonne after 50,000 revolutions in total) via PFI refining increased the tensile index to only 42.3 Nm/g. Laboratory refining imparted a similar effect, comparable to PFI refining, with respect to specific energy consumption. Subsequent homogenization of this refined pulp further increased the tensile index to 53.9 Nm/g while direct homogenization had less effect. The tensile index was only 52.5 Nm/g of tensile index after 10 passes in the homogenizer. Homogenization, even when coupled with refining, was not an efficient method to upgrade the whitewater fines, due to its high energy consumption.



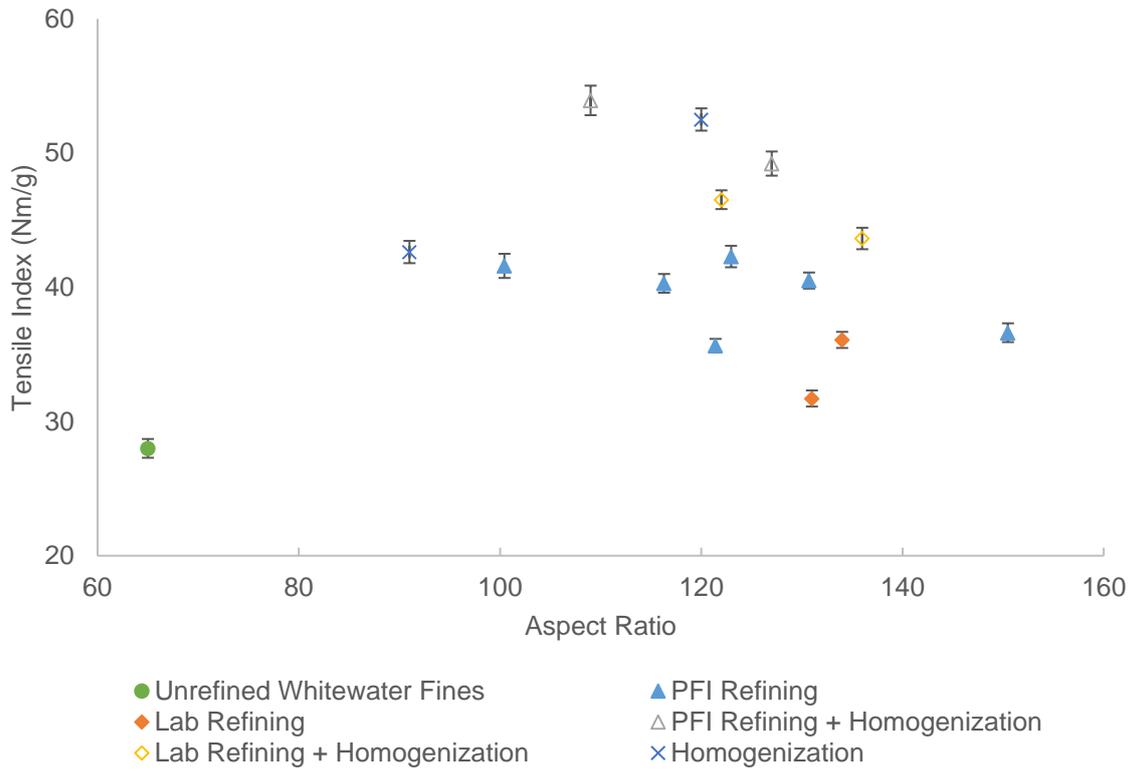
**Figure 6.5.** Change in tensile index with energy consumption. The error bars represent 95% confidence intervals.

The SEM images and fibre diameter analysis show that the median diameter reduced with the addition of energy. Therefore, one would expect the tensile index to increase continuously, rather than reach a plateau with continued fibrillation from refining and homogenization. Increased surface area through fibrillation should have increased the fibre-fibre bonds, and eventually be reflected in sheet strength. However, continued addition of energy through either refining and/or homogenization did not increase tensile strength significantly as it reached a plateau around 52-54 Nm/g. This suggests that median diameter is not correlated with tensile index. Interestingly, tensile strength appears to be following the trend set by both the aspect ratio and sheet density, which increases with initial addition of energy, but plateaus out after continued addition of energy- see Figures 6.6 and 6.7.

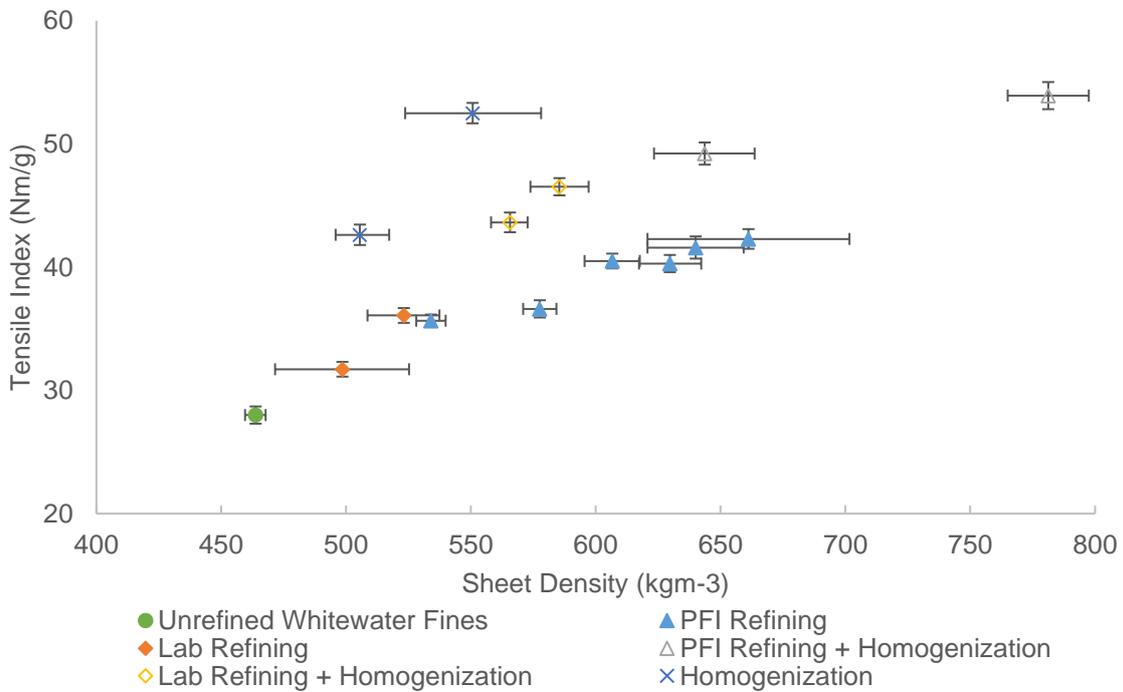
This agrees with the modified Page equation, Eq. 3, where tensile strength is related to the ratio of length of the fibre/width of the fibre, i.e. aspect ratio [39].

$$\frac{1}{T} = \frac{9}{8Z} + \frac{3w_f}{\tau_b l_f RBA} \quad [3]$$

Where, T is tensile strength, Z is the zero-span strength of the paper reflecting fibre strength,  $\tau_b$  is fibre-fibre bonding,  $w_f$  is width of the fibres,  $l_f$  is length of the fibres, RBA is relative bonded area which is proportional to sheet density.



**Figure 6.6.** Tensile Index Vs Aspect Ratio. The error bars represent 95% confidence intervals.



**Figure 6.7.** Tensile Index Vs Sheet Density. The error bars represent 95% confidence intervals.

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Fibre-fibre bonding,  $\tau_b$ , gives an indication of the quality of the bonds between the fibres. Kraft fibres which are almost pure cellulose, will have higher specific fibre-fibre bonding because of uninhibited hydrogen bonds. However, the TMP fibres have a surface that is covered with hemicellulose and lignin which hinders the potential of hydrogen bonding. Their surface is also covered with extractives which further inhibits the bonding. Whitewater fines are further affected by extractives. Whitewater fines are circulated in the process water system, resulting in adsorption of extractives on to the surface, and whitewater fines are considered to be of poor quality [9, 11, 40]. The presence of extractives reduces the tensile strength of the fines and even the slightest amount of surface coverage by extractives can reduce the tensile properties significantly [9, 41, 42]. The tensile properties can be completely restored when extractives are removed [43]. The surface of the whitewater fines recovered via dissolved air flotation is even more contaminated [10]. As the fines float up, the bubbles carry colloidal extractives along with the fines, which get adsorbed to the surface of the fines. This further hinders fibre-fibre bonding of whitewater fines. As observed in SEM images and subsequent diameter analysis, both refining and homogenization create new surface area. However, this is not reflected in the tensile strength. This is probably due to extractives redistributing themselves and covering the newly created surfaces.

It is important to consider the effect of sheet density as well. The increase in tensile index during initial refining in the PFI mill may be attributed to the increase in sheet density which increased the relative bonded area (RBA). Relative bonded area is also directly related to tensile strength. This could also explain why homogenization of both unrefined and refined whitewater fines didn't increase the tensile index relative to the energy consumption. As shown in Figure 6.4, homogenization didn't increase sheet density as efficiently as refining.

#### 6.4.3. Potential for upgrading

Untreated whitewater fines were added to bleached TMP pulp at a ratio of 1:9 (10% addition), without any retention aid as sheets were made on top of a Whatman Grade 541 filter paper. It resulted in a tensile index of 38.7 Nm/g which indicates that these whitewater fines are of poor quality and detrimental to paper quality if added to pulp directly. This is consistent with the decision of the mill to treat these fines as waste. Whitewater fines were homogenized for 5 passes and added to bleached TMP pulp at the same ratio. This resulted in a tensile index of 43.5 Nm/g. This value is higher than both bleached TMP pulp (40.6 Nm/g) and whitewater fines homogenized for 5 passes

(42.6 Nm/g), although this is within the experimental error, as we would expect the tensile strength to be in the range of 40.6 – 42.6 Nm/g. However, it is worthwhile to note that the drainage time was minimally affected by the addition of homogenized whitewater fines. The average drainage time for making a standard TMP handsheet (60 gsm) on the filter paper was 39 seconds. When unhomogenized whitewater fines were added to the furnish, drainage time increased slightly to 41 seconds. This could be due to the increased number of fines in the furnish. When homogenized whitewater fines were added, the drainage time was increased only to 43 seconds. This shows that the addition of homogenized whitewater fines increased the tensile index, but it doesn't affect the drainage time negatively. This could be due to the hydrophobic nature of the microfibrils produced.

The tensile strength results are comparable with the values reported by Wood et. al (2000). In that study, the tensile index of TMP pulp decreased from 50.4 to 46.3 Nm/g when 10% whitewater fines were added. They showed that the addition of whitewater fines which were refined in a 12-inch Sprout-Waldron single disc refiner had the same effect as the unrefined whitewater fines. However, ball milled whitewater fines maintained the tensile index at the same level as 100% TMP, 50.9 Nm/g, after their 10% addition to TMP. Nevertheless, this research proves that whitewater fines may be upgraded to remove the detrimental effects and to match the expected quality of commercial pulp.

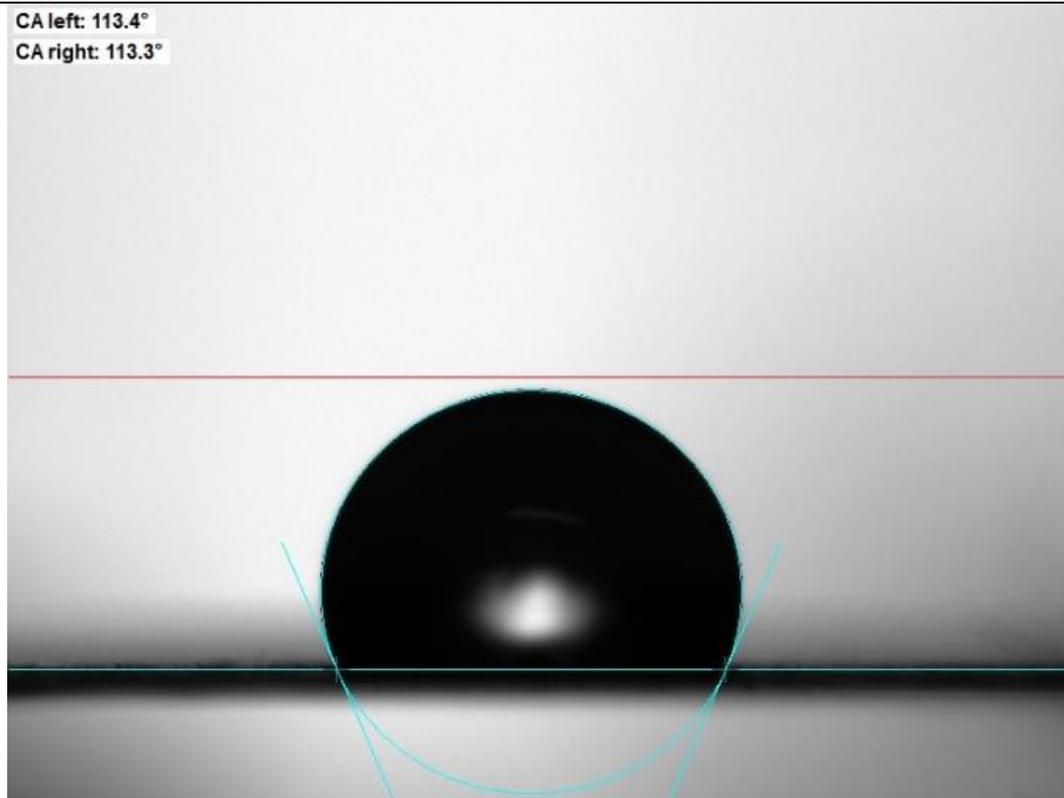
The addition of 3000 kWh/tonne of energy increased the tensile index to 40.6 Nm/g as shown earlier. This is probably a sensible target to set as the tensile index is at the same level as bleached TMP pulp and the energy addition was not much higher than the specific energy consumption of TMP pulp which is ~2,000 kWh/tonne. Further addition of energy via refining increased the tensile index even more, but began to reach a plateau (Figure 6.5). Further refining increased the drainage time significantly which is not desirable in paper making, (Figure 6.3). It is worth mentioning that large scale mill refiners have much higher efficiency than PFI or lab scale refiners which would further reduce the specific energy consumption needed to reach the set target. Even though, further refining requires further addition of energy into a pulp which has already consumed 2000 kWh/tonne, the potential benefits could offset the cost. Recovering and reusing the fines ensures that the initial application of 2000 kWh/tonne is not wasted. It would also reduce the load to the effluent treatment facility which in turn would reduce the cost of operation and environmental foot print of the facility. Moreover, this could potentially generate more income due to greater utilization of wood fibres.

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#### 6.4.4. Other applications

As seen earlier, the combination of PFI refining and homogenization can effectively produce nanofibers of diameters between 10 – 20 nm. These nanofibers have valued added applications such as membranes and composites. The nanofibre sheets made from whitewater fines exhibited hydrophobic characteristics. The sheets made from whitewater fines after 50,000 revolutions, were tested for contact angle using a DataPhysics Optical Contact Angle (OCA) 35 system. A deionised water droplet of 3  $\mu\text{L}$  was dropped on to the paper sheet and initial contact angle was measured using image analysis. The average contact angle of 10 measurements was 112.8 degrees. One single measurement is shown in Figure 6.8. Similarly, contact angles was observed for unrefined whitewater fines, whitewater fines after 20,000 revolutions, and whitewater fines after 40,000 revolutions, which were 105.1, 105.9, and 108.9 degrees respectively.

This hydrophobic nature arises from the chemical composition of these whitewater fines. Thermomechanical pulping process doesn't alter the chemical composition of wood fibres, and it retains the lignin and hydrophobic extractives. This makes the fines hydrophobic. As explained earlier, extractives can redistribute themselves on the newly created surface after refining and homogenization. This makes the nanofibers made from whitewater fines hydrophobic in nature. The contact angle value found in this experiment is actually slightly higher than the value reported by Rundlöf et al. (2000b) for Spruce TMP whitewater fines, which is 101°. [9]. Hydrophobic nanofibers can have advantage over the usual cellulosic nanofibers which are essentially hydrophilic due to hydroxyl groups. The hydrophilicity of conventional nanocellulose makes it difficult to integrate in non-polar composites and often requires surface chemical modification prior to integration with non-polar matrices such as polyethylene and other plastics. Ferrer et al used lignocellulosic nanofibrils obtained from residual empty palm fruit bunch and incorporated them to a polypropylene matrix using soy protein isolate as a coupling agent. Authors noted good levels of dispersions in the polypropylene matrix which resulted in improvement of thermo-mechanical behaviour of the composite [44]. Hydrophilic nanofibers also cause longer drainage times during sheet making due to their high water-retention. However, hydrophobic nanofibers can overcome these issues, and could be preferable.



**Figure 6.8.** Contact angle of sheets made of whitewater fines after 50,000 revolutions in the PFI mill

## 6.5. Conclusions

Waste TMP whitewater fines were mechanically treated using PFI refining, lab refining and high-pressure homogenization. The combination of PFI refining for 50000 revolutions and homogenization for 5 passes at 1000 bar was able to produce nanoscale fibres of 10 – 20 nm diameter and increased the hand sheet tensile index from 28 Nm/g to 53.9 Nm/g, a 90% increase. Lab refining had similar performance to PFI refining. One drawback is that homogenization, even coupled with refining, is not an energy efficient method to produce cellulose microfibrils, due to its high energy consumption, although refining alone can produce nanoscale fibres of sufficiently good quality. However, these upgraded waste whitewater fines can be added to the TMP newsprint without any adverse effects on either strength or drainage, or they could be used with non-polar matrices for nanocomposites.

## 6.6. Acknowledgments

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## 6.7. Raw Data

Raw data of this study can be found in the following online database.

Gunawardhana, Thilina; Batchelor, Warren; Patti, Antonio; Richardson, Desmond; Banham, Paul (2017), "Upgrading waste whitewater fines from a pinus radiata thermomechanical pulping mill - SEM Images", Mendeley Data, v1

<http://dx.doi.org/10.17632/zp45br69jp.1>

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# Chapter 7

Upgrading Thermomechanical Pulping  
Whitewater Fines through Chemical Treatment

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## Preface

Whitewater fines have inferior tensile properties compared to bleached thermomechanical pulp. These fines are generally considered as waste and sparingly used in the papermaking process. In the previous chapter, we looked into the possibility of upgrading whitewater fines through mechanical treatment. We proved that we could improve the whitewater fines back to the expected quality of newsprint by the addition of 3000 kWh/tonne. Whitewater fines could also be processed into hydrophobic lignocellulosic microfibrils with further addition of mechanical energy. However, the mechanical energy addition is hard to justify as these whitewater fines are the result of intensive mechanical energy addition. Therefore, we should investigate the means for reducing the mechanical energy consumption. In this chapter, we have investigated two chemical treatment methods: washing by ethanol and washing by caustic. The hypothesis is that washing process would decontaminate the fibres by removing the extractives, thus increasing their strength. Fibre properties are analysed. Sheets are made by treated fibres and tested for mechanical properties.

This chapter addresses objective A1.

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# Chapter 7 – Upgrading Thermomechanical Pulping Whitewater Fines through Chemical Treatment

Thilina Gunawardhana<sup>1</sup>, Paul Banham<sup>2</sup>, Desmond E. Richardson<sup>2</sup>, Antonio F. Patti<sup>3</sup>, Warren Batchelor<sup>1</sup>

<sup>1</sup>Bioresource Processing Institute of Australia (BioPRIA), Department of Chemical Engineering, Monash University, Clayton VIC 3800, Australia

<sup>2</sup>Norske Skog Paper Mills (Australia), Boyer, TAS 7140, Australia

<sup>3</sup>School of Chemistry, Monash University, Clayton VIC 3800, Australia

Corresponding Author: [warren.batchelor@monash.edu](mailto:warren.batchelor@monash.edu)

## 7.1. Abstract

Whitewater fines collected as the floats of the DAF unit are rarely used within the papermaking process at Norske Skog Boyer, because of their detrimental effect on sheet strength. In Chapter 6, we investigated the effect of mechanical treating the fines to upgrade them to the required strength. Treatment with 3000 kWh/t of refining energy increased the sheet strength by ~45% from 28 Nm/g to 40.5, which is higher than the strength of the sheets made from the main TMP pulp. In this chapter, the use of two chemical treatments to upgrade the fines to the required sheet strength is investigated.

The first treatment was washing in ethanol. This removed 10% of the mass of the fines as ethanol soluble extractives and increased the tensile index of the sheets made, from 28 Nm/g to 34.5 Nm/g. The second treatment was caustic washing/treatment. This was carried out at four different temperatures and four different caustic strength levels. Fibres, which were treated at room temperature and 0.5 M caustic strength, showed the best improvement. The standard hand sheets made out of these fibres showed a tensile index of 48.8 Nm/g, which is a ~ 74% increase from the untreated whitewater fines. The weight of extractives recovered from the caustic liquor after centrifugation was 5.5%. Treated whitewater fines could then be added to the thermomechanical pulp to improve the strength. However, further experiments and studies are needed to further optimize the properties.

## 7.2. Introduction

TMP whitewater has presented many challenges to newsprint industry. Whitewater system contains the water filtered through meshes in pulp thickening processes and water filter through papermaking meshes. Whitewater brings along fines and extractives as they filter through the meshes. The extractives in whitewater can cause damage to newsprint if they coalesce into pitch. However, extractives in whitewater contains valuable group of phytochemicals, resin acids, which could be extracted as by-products. Our recommendations to remove extractives and extract resin acids are given in Chapter 8.

Norske Skog – Boyer Mill uses a dissolved air flotation (DAF) unit to clarify whitewater. Whitewater fines are floated along with the air bubbles and colloidal extractives are bound to the fibres in the process. Refer to section 2.2.2 for more details on the Norske Skog – Boyer Facility and the DAF unit. The collected whitewater fines are sparingly used in paper making process and often discarded to the effluent treatment facility as waste. Whitewater fines are often regarded as of poor quality due to various reasons such as: enrichment of extractives on surface, enrichment of ray-parenchyma cells and fragments etc. Further details on whitewater fines can be found in section 2.2.2.1.

We have studied how mechanical refining can upgrade the whitewater fines back to the quality of TMP newsprint in Chapter 6 and in our published work [1]. We found out that a specific energy input of 3000 kWh/t would improve the tensile strength of whitewater fines from 28 Nm/g to 40 Nm/g. We also found out that subsequent homogenization could produce nano-scale lignocellulosic microfibrils which could be advantageous in applications such as a composite material in non-polar matrices. However, the energy consumption should be further reduced in order to upgrade the whitewater fines in an economical manner.

In this chapter, we have investigated how different chemical treatments alone can improve the properties of whitewater fines, something which only a very few researchers have investigated so far. Wood et al treated the ray cells fraction recovered from whitewater using alkaline peroxide and mechanically treated them using ball milling and refining [2]. Then they added the treated fibres into TMP newsprint at 1:10 ratio and observed significant increase in strength properties. In this study, we used an ethanol-washing process and a series of caustic treatment to upgrade the whitewater fines.

### 7.3. Materials

Whitewater fines were collected from the floats of the DAF unit in Norske Skog – Boyer facility at a consistency of 2.6%. The pH of the fines was measured at 7.26. Ethanol 96% was supplied by Ajax Finechem (AJA1046-2.5LPL).

### 7.4. Methodology

#### 7.4.1. Ethanol Washing

Whitewater fines were thickened to ~ 17 wt. % prior to ethanol washing.

Ten grams (dry weight) of thickened whitewater fines (17 wt. %) was put into a 2 L Schott glass bottle and filled with 2 L of ethanol. The suspension inside was stirred using a magnetic stirrer over night with the lid loosely on. Fibres were then filtered out and washed twice with 2 L of deionised water. The ethanol filtrate was then transferred into a dried and weighed round bottom flask. Ethanol was then evaporated using a rotary vacuum evaporator. The round bottom flask was then weighed again after oven drying, to calculate the weight of the “ethanol washable extractives”.

#### 7.4.2. Caustic Treatment

Caustic treatment was done at three different temperatures: room (~20 °C), 40 °C and 80 °C, and two caustic strengths 0.5 M and 3 M. However, two additional caustic strength tests were run at room temperature, 0 M and pH 9.5. All room temperature treatments were carried out in a high-shear dispermat at 1500 rpm for 1 hr. All the treatments done at 40 °C and 80 °C were carried out in an air bath reactor for 1 hour. This air bath reactor rotates around its axis to provide agitation. In a separate study, another treatment was carried out at 160 °C at 3 M caustic loading in the same air bath reactor for 1 hour. The temperature in this reactor was manually controlled within  $\pm 3$  °C for 1 hr. 1 kg of whitewater fines suspension at 2.6% was used for each treatment. The table 7.1 summarizes the conditions of each caustic treatment.

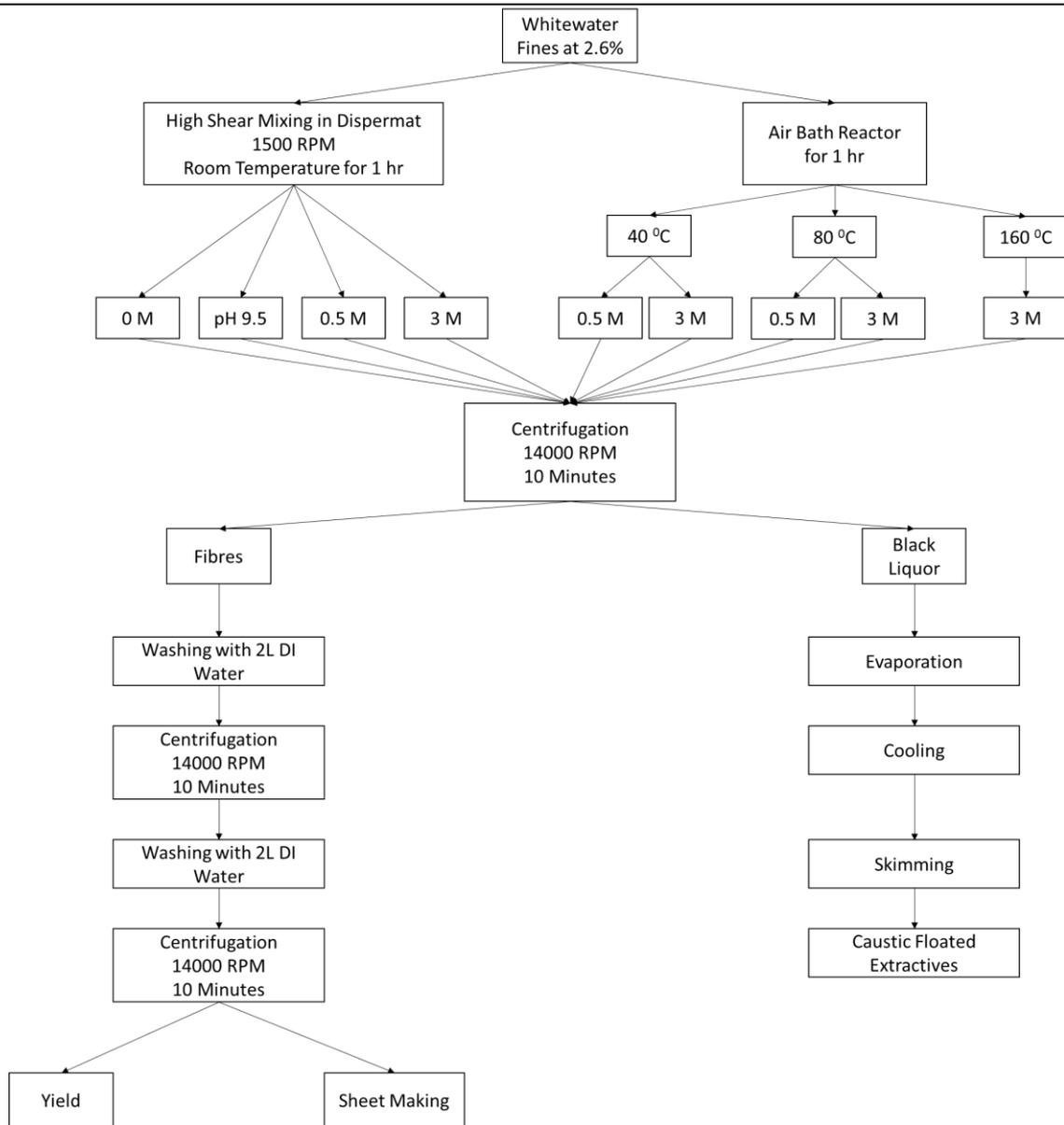
**Table 7.1.** *Different Caustic Treatment Conditions*

Temperature	Level of Caustic Treatment				Apparatus
Room (20 °C)	0 M	pH 9.5 (3.1623 x 10 <sup>-5</sup> M)	0.5 M	3 M	Dispermat
40 °C	-	-	0.5 M	3 M	Air Bath Reactor
80 °C	-	-	0.5 M	3 M	Air Bath Reactor
160 °C	-	-	-	3 M	Air Bath Reactor

After caustic treatment, the fibre suspension was centrifuged at 14000 rpm for 10 minutes to separate the fibres. Fibres were then washed twice with 2 L of deionised water and centrifuged. Each sample was then suspended in 2 L of deionised water. Consistency of these suspensions were measured, and then total amount of fibres was estimated using the measured consistency. This was used to estimate the yield from each treatment.

#### 7.4.2.1. Extractive Recovery

Supernatant after centrifugation of treated fibre suspensions was used to recover extractives. The supernatant was dark brown in color and referred to as 'black liquor' here onwards. Black liquor sample (~ 1L) was heated in an open beaker at 150 °C while being stirred using a magnetic stirrer, to evaporate the water away until the volume is half of the original volume (~ 500 mL). Then the concentrated black liquor was cooled down overnight. It was then filtered on a Whatman 114 filter paper to recover the floating extractives. Extractives were then oven dried at 105 °C for 4 hours and weighed. See Figure 7.1 for a flow diagram for caustic treatment.



**Figure 7.1.** Flow Diagram for Caustic Treatment

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### 7.4.3. Fibre Characterization

#### 7.4.3.1. Aspect Ratio

Aspect ratio (length/diameter) after each treatment stage was evaluated by estimating the gel point of the fibre suspension through sedimentation, as described by Varanasi et al. [3]. In this method, a series of dilute suspensions, often from 0.01 – 0.1 wt% suspensions of MFC are prepared and poured equal volumes to a series of measuring cylinders, and the initial height of the suspension is recorded. The suspensions were allowed to settle > 48 hours and final sediment heights were measured. The ratio of final sediment height to initial suspension height is plotted against the consistency of the suspension, and a quadratic fit is found. The linear coefficient of this quadratic equation gives the gel point consistency which is then used to estimate the average aspect ratio of the fibres using a set of empirical equations as given in Varanasi et al. When calculating the aspect ratio, it was assumed that the density of the fibres was  $1333 \text{ kgm}^{-3}$  and the respective equation according to effective medium theory (EMT) was used. The aspect ratio is calculated using the following equation, by Varanasi et al. (2013) [3], where  $A$  is the aspect ratio of the fibres, and  $C_c$  is the solid concentration corresponding to gel-point.

$$A = 2.98C_c^{-0.58}$$

#### 7.4.3.2. Scanning Electron Microscopy

Scanning electron microscopy (SEM) images of the fibres in the different nanofibre suspensions were taken using a FEI Magellan 400 FEGSEM and a FEI Nova NanoSEM 450 to observe the fibre morphology. SEM samples were prepared by evaporating a droplet from a very dilute (~0.001 wt. %) suspension on a silicon chip mounted on a carbon tab. Sample dilution was done with MilliQ water. Once dried, samples were coated with 2 nm layer of Iridium. Images were acquired at 3 kV and different magnifications (5,000 – 100,000X).

#### 7.4.4. Sheet Making

The consistency of the suspension was adjusted to 0.2 wt.% and 60 gsm sheets were made by taking 600 g of the suspension. No retention aid was added, and all the sheets were made on Whatman Grade 541 filter paper using a standard automatic British Hand Sheet Maker. Drainage time (seconds) was measured from the start of the “Drain” cycle in the hand sheet maker until the sheet was fully drained, which was visually estimated from when the water disappeared from the whole surface of the sheet. After draining, the sheet was then couched manually by placing two new blotting papers and the couching plate, in that order, on top of the sheet and pressing with a rolling pin according to the TAPPI standard T205. Then, the filter paper was lifted off the mesh, with the sheet, two

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blotter papers and the couching plate still on top of it. The filter paper was then carefully removed from the sheet and the bottom most blotting paper was replaced with a new blotting paper. A gloss pressing plate was carefully placed on top the sheet and another blotting paper was put on top of it. It was then pressed at 345 kPa for 5 minutes between two square metal plates, using an automatic sheet press. After the first press, the hand sheet was then transferred onto a new blotting paper along with gloss pressing plate and pressed again for 2 minutes at the same pressure. Sheets were then air-dried in a conditioned testing room (25 °C and 50% RH), under restraint and stored there until further use.

#### 7.4.5. Sheet Testing

Oven dry weight (g) was measured by measuring the total sheet weight after drying them at 105 °C for 4 hours. Sheets were weighed using a balance with 0.001g sensitivity.

Thickness ( $\mu\text{m}$ ) was measured using an L&W Micrometer 51. Twenty measurements were taken from each sheet. Air permeability ( $\mu\text{m}/\text{Pa}\cdot\text{S}$ ) was measured using an L&W Air Permeance Tester. Tensile testing was done on 15 mm wide strips and a 100-mm test span with 10 mm/min extension rate, using an Instron 5566 Tensile Tester. Approximately 24 strips were measured for each refining and homogenization level. Force (N) and elongation at break (mm) were recorded. The strength results were expressed as tensile index, calculated by dividing the maximum tensile load (at break) by the width of the strip (15 mm) and by grammage of the paper sheet ( $\text{g}/\text{m}^2$ ).

### 7.5. Results & Discussion

#### 7.5.1. Yield

The lowest intensity of treatment used was stirring at room temperature with no caustic addition. This was followed by centrifugation to separate the fibres from the suspension and washing twice with deionised water. Interestingly, this process resulted in only an 89.1% yield. See table 7.2. This is because of the highly colloidal nature of the whitewater fines stream collected as floats in the dissolved air flotation unit. The colloids will stay suspended while the fines will sediment under the centrifugal force. The original consistency of the suspension, 2.6 wt. %, was calculated by oven dry method. Centrifugation separates the dissolved and colloidal extractives from fibres. This could be the reason for the reduction in yield.

The yield was further reduced when we increased the pH to 9.5. This was because more extractives, more specifically resin acids were removed from the fibres into the soluble phase. This phenomena is further explained in Chapter 8 in detail. Further increase of

caustic strengths to 0.5 M and 3 M, which were pH 13.69 and ~ 14 respectively, decreased the yield even further to 82.2% and 79.5%. This was due to the degradation of lignin at higher caustic strengths. This was also consistent with the observations when increased the temperature as the activity of the hydroxyl ion increases at higher temperatures and lignin is degraded at a higher rate.

**Table 7.2.** Yield from Caustic Treatment: Average of Duplicate Runs  $\pm$  [Min/Max – Average]

Treatment	Fibre Yield (wt. %)	Caustic Floated Extractives (wt. %)	Ethanol Washable Extractives (wt. %)	Dissolved + Colloidal Substances (Extractives + Dissolved Lignin) (wt. %) [Calculated]
Untreated	100	-	-	-
Ethanol Washing	90 $\pm$ 0.5	-	10 $\pm$ 0.5	-
Room Temp + 0 M	89.1 $\pm$ 1.1	0.0	-	10.9 $\pm$ 1.1
Room Temp + pH 9.5	86.6 $\pm$ 1.2	0.0	-	13.4 $\pm$ 1.2
Room Temp + 0.5 M	82.2 $\pm$ 1.2	5.5 $\pm$ 0.9	-	12.3 $\pm$ 0.3
Room Temp + 3 M	79.5 $\pm$ 1.2	8.4 $\pm$ 1.0	-	12.1 $\pm$ 0.2
40 °C + 0.5 M	81.1 $\pm$ 1.1	6.2 $\pm$ 0.8	-	12.7 $\pm$ 0.3
40 °C + 3 M	78.9 $\pm$ 0.9	8.9 $\pm$ 1.1	-	12.2 $\pm$ 0.2
80 °C + 0.5 M	76.4 $\pm$ 1.0	7.7 $\pm$ 0.7	-	15.9 $\pm$ 0.3
80 °C + 3 M	73 $\pm$ 1.3	9.4 $\pm$ 0.8	-	17.6 $\pm$ 0.5
160 °C + 3 M	39.1 $\pm$ 0.2	12.9 $\pm$ 0.3	-	48.1 $\pm$ 0.1

However, the yields were still quite high at these low and medium intensity caustic strength levels. Therefore, we could consider this operation as a high yield operation, even at 80 °C and 3 M caustic strength, the yield is 73%. However, when we increased the temperature to 160 °C with caustic strength of 3 M, the yield was only 39.1 $\pm$ 0.2%. The concentration of fines in this treatment was 5 wt%, meaning it had a higher fibres/caustic ratio. Regardless, the increase in temperature led to a significant decrease in yield. This means that the temperature has a non-linear effect on the yield.

Extractives concentration reach the critical micelle concentration when water is evaporated away. Even at concentrations above the critical micelle concentration, extractives remain suspended in black liquor when the suspension is hot. However, when

the suspension is cooled down, the extractives float to the top. These extractives can be easily collected by filtration. The extractive yield at 0.5 M caustic treatment was 5.5 % based on the dry weight of the fibres. See Table 7.1. More extractives were removed when the caustic strength is increased to 3 M. Even more extractives can be recovered when fibres are treated at higher temperature. Generally, extractive recovery increases with the intensity of the treatment. This was further verified in 160 °C and 3 M caustic strength treatment, where the extractive recovery was 12.9%. Higher intensity of treatment will expose more fibre surface due to removal of lignin. This releases more extractives into the suspension. Extractives can be a valuable by-product in this proposed process to upgrade the quality of the whitewater fines.

Ethanol washing removed 10% by weight of the sample as extractives, which was close to the floatable extractives produced with 3M caustic treatment. However, extractive recovery using ethanol could be problematic, as high volumes of flammable organic liquid are needed, which is undesired in a mill environment.

### 7.5.2. Effect of Treatment on Fibre & Sheet Properties

#### 7.5.2.1. Aspect Ratio

Aspect ratio can tell valuable information of the quality of the fibres. The higher the aspect ratio, the higher the tensile strength of the fibres according to the modified Page equation [4]. Aspect ratio of the untreated whitewater fines is 65. See table 7.3. Simple high shear mixing and washing of the fibres increased the aspect ratio to around 100. This value is significantly higher than the aspect ratio of untreated fibres. A possible explanation would be that extractives that are adsorbed on to the fibre surface could form a double-layer. This results in an 'increased' diameter that ultimately lowers the apparent aspect ratio. Extractives may also have adhered fibres and fibre fragments together to reduce aspect ratio. During the washing at room temperature, the fibres are collected after centrifuging and two subsequent washing steps with deionised water. This reduced the absorption of colloidal extractives and cleaned the fibre surface even more. This removed any double layer creation by adsorption of extractives as well as agglomeration into bundles, which is reflected by a higher aspect ratio. Further cleansing of fibre surface by raising the pH to 9.5 did not seem to have any significant impact on aspect ratio.

Ethanol washing however did not result in an increase in aspect ratio. In fact, the aspect ratio was reduced. This could be due to possible fibre cleaving and swelling due to ethanol. However, this should be further investigated as subsequent SEM analysis showed that

ethanol washing might have separated loosely bound individual fibres from fibre bundles. See section 7.5.2.2.

It was notable that the caustic treatment at higher strengths has significantly reduced aspect ratio. This was observed at all three different temperatures. This suggested that caustic treatment did cleave the fibres, possibly via hydrolysis. At 3 M caustic strengths, the effect seemed to be intensified.

**Table 7.3.** Aspect Ratio Development with Caustic Treatment

Temperature (°C)	Aspect Ratio					
	Untreated	Ethanol Washed	Caustic Strength			
			0 M	pH 9.5	0.5 M	3 M
Room	65	55	100	98	79	57
40	NA	NA	NA	NA	67	59
80	NA	NA	NA	NA	71	60
160	NA	NA	NA	NA	NA	68

#### 7.5.2.2. Scanning Electron Microscopy

SEM images show the effect of different treatment intensities on whitewater fines. See figure 7.2. Ethanol washing appeared to have separated loosely bound individual fibres from fibre bundles. This liberates more fibre surfaces for fibre-fibre bonding. It was difficult to gauge to the degree of surface cleaning through SEM images. However, we could observe colloidal sticky like material on the unwashed fibre surfaces.

SEM images from both 0 M and pH 9.5 treatment at room temperature shows the fibres have no significant contamination by colloidal extractives. Treatment at 0.5 M caustic strength did not show any significant differences in the SEM images. However, we could still observe fragments of ray parenchyma cells and they seem to be unaffected by treatment at even 80 °C and 3 M caustic strength. Interestingly, the treatment at 3M caustic strength appeared to have damaged the fibres quite intensively. Fibres were curled and many kinks were visible. Fibres also seemed to have been cleaved and shortened by the higher caustic strength. This is the cause for the shorter aspect ratio of fibres treated 3 M caustic strength.

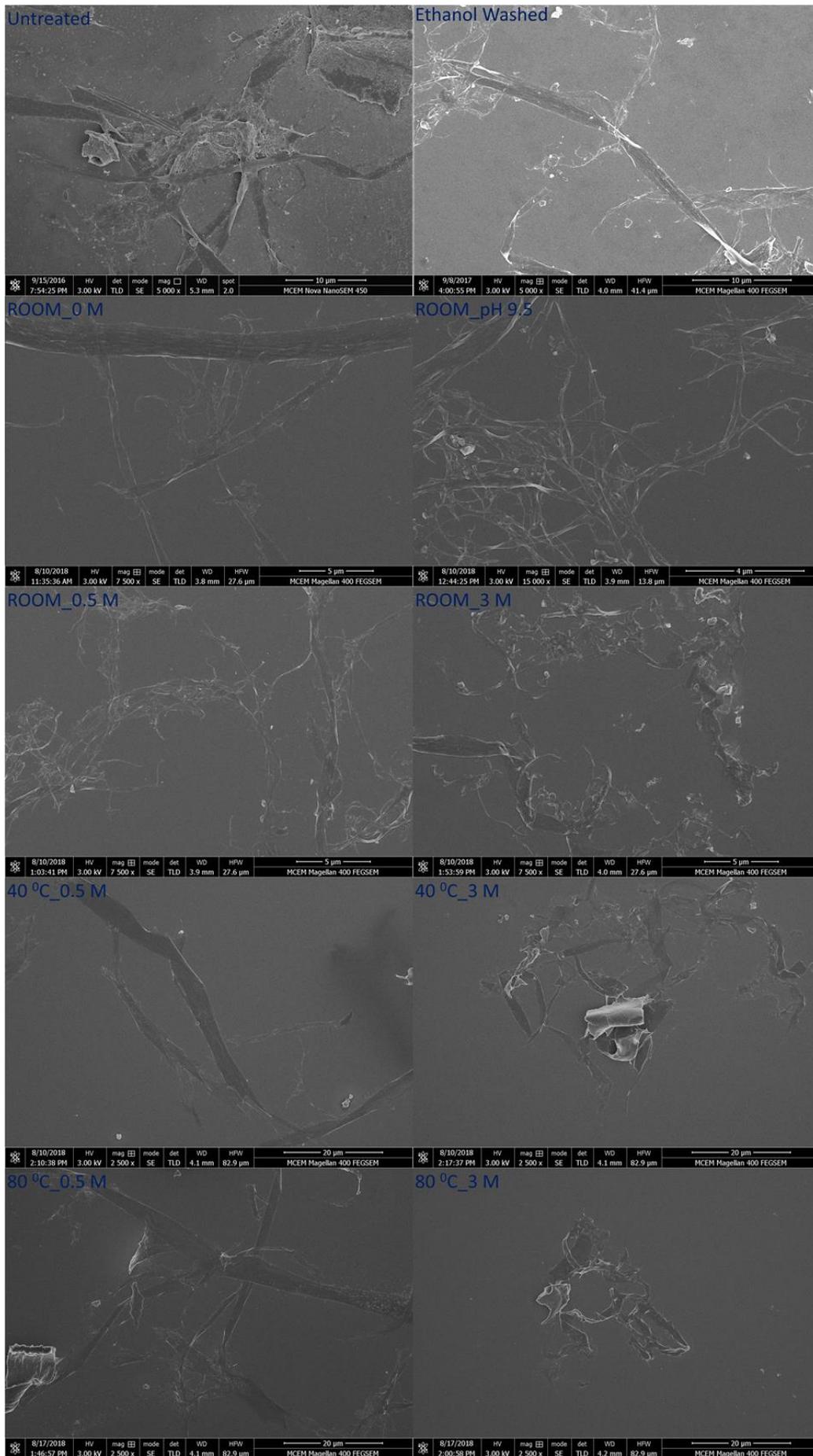


Figure 7.2. SEM Images of Treated Fibres

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### 7.5.2.3. Drainage Time

The drainage time increased when fibres were mixed in the dispermat and washed with deionised water. This could be due to removal of extractives from the surface and high shear mixing might be exposing and creating new surface by fibrillation. The drainage time further increased when fibres are treated at pH 9.5 at room temperature. This was due to more extractives (resin acids) being removed from the surface and fibres becoming less hydrophobic or more hydrophilic. See table 7.4. Resin acids are selectively removed from colloids and fibre surfaces when pH is increased beyond their colloidal  $pK_a$  values as explained in Chapter 1. This could have caused the slight increase in drainage time.

Ethanol washing however did not increase the drainage time significantly. This was unexpected as ethanol washing removes a significant amount of extractives. This should have increased the drainage time. One possible explanation is that ethanol washing removes mostly hydrophilic compounds; however, significant levels of hydrophobic compounds might be remaining on the fibre surface. This could have caused the low drainage time, and should be investigated further in a future study.

The drainage time significantly increased when fibres were treated at 0.5 M caustic strength. This could be due to removal of lignin and exposing more hydrophilic cellulose and hemicellulose surfaces. The drainage times at 0.5 M caustic treatments across all three temperatures were similar. However, when the caustic strength was increased to 3 M, the drainage time is decreased drastically. Ideally, higher caustic strength should remove more lignin and expose more and more of cellulose and hemicellulose making fibres more hydrophilic. This should ideally have increased the drainage time. However, the result is quite the opposite. Drainage time has significantly reduced. This could be explained by going back to the SEM images at 3 M caustic strength. The fibres are curled and deformed by the high caustic strength, which could cause the fibres to pack in a less tight manner eventually leading to higher porosity. This could decrease the drainage time significantly. However, further investigation is needed to understand this phenomenon.

However, the drainage time was high when fibres were treated at 160 °C. The fibre yield was 39.1% and it means that more lignin was removed at higher temperatures. This suggested that the fibres were probably mostly cellulose. This could have increased the hydrophilicity of the fibres, which was reflected in higher drainage time.

**Table 7.4.** Effect of Caustic Treatment on Drainage Time: Average  $\pm$  Standard Deviation

Temperature (°C)	Drainage Time (S)					
	Untreated	Ethanol Washed	Caustic Strength			
			0 M	pH 9.5	0.5 M	3 M
<b>Room</b>	35 $\pm$ 2.5	37 $\pm$ 2.5	94 $\pm$ 3	109 $\pm$ 3	181 $\pm$ 3	71 $\pm$ 10
<b>40</b>	NA	NA	NA	NA	187 $\pm$ 2	68 $\pm$ 4
<b>80</b>	NA	NA	NA	NA	193 $\pm$ 2	72 $\pm$ 10
<b>160</b>	NA	NA	NA	NA	NA	203 $\pm$ 16

#### 7.5.2.4. Sheet Density

Sheet density was increased significantly when fibres were washed with ethanol. See Table 7.5. This could be due to the separation of individual fibres from fibre bundles as observed in SEM analysis. High shear mixing and washing with deionised water increased the density slightly and it was further increased slightly when pH was increased to 9.5. The most significant increase in sheet density was observed when fibres were treated with 0.5 M caustic strength. This was due to the removal of extractives and also lignin, which resulted in lower fibre diameter causing the fibres to pack tighter. Sheet density further increased slightly when caustic strength was increased to 3M, indicating more lignin have been removed from the fibres. This was further observed when fibres were treated at 160 °C at 3 M caustic strength.

**Table 7.5.** Effect of Caustic Treatment on Sheet Density: Average  $\pm$  Standard Deviation

Temperature (°C)	Sheet Density (kg/m <sup>3</sup> )					
	Untreated	Ethanol Washed	Caustic Strength			
			0 M	pH 9.5	0.5 M	3 M
<b>Room</b>	417 $\pm$ 9	495 $\pm$ 3	444 $\pm$ 11	454 $\pm$ 7	614 $\pm$ 4	662 $\pm$ 6
<b>40</b>	NA	NA	NA	NA	610 $\pm$ 5	665 $\pm$ 3
<b>80</b>	NA	NA	NA	NA	654 $\pm$ 4	696 $\pm$ 6
<b>160</b>	NA	NA	NA	NA	NA	785 $\pm$ 8

#### 7.5.2.5. Air Permeance

Air permeance followed a similar trend to sheet density as expected as showed in Table 7.6. The air permeance values received at 3 M caustic strength were slightly higher than the values received at 0.5 M caustic strength. This indicated the higher porosity of sheets when fibres were treated at 3 M caustic strength. Air permeance was decreased as temperature was increased, at both 0.5 M and 3 M caustic strengths. More lignin was removed at higher temperatures. This resulted in reduced diameter and increased fibre-fibre bonding, which in turn resulted in a tighter pore structure and low air permeance.

**Table 7.6.** Effect of Caustic Treatment on Air Permeance: Average  $\pm$  Standard Deviation

Temperature (°C)	Air Permeance ( $\mu\text{m}/\text{Pa}\cdot\text{S}$ )					
	Untreated	Ethanol Washed	Caustic Strength			
			0 M	pH 9.5	0.5 M	3 M
Room	0.327 $\pm$ 0.124	0.105 $\pm$ 0.038	0.133 $\pm$ 0.009	0.105 $\pm$ 0.006	0.011 $\pm$ 0.001	0.028 $\pm$ 0.005
40	NA	NA	NA	NA	0.011 $\pm$ 0.001	0.014 $\pm$ 0.001
80	NA	NA	NA	NA	0.004 $\pm$ 0.001	0.013 $\pm$ 0.003
160	NA	NA	NA	NA	NA	0.003 $\pm$ 0.000

### 7.5.2.6. Tensile Properties

Ethanol washing alone improved the tensile properties quite significantly. Tensile index increased from 28 $\pm$ 1.4 Nm/g to 39.3 $\pm$ 1.9 Nm/g. Ethanol removes most of the hydrophobic compounds from fibre surface and cleans the surface. This allows the fibres to create more hydrogen bonding between the fibres, improving the tensile strength of the sheets made.

Tensile properties of caustic treated fibres showed interesting results and some unexpected results. The tensile index of sheets made by fibres that were washed at room temperature was 34.5 Nm/g. See Table 7.7. This value was higher than the tensile index of untreated fibres, which was 28 Nm/g. Untreated fibre were loaded with extractives as confirmed by ethanol washing. This is also reported previously in literature [2, 5]. When fibres were washed, it decontaminated the fibre surface and increased the tensile strength. However, when fibres were treated at pH 9.5, the tensile index was not improved significantly compared to 0 M. In both occasions, the yields were similar and no floatable extractives were recovered.

**Table 7.7.** Tensile Strength Development with Caustic Treatment: Average  $\pm$  Standard Deviation

Temperature (°C)	Tensile Index (Nm/g)					
	Untreated	Ethanol Washed	Caustic Strength			
			0 M	pH 9.5	0.5 M	3 M
Room	28 $\pm$ 1.4	39.3 $\pm$ 1.9	34.5 $\pm$ 2.2	35.3 $\pm$ 2.3	48.8 $\pm$ 2.4	36.5 $\pm$ 2.6
40	NA	NA	NA	NA	48.6 $\pm$ 2.0	36.1 $\pm$ 1.9
80	NA	NA	NA	NA	52.1 $\pm$ 3.2	38.0 $\pm$ 3.4
160	NA	NA	NA	NA	NA	73.2 $\pm$ 2.5

However, when caustic strength was increased to 0.5 M, tensile strength improved significantly, ~ 40% compared to 0 M treatment. This is because lignin is removed from fibres in addition to the extractives that are removed at 0 M. This improves fibre-fibre

bonding and tensile strength is improved as a result. Tensile strength not change significantly when increasing the temperature at 0.5 M caustic strength. Although, a slight trend of increase was observed when temperature is increased to 80 °C. However, it is not statistically significant.

Tensile strength did not increase significantly when 3 M caustic strength was used. However, the results could be explained when we look at the aspect ratio data and SEM images. Aspect ratio of the fibres treated at 3 M caustic strength was lower than the fibres treat 0.5 M caustic strength. SEM images also show that fibres are curled and damaged at 3 M caustic strengths compared to 0.5 M. These deformations reduced effective fibre-fibre bonding. In fact, the sheet strength is similar to the 0M treated fibres. These results are further verified when we look at the strain at break data in Table 7.8. The strain at break in sheets at 3 M caustic strength was significantly lower than the sheets at 0.5 M caustic strength. Curled and deformed fibres are not able to bind to each other effectively as straight and undeformed fibres. This caused the fibres to break quicker and at a lower strain. This behaviour of reduced quality at higher caustic strengths was previously observed in literature. Wan Rosli et al observed that there is an optimum level of alkali charge to get the best tensile properties of pulp [6]. According to the authors, when alkali charge was increased beyond the optimum value, tensile properties decreased due to fibre damage.

**Table 7.8.** Effect of Caustic Treatment on Strain at Break: Average  $\pm$  Standard Deviation

Temperature (°C)	Strain at Break (%)					
	Untreated	Ethanol Washed	Caustic Strength			
			0 M	pH 9.5	0.5 M	3 M
Room	1.40 $\pm$ 0.13	1.50 $\pm$ 0.15	1.93 $\pm$ 0.15	1.99 $\pm$ 0.34	1.76 $\pm$ 0.25	1.22 $\pm$ 0.16
40	NA	NA	NA	NA	1.95 $\pm$ 0.51	1.19 $\pm$ 0.12
80	NA	NA	NA	NA	1.68 $\pm$ 0.23	1.24 $\pm$ 0.15
160	NA	NA	NA	NA	NA	2.30 $\pm$ 0.34

However, when fibres were treated at 160 °C and at 3 M caustic strength, the tensile index improved significantly. This was probably because the yield was now so low that the remaining material was largely cellulose, which resulted in higher tensile strength via increased hydrogen bonding. This was also reflected in strain at break.

### 7.5.3. Feasibility of Different Treatment Methods

Caustic treatment process can improve the quality of the fibres significantly without any further mechanical energy addition. Simple washing of the fines improved the tensile

index from 28 Nm/g to 34.5 Nm/g. This is a good achievement considering there is no chemical addition. However, this value is still lower than that of bleached TMP newsprint, 40.6 Nm/g, as reported in Chapter 5.

The best conditions out of all the conditions tested was 0.5 M caustic treatment at room temperature. This resulted in a tensile index of 48.8 Nm/g. This was a ~40% increase in strength compared to the same treatment with no caustic addition. However, this was a ~ 74% increase when we compare with the sheets made of whitewater fines which have a tensile index of just 28 Nm/g. The tensile strength achieved by this treatment was significantly higher than that of bleached TMP newsprint as reported in Chapter 5. This suggests that treated whitewater fines could be added to the TMP newsprint without any detrimental effects on the tensile properties. The extractives recovered can be a valuable by-product as discussed in the literature review. However, the caustic strength used, 0.5 M, may or may not be the optimum. Therefore, further experiments and studies are needed to find the optimum conditions to achieve the best tensile properties and maximize the extractive recovery. Further studies are also needed to confirm the composition of both treated fibres and extractives in each phase. The treated whitewater fines could be good source to produce microfibrillated cellulose in a continuation of this project.

## 7.6. Conclusions

Whitewater fines contains extractives and lignin, which reduces the quality. Whitewater fines could be upgraded back to the desired quality of TMP newsprint with chemical treatment and without any further addition of mechanical energy. Ethanol washing improved the tensile strength from 28 Nm/g to 39.3 Nm/g. However, caustic washing could be more practical to implement in an existing TMP pulping mill and light treatment at ambient conditions could improve the strength quite significantly. Caustic treatment at room temperature and at 0.5 M caustic strength improved the tensile index to 48.8 Nm/g. This represents ~ 74% increase in tensile strength when compared to untreated whitewater fines. Extractives could also be recovered from the black liquor as a by-product similar to tall oil in Kraft pulping mills. However, further experiments and studies are needed to further optimize the caustic strength to get the best tensile properties and extractive yield. Treated whitewater fines could easily be added to the TMP newsprint without any detrimental effects to the tensile properties and they could be a good source to investigate the production of microfibrillated cellulose.

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## **Chapter 8**

Recovery of Resin Acids and Terpenes from  
Thermomechanical Pulp Mill Process Water  
Using Membrane Filtration

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# Preface

Process water streams of thermomechanical pulping mills contain phytochemicals that could be extracted as value-added products. During the initial analysis of the Norske Skog – Boyer Facility, the subnatant of the dissolved air flotation unit was selected as an ideal candidate for recovering resin acids, while the plug screw pressate and the primary refiner steam condensate were selected as the prime candidates for terpenes recovery. The subnatant was analysed for resin acids using gas chromatography following lipophilic extraction. The plug screw pressate and the primary refiner steam condensate were analysed using headspace gas chromatography and/or solid-phase micro-extraction. Micro- and ultrafiltration were used to evaluate the possibility of selectively concentrating resin acids. Ultrafiltration was tested for the feasibility of recovering and concentrating terpenes.

This work addresses objectives B1 and B2.

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# Chapter 8 - Recovery of Resin Acids and Terpenes from Thermomechanical Pulping Mill Process Water Using Membrane Filtration

## 8.1. Abstract

Resin acids and terpenes are important constituents of wood extractives in pulp paper industry, and have many value added applications as pharmaceuticals, anti-oxidants and starting material for fragrances and polymers. Resin acids and terpenes come out the wood during the primary processing in thermomechanical pulping. Recovering these chemicals from thermomechanical pulping process water system could be a way to implement biorefining. In this chapter, the potential of recovering resin acids from whitewater and terpenes from plug screw pressate using ultrafiltration is reported. Two-stage ultrafiltration is proposed; membrane filtration of thermomechanical pulp mill whitewater at pH 9.5 through a 100-kDa regenerated cellulose membrane, and membrane filtration of permeate from Stage 1 at pH 4.5 through a 30-kDa membrane regenerated cellulose. The proposed process can recover 64% of resin acids present in the original whitewater stream with 77% enrichment of resin acids. Terpenes could completely isolated and concentrated in the retentate by using ultrafiltration. The concentrated retentate could be an efficient feed to subsequent unit operations to separate terpenes.

## 8.2. Introduction

Resin acids and terpenes are two essential components in extractives in radiata pine. Wood extractives are discussed in detail in section 1.2.5. Removal of non-volatile extractives from thermomechanical pulping (TMP) process water streams is critical. Colloidal extractives cause 'pitch' when they are unstable in whitewater. Pitch and colloidal stability are discussed in detail in section 1.2.5.1. We have identified resin acids as the potentially most valuable component in wood extractives in Chapter 1. The potential value-added applications of resin acids are mentioned in section 1.2.5.3. Terpenes can be separated from the plug screw pressate and/or TMP primary refiner steam condensate as discussed earlier. Terpenes can be valuable raw materials for production of fragrances, biopharmaceuticals, and polymers. See section 1.2.5.4.

#### 8.2.2.1. Colloidal Nature of Resin Acids

Resin acids exist in three different forms in TMP whitewater as discussed earlier in section 1.2.5, and it is dependent on the pH and temperature. TMP pulping is often carried out in neutral or near-neutral pH. At these temperatures, resin acids mostly exist in their colloidal form and often in complex colloidal structure as shown in Figure 1.8. Resin acids exist in the outer layer of the colloid and can be moved out of the colloid and solubilized at pH values above their colloidal  $pK_a$  values [1, 2]. Depending on the pH, almost 100% of the resin acids could be removed from the colloid and be moved to the soluble phase [1, 3, 4]. The Table 1.3 in section 1.2.5.1, shows the colloidal  $pK_a$  values of some resin acids at 20 °C and 50 °C [1].

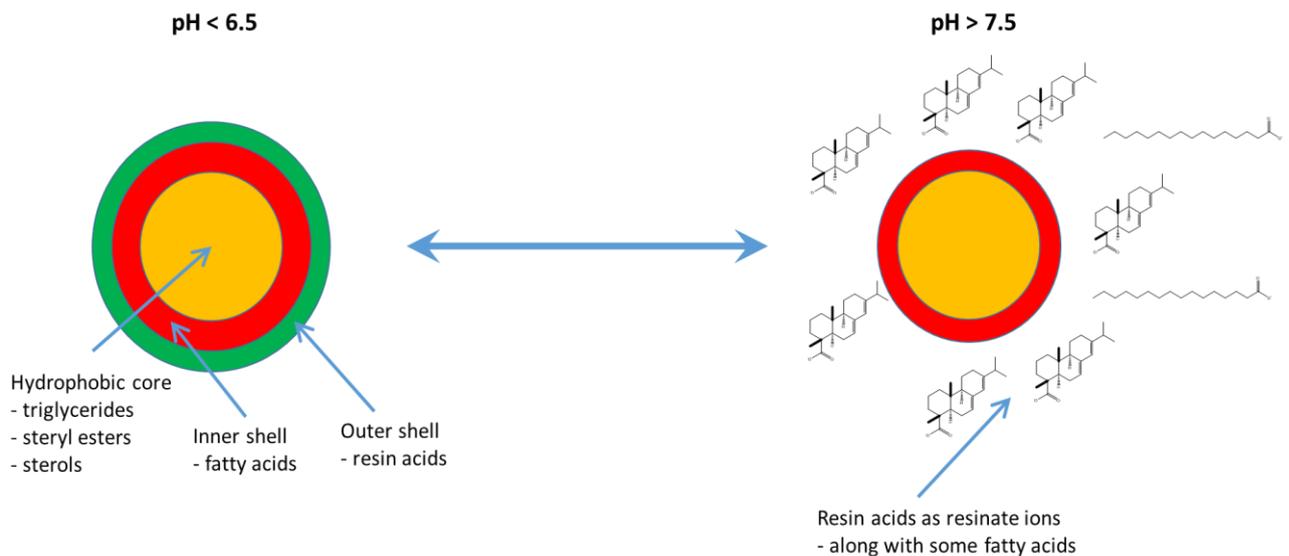
It can be expected that most of the resin acids would become soluble at pH above 8.0. However, along with resin acids, fatty acids can also become liberated from the colloids with the increase of pH, even though the  $pK_a$  values of fatty acids are slightly higher than those of resin acids. See Table 1.4 in section 1.2.5.1. Therefore, some fatty acids could be solubilized with the increase of pH. Therefore, optimum pH ranges should be investigated to reduce the fatty acid concentration in soluble phase.

#### 8.2.2.2. Manipulation to Isolate Resin Acids

In order to isolate the resin acids, their encapsulation in a mixed colloid was the most critical barrier to overcome. As explained earlier, resin acids form complex colloids with fatty acids, triglycerides and other components that are often referred to as neutrals. If resin acids could be isolated from the colloids, it would make it possible to recover them and to purify them further into individual resin acids. This could be achieved by manipulating the pH. However, as discussed in section 1.2.5.1, some fatty acids could also be liberated alongside the resin acids. Therefore, pH must be optimized to reduce the amount of fatty acids liberated with resin acids. However, the colloidal  $pK_a$  values reported in Tables 1.3 and 1.4 are for pure resin acids or fatty acids mixtures. The colloidal  $pK_a$  of resin acids in complex colloids in whitewater could be different from the value of reported in Tables 1.3 and 1.4, and the same applies for fatty acids. Therefore, it is not possible to refer to the Tables 1.3 and 1.4 to determine a pH that will liberate the resin acids while minimizing the fatty acid content. This demands that a proper experimental study is necessary to determine efficient methods to isolate resin acids from TMP whitewater.

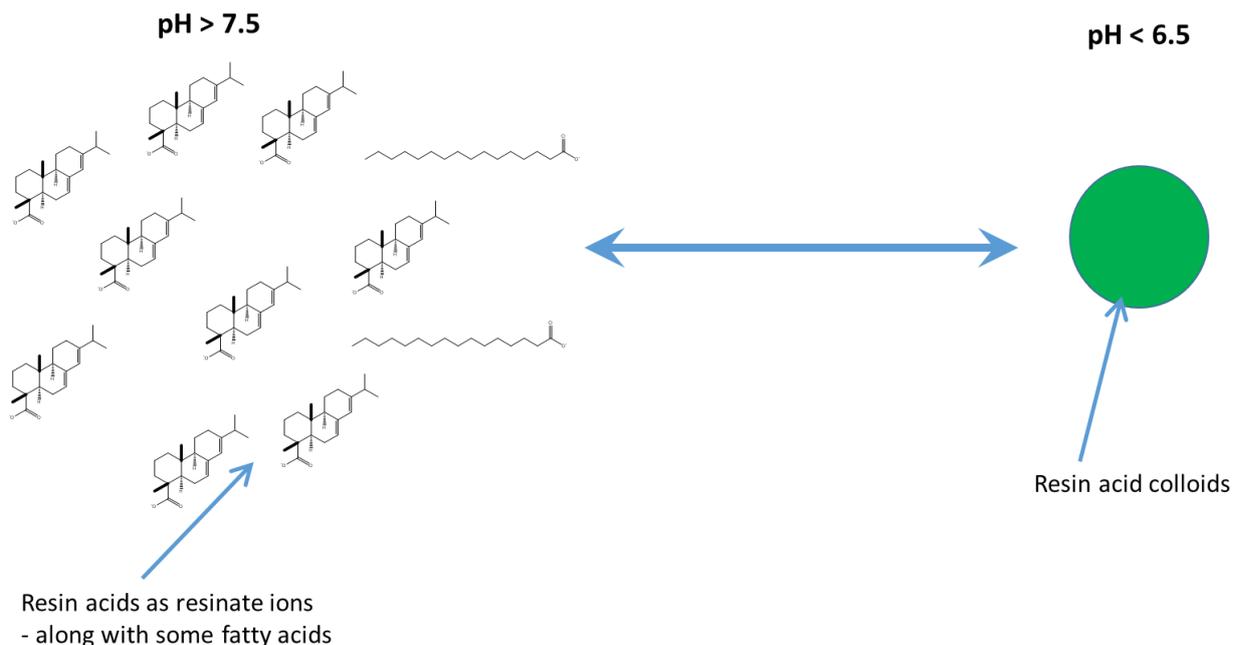
The following process is proposed to isolate resin acids effectively using efficient manipulation of pH and membrane separation.

TMP whitewater contains fines that could complicate the downstream processing. Therefore, the first stage is to remove fines using centrifugation or filtration. Then, we could increase the pH to move resin acids out of the colloids as shown in Figure 8.1.



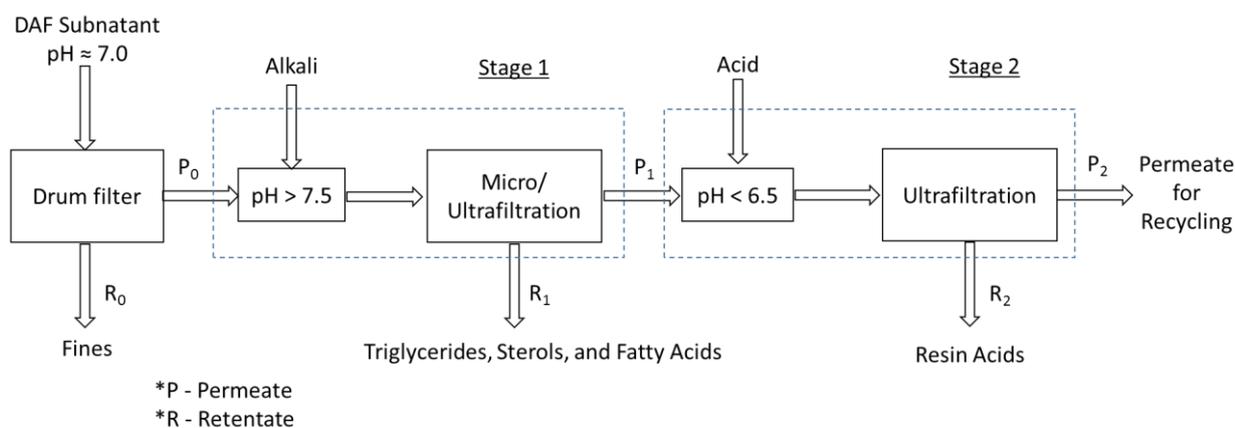
**Figure 8.1.** Stage 1 – Isolation of Resin Acids from Colloids

Subsequently membrane filtration, either micro- or ultrafiltration was used to separate the colloids which contained the triglycerides and some fatty acids to produce a stream containing mostly resin acids. Reduction of the pH of this stream to values below the colloidal  $pK_a$  of resin acids effectively moves these resin acids back into their colloidal form. See Figure 8.2.



**Figure 8.2.** Stage 2 – Further Isolation of Resin Acids

A further membrane filtration stage was used to further isolate the resin acid colloids and concentrate the stream. The purified water stream contains mostly hydrophilic compounds that are not detrimental to the process chemistry of TMP mills and could be readily circulated to close the loop. The following flow diagram summarizes the proposed process. See Figure 8.3.



**Figure 8.3.** Proposed Process to Isolate Resin Acids from TMP Whitewater

In this study, the effectiveness and efficiency of this proposed process to isolate resin acids and produce a concentrated resin acid-rich aqueous flow was evaluated. This could then be further processed into a pure resin acid mixture or individual resin acids.

Using membrane filtration to recover wood extractives from TMP process water is not a novel concept. This has been used to many extents by various researchers to purify the TMP process water and close the water loop in the mills. However, membrane filtration is seldom used to recover extractives as value added product [5, 6]. Furthermore, membrane filtration has not yet been used to isolate resin acids and recover them as a valuable chemical from TMP whitewater. This underlines the significance of the research carried out in this work.

### 8.3. Materials

At Norkse Skog – Boyer, TMP whitewater water stream is clarified using a dissolved air flotation (DAF) unit. The main purpose of this unit is to remove colloidal extractives and whitewater fines that are of poor quality. The subnatant of this DAF process, which hereafter is referred to as DAF subnatant, is then recirculated in the process water loop. However, the studies by the mill have found that this stream still contains significant amounts of resin acids. This stream also contains some fine fibrous materials. The DAF subnatant was used for investigating the possibility of recovering resin acids.

Plug screw pressate and primary refiner condensate from the TMP2 mill of the same facility was used for investigating the recovery of terpenes using membrane filtration.

All the samples were frozen upon receipt and used as necessary.

## 8.4. Methodology

### 8.4.1. Membrane Filtration Set-up

A solvent-resistant stirred cell membrane filtration setup (XFUF07601, Merck-Millipore) was used for all the membrane filtrations in this work. Membrane was cut into 76 mm diameter circle using a laser cutter (Helix, Epilog) to fit into the stirred cell when the membrane supplied was more than 76 mm in diameter. Membrane was gently washed and wetted with a horizontal flow of deionised water prior to fitting in the stirred cell. High purity compressed air (Air Liquide) was used to apply a 3-bar gauge pressure difference across the membrane.

Deionised water was passed through each membrane type prior to membrane separation of process water samples, to measure the pure water flux. This was later used to calculate the level of fouling.

### 8.4.2. Resin Acids

Four different membrane types were tested for the Stage 1 process. Two microfiltration membranes were used; Regenerated cellulose (RC) and polyethersulfone (PES) membranes each with 0.2  $\mu\text{m}$  pore size. RC microfiltration membrane was supplied by Whatman (RC58) while the PES microfiltration membrane was supplied by Sterlitech (PES029025). Two ultrafiltration membranes were also used, made of the same two materials, with 100kDa molecular weight cut off. Both ultrafiltration membranes were supplied by Merck-Millipore (Ultracel 100kDa – PLHK07610, Biomax 100kDa – PBHK07610).

#### 8.4.2.1. Stage 1

For stage 1, 100 g of the DAF subnatant was used in each membrane filtration and four (4) different pH values were investigated: 7.5, 8.5, 9.5 and 10.5. 2% NaOH was used for pH adjustment. Membrane separation was carried out until a concentration factor of 8-10 was achieved in the retentate. The flux was measured electronically using a weighing balance that was connected to data acquisition software and average flux was calculated at the end of each membrane separation. Permeate and retentate were collected, labelled and stored in a freezer until further use. The membrane was removed from the setup and gently washed by a horizontal flow of deionised water. Then it was put back in the

membrane setup and deionised water was passed through the membrane under similar conditions to calculate the pure water flux after membrane separation. This was used to calculate the percentage of fouling according to the following equation as reported by several researchers in the literature [7, 8].

$$\text{Percentage of fouling (\%)} = \frac{(\text{pure water flux before} - \text{pure water flux after})}{\text{Pure water flux before}} \times 100 \%$$

Membrane filtrations were run in duplicate.

#### 8.4.2.2. Stage 2

The optimum conditions from the stage 1: membrane material, membrane type (micro- or ultrafiltration), and pH were selected to produce permeate for the stage 2. Then, membrane was filtration carried out with a RC 30kDa ultrafiltration membrane (Ultracel 30kDa – PLTK07610, Merck-Millipore) at four (4) different pH values: 6.5, 5.5, 4.5 and 3.5. HCl acid of 2% was used for pH adjustment. Similar concentration factors were achieved, and fouling intensity was calculated as described above. Membrane filtrations were run in duplicate.

#### 8.4.2.3. Extractive Analysis

##### 8.4.2.3.1. Liquid – Liquid Extraction

5 ml of DAF subnatant was measured into a Teflon centrifuge tube using a positive displacement pipette. The pH was adjusted to 3.5 by the addition of drops of 2% HCl. An internal standard solution (100 µL) containing known amounts of pentadecanoic acid (P6125 – Sigma Aldrich), heptadecanoic methyl ester (H4515 – Sigma Aldrich), cholesteryl palmitate (C6072 - Sigma Aldrich) and glyceryl triheptadecanoate (T2151 - Sigma Aldrich), was add into the centrifuge tube. This solution was made by dissolving known amounts of above compounds in toluene (100849100 – Merck). Then 2.5 ml of tert-butyl methyl ether (tBME, 1019952500 – Merck) was added to the to the centrifuge tube and shaken vigorously for 2 minutes with the lid tightly closed. The resulting emulsion was centrifuged at 2500 RPM for 10 min. The tBME layer was carefully pipetted out to a marked GC vial, without disturbing the fines below it. Solvent in GC vial was completely evaporated using a nitrogen blower. The extraction was repeated with fresh 1.5 ml of tBME without any internal standard and solvent layer was pipetted out to the same marked GC vial and solvent was evaporated completely again. A calibration standard GC vial was prepared by adding 100 µl of internal standard solution and another 100 µl of ‘spike’ solution, containing known amounts of petroselenic acid (P8750 - Sigma Aldrich), dehydroabietic acid (R001 – CanSyn Canada), and glyceryl trioleate (T7140 - Sigma

Aldrich), and the solvent was completely evaporated using nitrogen blower. Similarly, calibration standard GC vials containing 25, 50, 75, 125, 150 and 200  $\mu\text{L}$  each of both internal standard and 'spike' solution were prepared. Toluene (750  $\mu\text{L}$ ) was added into each GC vial and mixed thoroughly before analysis via GC.

All the extractions were duplicated. All the retentate samples were diluted ~8 times prior to extraction using the similar method described above.

#### 8.4.2.3. 2. Quantitative analysis by GC - FID

The GC column used for the quantitative determinations of major components and/or component groups was a large diameter (15 m X 0.53 mm i.d.) open tubular column coated with dimethyl polysiloxane ZB-1 (Phenomenex), film thickness 0.15  $\mu\text{m}$ ; carrier gas He -24.2 ml/min; temperature program of column oven: 80  $^{\circ}\text{C}$  (1.50 min) – 12  $^{\circ}\text{C}/\text{min}$  – 340  $^{\circ}\text{C}$  (10 min); injector: 80  $^{\circ}\text{C}$  (0.5 min) – 200  $^{\circ}\text{C}/\text{min}$  – 345  $^{\circ}\text{C}$  (20 min); FID detector: 350  $^{\circ}\text{C}$ . The injection mode was cold-on-column. The gas chromatograph equipment used was an Agilent 7890B instrument. The peak areas were measured relative to the internal standard.

The response factors of fatty acids and unidentified peaks before fatty acids were taken as that of heptadecanoic methyl ester. The response factors of resin acids were taken from dehydroabietic acid while the response factors for neutrals (sterols) between fatty acids and triglycerides were taken from cholesteryl palmitate. The response factors of triglycerides were assumed be the same as that of glyceryl trioleate.

Extraction coefficients between tBME and water for fatty acids, unidentified peaks before fatty acids and resin acids were assumed to be the extraction coefficient of heptadecanoic methyl ester. The extraction coefficient of neutrals (sterols) from resin acids to triglycerides was calculated from recovered cholesteryl palmitate while for triglycerides, glyceryl triheptadecanoate was used.

Total resin acids, fatty acids, unknowns, neutrals and triglycerides were all calculated using group peak integrations.

Resin acid recovery in permeate (%) in stage 1 was calculated using the mass balance.

*Resin Acid Recovery in Permeate (%)*

$$= \frac{\text{Concentration of Resin Acids in the Permeate} \left( \frac{\text{mg}}{\text{mL}} \right) \times \text{Mass of Permeate Collected (g)}}{\text{Concentration of Resin Acids in the Feed} \times 100 \text{ g}}$$

Resin acid recovery in permeate (%) in stage 2 was calculated using the same equation as above. This was used to calculate the resin acid recovery in retentate, assuming no loss of resin acids in the process.

$$\text{Resin Acid Recovery in Retentate (\%)} = 100 - \text{Resin Acid Recovery in Permeate (\%)}$$

### 8.4.3. Terpenes

#### 8.4.3.1. Terpene Analysis

Both plug screw pressate and the TMP primary refiner steam condensate were both analysed for terpenes using headspace gas chromatography. Solid Phase Micro-Extraction (SPME) GC was also used for TMP primary refiner steam condensate.

##### 8.4.3.1.1. Headspace Gas Chromatography

Plug screw pressate was analysed using headspace GC according to the following method. A 20mL volume headspace GC vial was filled with 0.5 mL of the sample and 0.5 mL of 0.2 M Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O pH 7.0 buffer solution. Buffer solution was prepared by dissolving 3.58 g of Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O and adding 50 g of deionised water. The pH of the buffer solution was adjusted using 1:1 phosphoric acid. The buffer solution was used with all the samples to normalize the pH. To each sample was added 20 µL of α-terpine-d<sub>3</sub>-ol (D-2707 – CDN Isotopes, Canada) of known concentration as internal standard. Calibration standards were prepared by adding 2 – 25 µL amounts of terpene mixture (α-pinene, β-pinene, d-limonene and α-terpine-d<sub>3</sub>-ol of known concentrations) to headspace vials containing 0.5 mL of buffer solution and 0.5 mL of deionised water. Internal standards, α-pinene (N-10984), β-pinene (N-11120) and d-limonene (N-11560) were all acquired from Chemservice Inc, USA.

TMP primary refiner condensate was also analysed using the same method as above, however 5 mL of sample was used in the headspace vial together with 5 mL of buffer solution.

The sample was then incubated in the headspace vial for at 80 °C for 6 mins prior to drawing a gas phase sample at 15 mm syringe penetration depth. Then, 0.5 mL of the sample was auto-injected into the column. The column conditions are as follows; 5%phenyl 95%dimethylsiloxane (DB-5MS UI, 112-5532UI, 30 m x 0.25 mm id, 0.25 µm film thickness, Agilent USA) capillary column, carrier gas He – 1 mL/min with 10:1 split ratio, temperature program of the column oven: 40 °C (0 min) – 5 °C/min – 120 °C (0 min) – 25 °C/min – 325 °C (2 min), total GC run time of 26.2 mins, MSD detector – 260 °C. The gas chromatograph equipment used were Agilent 7890B and Agilent 5977 MSD. The peak areas were measured relative to the internal standard.

#### 8.4.3.1.2. Solid Phase Micro-Extraction

TMP primary refiner steam condensate was analysed using SPME GC according to the following method. The fibre used was Polydimethylsiloxane (PDMS) – autosampler. A 20 mL headspace vial was filled with 5 mL of sample and internal standard, 20  $\mu$ L of  $\alpha$ -terpine-d<sub>3</sub>-ol (D-2707 – CDN Isotopes, Canada) of known concentration was added to the sample prior to incubating for 5 minutes at 30 °C. The fibre was then inserted into the headspace vial up to a penetration depth of 40 mm and then the sample was extracted for 40 minutes. Then the sample was injected into the GC column and desorbed for 12 seconds. The GC program used was as follows; narrow bore (30 m x 0.25 mm id) open tubular column, carrier gas He – 1 mL/min with 1:1 split ratio, temperature program of the column oven: 40 °C (0 min) – 5 °C/min – 120 °C (0 min) – 25 °C/min – 250 °C (2 min), total GC run time of 26.2 mins, MSD detector – 260 °C. The gas chromatograph equipment used were Agilent 7890B and Agilent 5977 MSD. The peak areas were measured relative to the internal standard.

#### 8.4.3.2. Membrane Filtration

Membrane filtration of plug screw pressate was carried out using two ultrafiltration membranes; RC 100 kDa and PES 100 kDa, and three different pH levels; 3.5, 7.0, and 10.5, using the same method as described in 8.4.2.1. Plug screw pressate was centrifuged to remove fibres, fibre bundles, and sand prior to ultrafiltration. The original pH of the plug screw pressate was measured as 5.5. 2% HCl and 2% NaOH were used for pH adjustment.

Retentate samples were diluted 1:10 prior to GC analysis. Otherwise, they were analysed using the exact same method described above in 8.4.3.1.1. Permeate samples and the original were analysed using the same method described above, however, 5 mL of the sample was used along with 5 mL of the buffer solution. Membrane filtrations were run in duplicates.

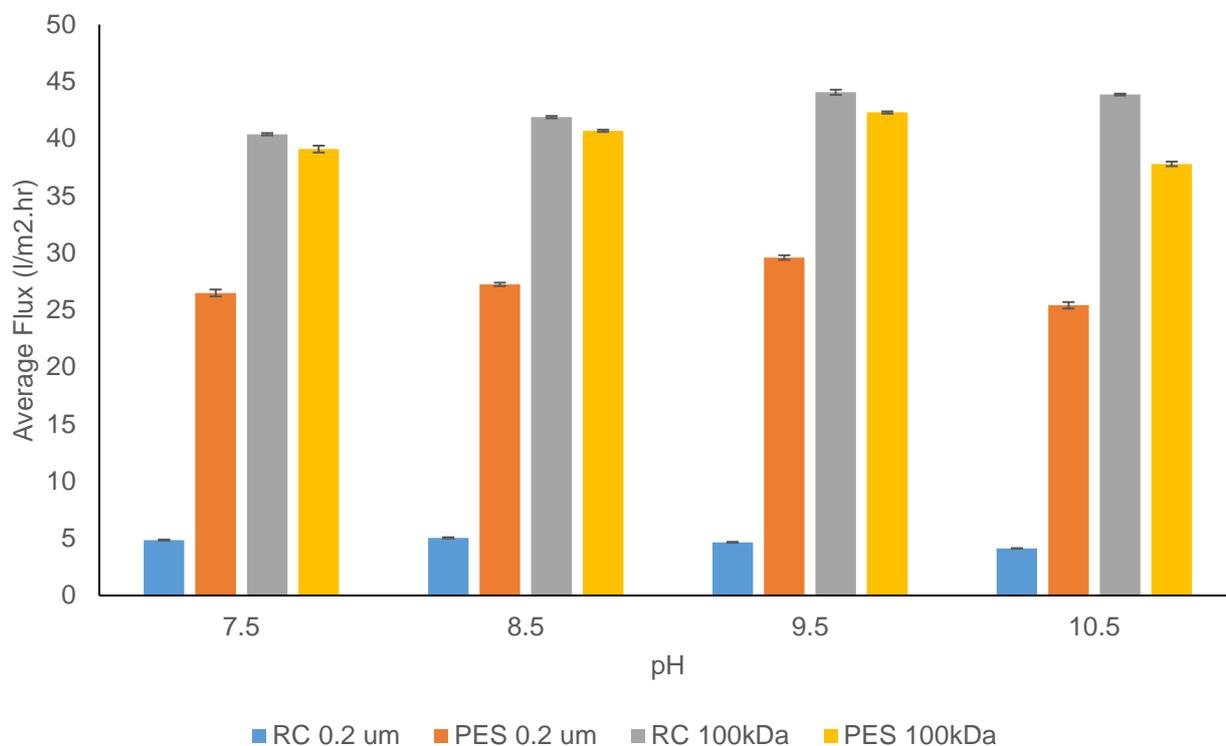
## 8.5. Results & Discussion

### 8.5.1. Resin Acids

#### 8.5.1.1. Membrane Filtration – Stage 1

Both microfiltration membranes performed significantly worse than ultrafiltration membranes in stage 1. See Figure 8.4. Their flux was very low and was not suitable for this application. Microfiltration membranes have a higher pore size than ultrafiltration membrane. This would indicate that flux should be higher through microfiltration membranes rather than ultrafiltration membranes. However, their higher pore size is also

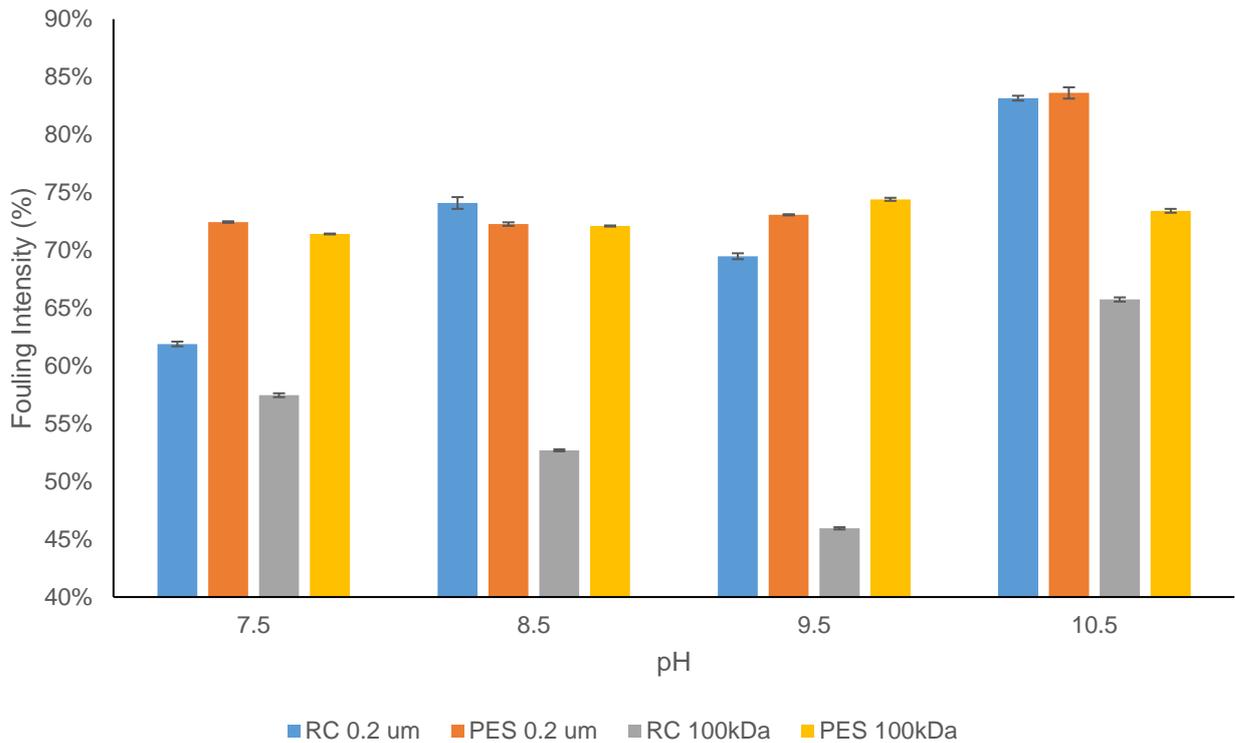
their weakness. This causes colloids to be trapped in the pores especially in a dead-end filtration setup like the one used in this work. This results in lower average flux rate than ultrafiltration membranes, which are not easily clogged.



**Figure 8.4.** Average Flux through Membranes in Stage 1: Error bars represent values from the two individual runs

However, the very low flux of the regenerated cellulose microfiltration membrane was because that particular membrane expanded when wetted. The expansion might have been not only outward, but also inward. This would cause the pores to shrink and eventually cause low flux rates.

The RC ultrafiltration membrane performed slightly better than the PES ultrafiltration membrane. This is further evident when we look at the fouling intensity. See Figure 8.5.



**Figure 8.5.** Fouling Intensity in Membranes in Stage 1: Error bars represent values from the two individual runs

RC membranes were less fouled compared to PES membranes. This was due to the hydrophilic nature of the regenerated cellulose and hydrophobic nature of polyethersulfone [6]. The colloids in TMP whitewater are hydrophobic and the RC membrane would repel them away from the surface, while the colloids will get attracted towards the PES membrane [6]. This resulted in lower fouling in RC membranes compared to PES membranes.

Fouling reduced in RC ultrafiltration membrane when the pH was increased from 7.5 to 9.5. This could be due to the gradual removal of resin acids from the colloid surface, which increase the hydrophobicity of the colloid. However, the colloid might be too small and could be clogging the membrane.

These results suggested that regenerated cellulose is the optimum membrane material and pH 9.5 might be the optimum based on the flux and fouling. However, this should be confirmed by the analysis of resin acids in the permeates and the retentates. The flux and fouling could definitely be improved in an industrial scale membrane filtration set up which is more resistant to fouling, such as cross flow filtration or vibrating membrane filtration setup [9].

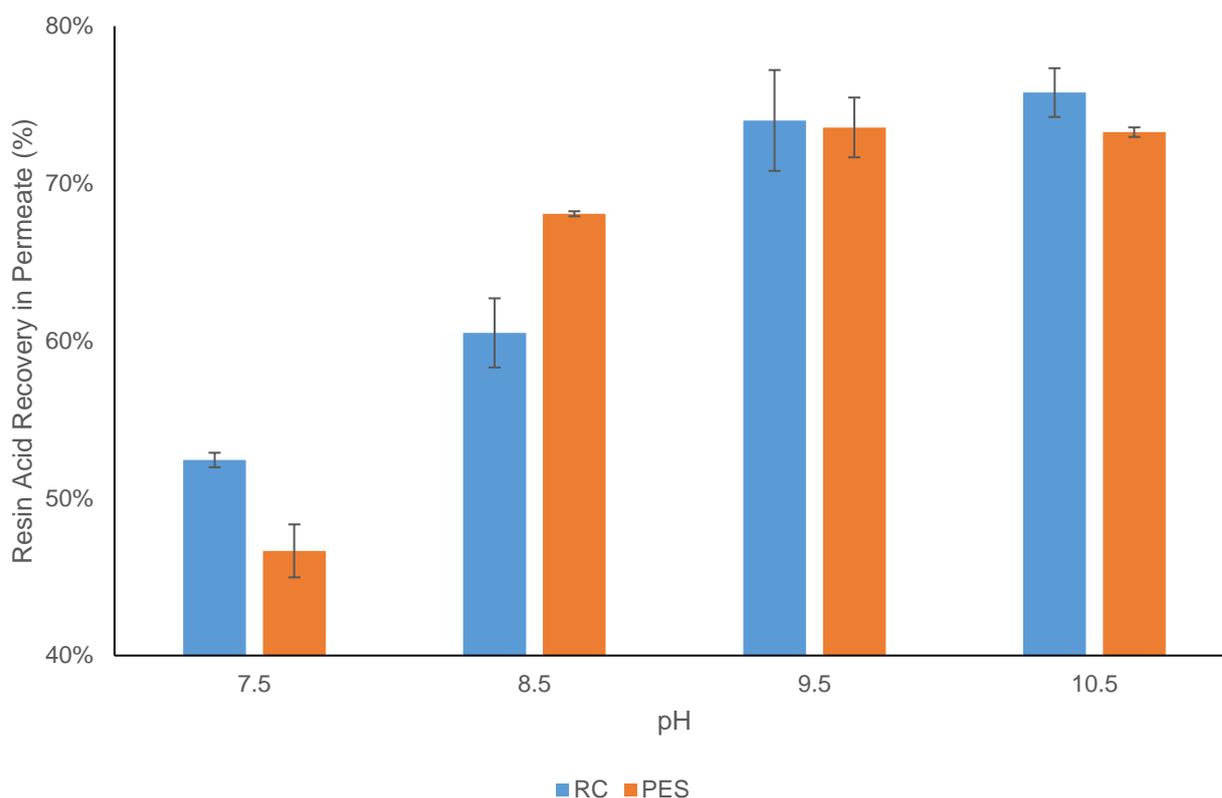
## 8.4.1.2. GC Analysis – Stage 1

The original DAF subnatant sample, P<sub>0</sub>, used for the stage 1 had the following concentrations. Resin acids were the most significant component with 41% of the total lipophilic compounds.

**Table 8.1.** Average Concentration of Extractives in DAF Subnatant – Stage 1

Component		Average Concentration (mg/L)
Resin Acids	Pimaric Acid	6.18
	Isopimaric Acid	1.84
	Unidentified Resin Acid	2.09
	Palustric + Levopimaric Acids	14.17
	Dehydroabiatic Acid	27.53
	Unidentified Resin Acid	1.91
	Abietic Acid	12.01
	Unidentified Resin Acid	1.91
	Neoabiatic Acid	3.68
β-Sitosterol		5.18
Triglycerides	Triglyceride - Unknown	8.89
	Glyceryl Trioleate	23.91
Total Fatty Acids		16.93
Total Resin Acids		87.16
Total Unknowns		32.96
Total Neutrals		30.22
Total Triglycerides		46.26

Resin acid concentrations in retentate and permeate was analysed. Based on these concentrations, the percentage of resin acids recovery in permeate was calculated for each ultrafiltration membrane type and each pH level. The results are shown below in Figure 8.6.



**Figure 8.6.** *Percentage Recovery of Resin Acids in Permeate: Error bars represent values from the two individual runs*

The results show that pH 9.5 and pH 10.5 are the best pH levels for the highest recovery of resin acids in the permeate. However, pH 9.5 was selected as the best pH based on the flux and fouling data reported above. At all of the pH levels tested, including pH 9.5 and 10.5, there were no triglycerides or  $\beta$ -sitosterol in the permeate. However, there was still a significant amount of fatty acids. The concentration of extractives in the permeate produced at pH 9.5 using RC 100 kDa membrane is given in Table 8.2.

**Table 8.2.** Average Concentration of RC 100 kDa Permeate at pH 9.5

Component		Average Concentration (mg/L)
Resin Acids	Pimaric Acid	4.45
	Isopimaric Acid	0.76
	Unidentified Resin Acid	1.72
	Palustric + Levopimaric Acids	13.45
	Dehydroabietic Acid	21.33
	Unidentified Resin Acid	1.25
	Abietic Acid	8.34
	Unidentified Resin Acid	0.81
	Neoabietic Acid	3.57
β-Sitosterol		0.00
Triglycerides	Triglyceride - Unknown	0.00
	Glyceryl Trioleate	0.00
Total Fatty Acids		10.10
Total Resin Acids		72.94
Total Unknowns		23.19
Total Neutrals		12.05
Total Triglycerides		0.00

The percentage of resin acids in this permeate was 62%, with unknowns and neutral compounds making up the majority of the rest.

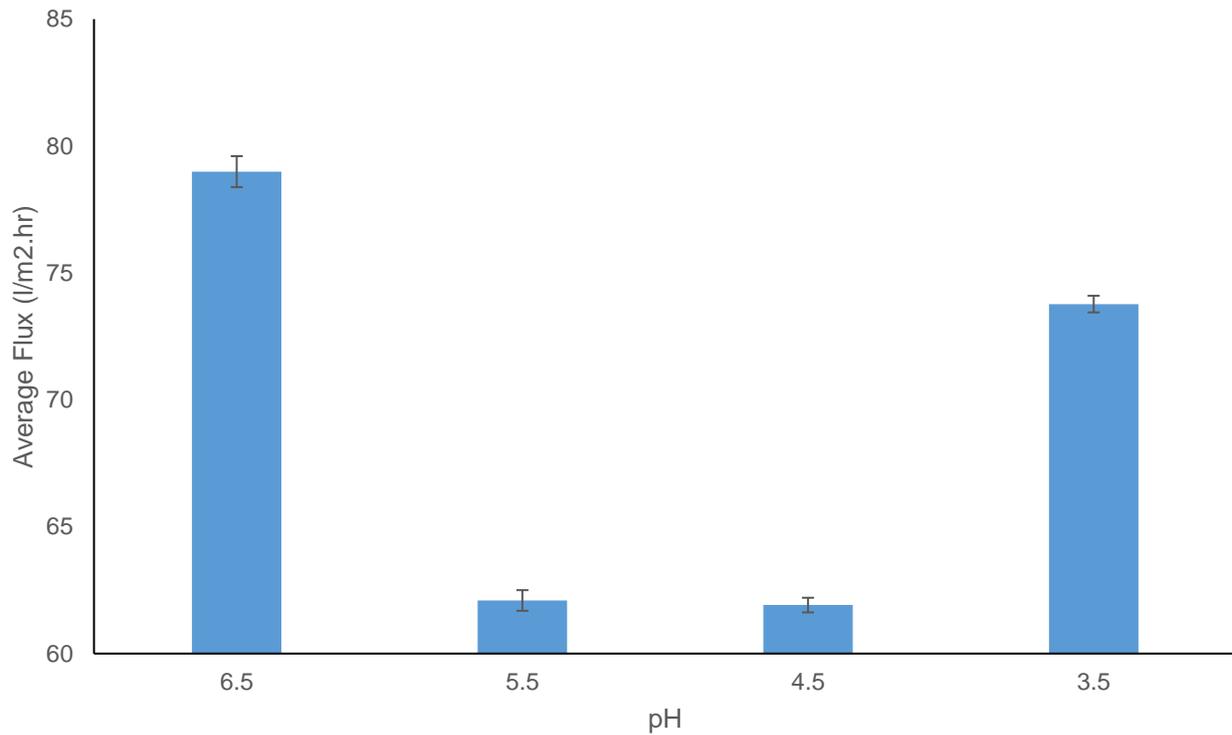
#### 8.4.1.3. Membrane Filtration – Stage 2

The feed to the second stage of membrane filtration was produced by passing a DAF subnatant at pH 9.5 through a RC 100kDa membrane, as described in 8.4.2.2. The percentage of resin acids in this feed was 65%. This was slightly higher than the value reported in previous section. This was because of the higher concentration of resin acids in the DAF subnatant sample used for Stage 2. The concentration of the feed to stage 2 is given below in Table 8.3.

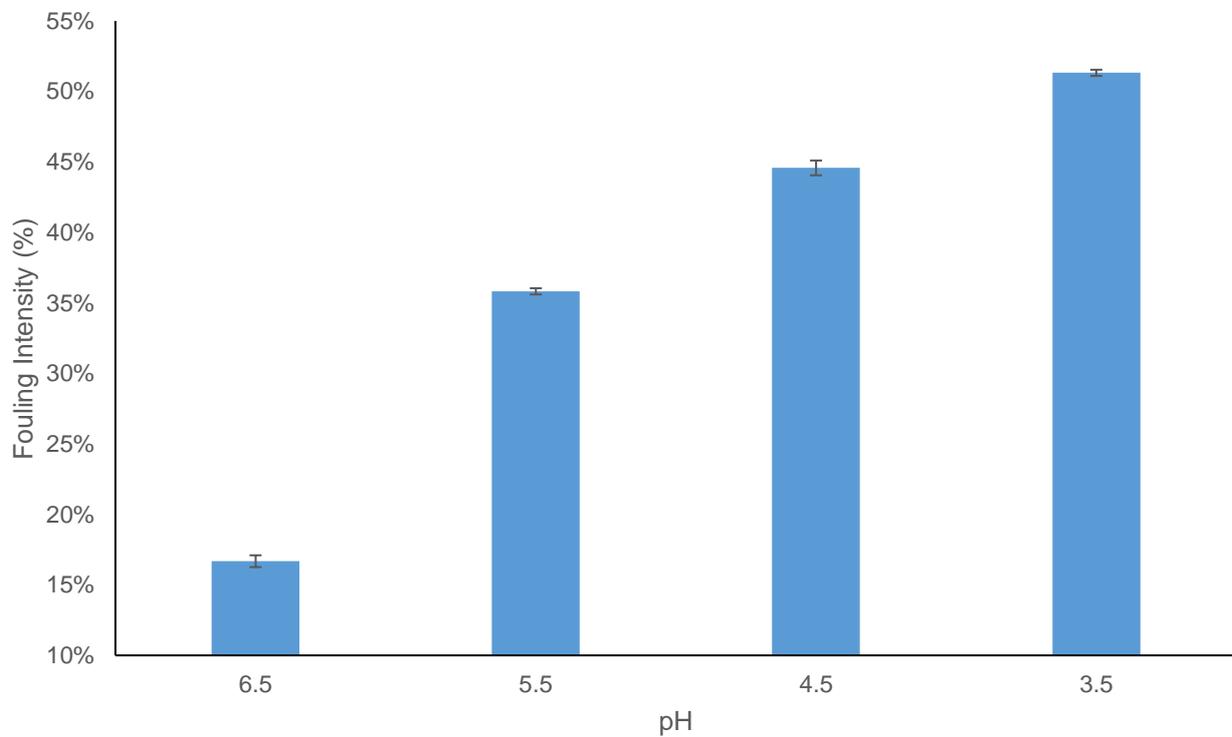
**Table 8.3.** Concentration of Extractives in Feed to Stage 2

Component		Average Concentration (mg/L)
Resin Acids	Pimaric Acid	4.02
	Isopimaric Acid	0.75
	Unidentified Resin Acid	1.07
	Palustric + Levopimaric Acids	18.94
	Dehydroabietic Acid	18.01
	Unidentified Resin Acid	1.07
	Abietic Acid	9.00
	Unidentified Resin Acid	0.91
	Neoabietic Acid	5.59
$\beta$ -Sitosterol		0.00
Triglycerides	Triglyceride - Unknown	0.00
	Glyceryl Trioleate	0.00
Total Fatty Acids		9.88
Total Resin Acids		75.32
Total Unknowns		19.85
Total Neutrals		10.85
Total Triglycerides		0.00

The flux was highest at pH 6.5 while the fouling intensity was lowest as expected. See Figures 8.7 and 8.8. At pH 6.5, most of the resin acids will still be in soluble phase. When the pH was decreased, resin acids will start moving more and more into the colloid phase. This increases the fouling intensity and reduces the flux due to pore clogging. This was observed at both pH 5.5 and 4.5. Gel formation on top of the membrane was observed at pH 4.5 and 3.5 with increasing intensity [10]. However, this does not explain why the flux rate increases at pH 3.5. The flux rate pH 4.5 was approximately 60 l/m<sup>2</sup>.hr and it is a significantly higher flux rate than what was achieved in stage 1.



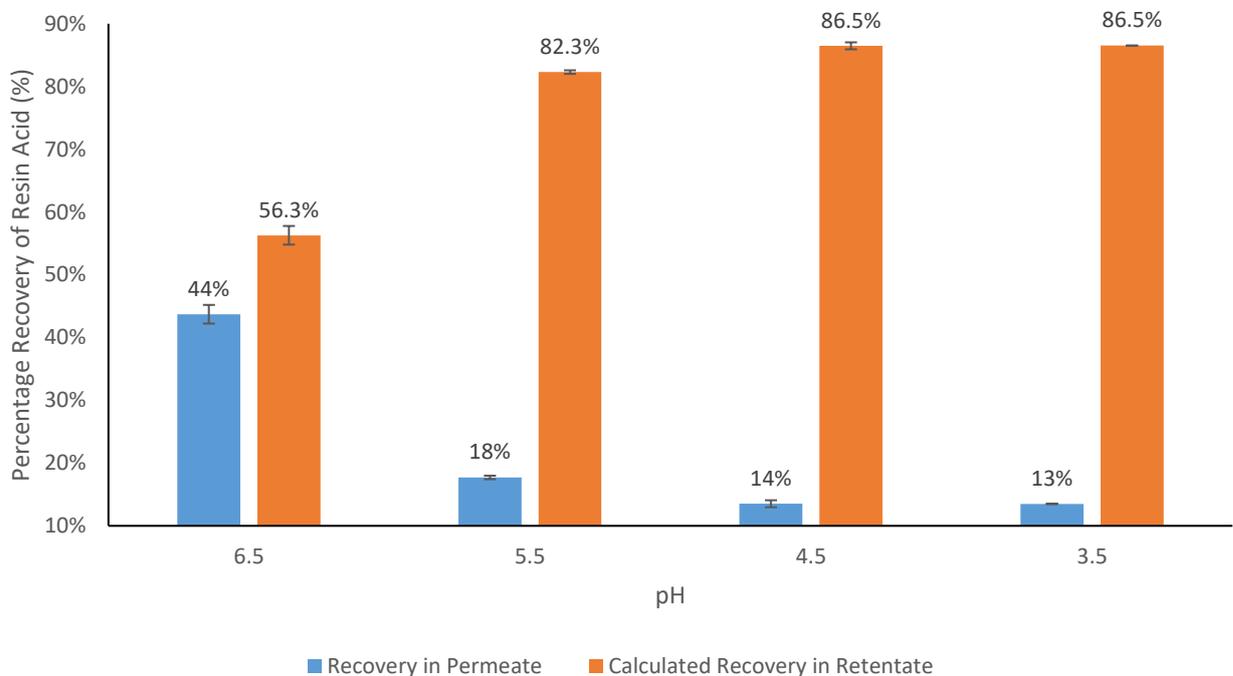
**Figure 8.7.** Average Flux through RC 30 kDa Membrane: Error bars represent values from the two individual runs



**Figure 8.8.** Fouling Intensity in RC 30 kDa Membrane

#### 8.4.1.4. GC Analysis – Stage 2

The observations in flux and fouling studies are further confirmed in GC analysis. There is a significant portion of resin acids in permeate, with 44% in the permeate and the rest 56% is calculated to be in the retentate. It was the intention to measure the concentration of resin acids in retentate and calculate the mass balance. However, it was not possible to accurately measure the concentration of extractives in the retentates, especially at pH 4.5 and 3.5. This is due to the loss of material due to fouling and gel formation on top of the membrane. It made any efficient recovery of the retentate very difficult and almost impossible. However, this was not an issue with the permeate. Therefore, the amount of resin acids found in the permeate was used to calculate the percentage recovery of resin acids in the retentate using mass balance equations.



**Figure 8.9.** Percentage Recovery of Resin Acids in Stage 2: Error bars represent values from the two individual runs

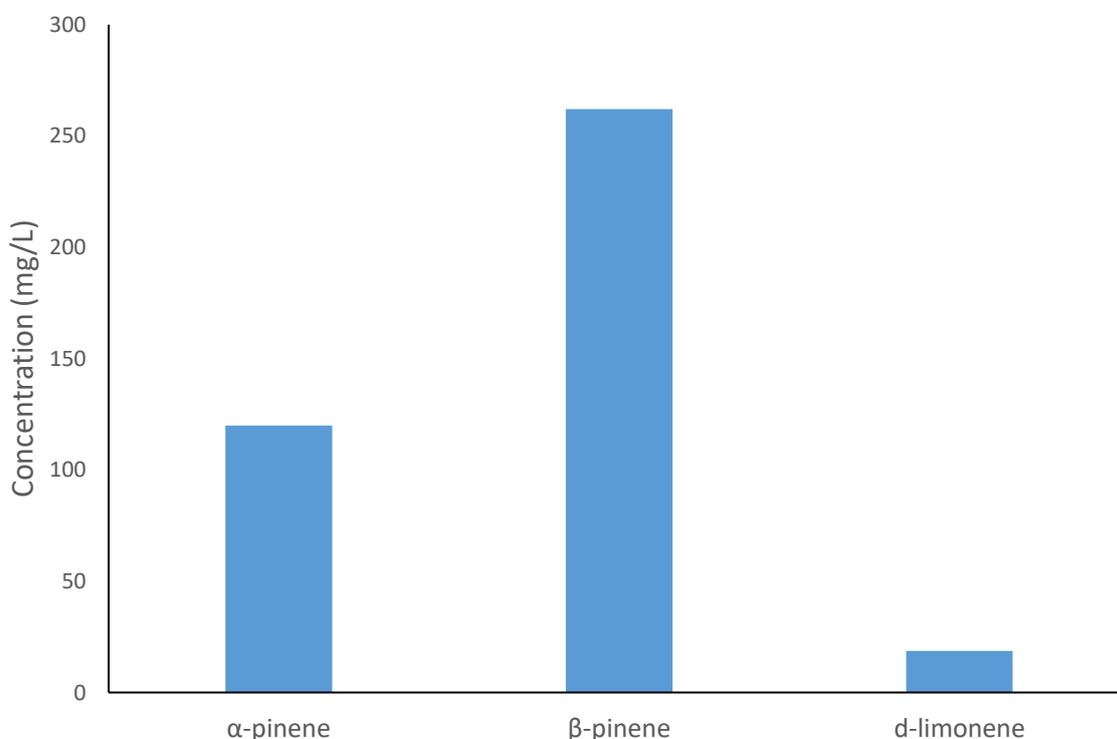
Membrane filtration at pH 4.5 was the optimum when considering the resin acid yield and amount of acid required for pH adjustment. The permeate at pH 4.5 contained only 14% of the resin acids and therefore 86% of the resin acids are recoverable in the retentate. The amount of resin acids lost due to fouling and gel formation could be avoided by using a better filtration design such as a cross flow filtration or a vibrating membrane filtration [9].

The total recovery of resin acids based on the yields (recoveries) of both stages is 64%, and the purity of resin acids is estimated as 77% based on the mass balance. These values can definitely be improved by using a more efficient membrane filtration setup with less fouling and aiming for a higher concentration factor, for example 20 instead of 10. The flux rate can be improved by increasing the pressure difference. Therefore, there is potential to isolate and recover resin acids using ultrafiltration. However, the economies of the separation can only be guaranteed if the feed to the membrane separation has adequate concentration of resin acids to justify the cost of membrane separation. The concentration of the resin acids in the feed to the stage 1 was 87.2 mg/L, which is a very low amount. Another DAF subnatant sample contained 259 mg/L of resin acids, indicating the variability in the whitewater. A pilot scale study is necessary to estimate the economies with yields achieved through a better optimised and efficient membrane separation process.

## 8.5.2. Terpenes

### 8.5.2.1. Plug Screw Pressate

Plug screw pressate contained significant levels of terpenes, and this stream was enriched with  $\beta$ -pinene, 65% and  $\alpha$ -pinene, 35%. The average concentrations are given below in Figure 8.10.



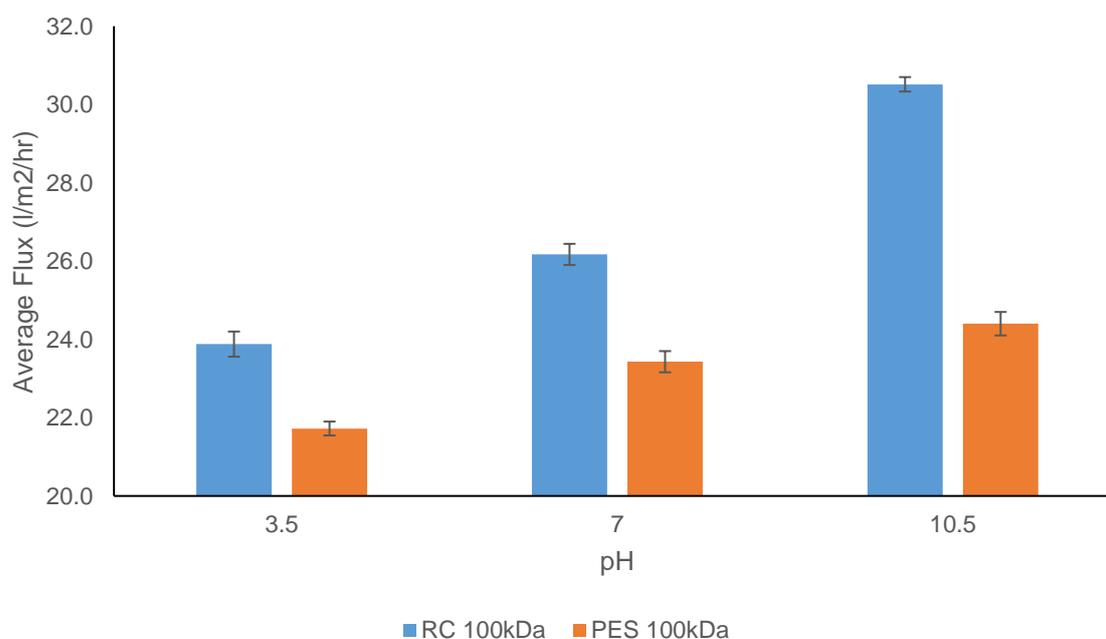
**Figure 8.10.** Terpene Concentrations in Plug Screw Pressate: Error bars represent values from the two individual runs

### 8.5.2.2. TMP Primary Refiner Steam Condensate

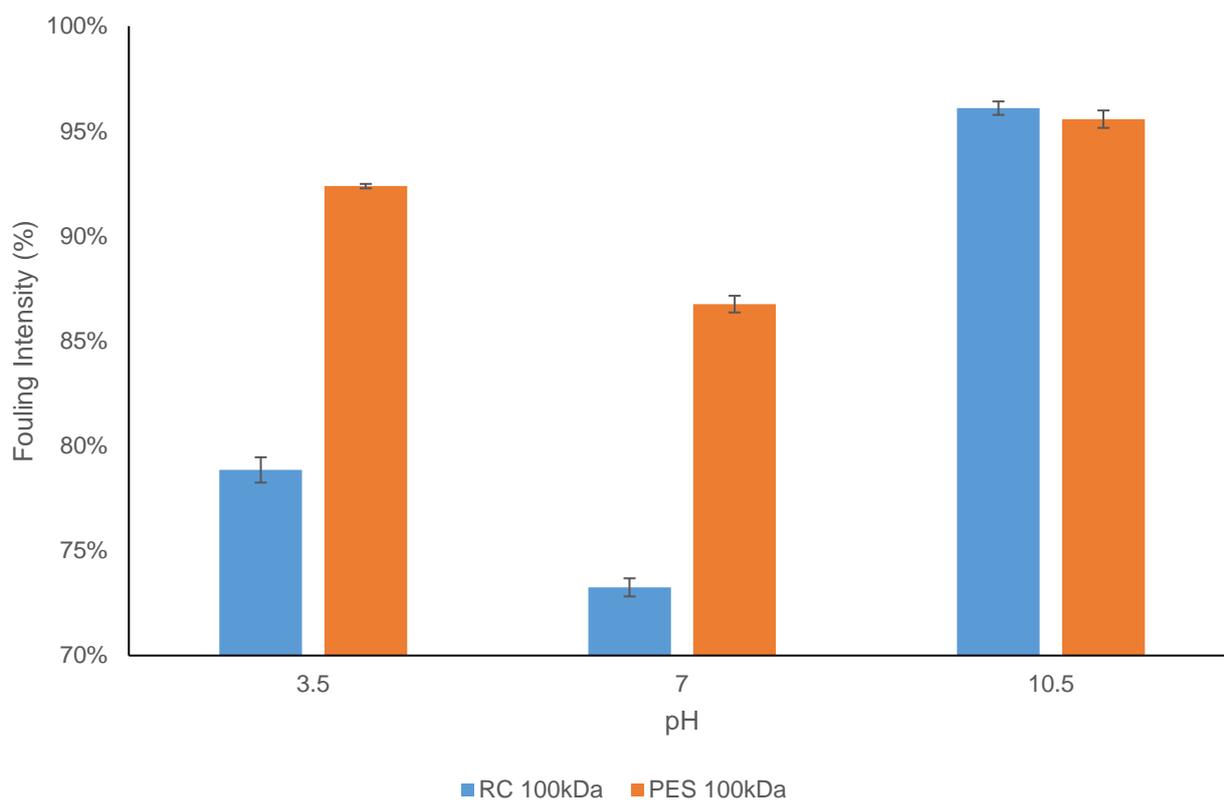
Headspace GC analysis indicated that the primary refiner steam condensate contained no significant levels of terpenes. Therefore, a solid phase micro extraction (SPME) was used, as it is a more sensitive technique to analyse volatile organic compounds. SPME technique concentrates volatile organic compounds onto 'adsorbent fibre', which can then be desorbed onto the GC column. The SPME method confirmed the results of headspace GC. Primary refiner steam condensate did not have any significant levels of terpenes. This indicates that the plug screw pressate removes almost all of the volatile extractives from wood chips prior to primary refining. The process flow diagram of the primary treatment of wood chips at Norske Skog – Boyer is shown in Figure 2.3 at section 2.2.3. Therefore, primary refiner steam condensate was deemed unsuitable for extraction of terpenes. Membrane separation were carried out using the plug screw pressate samples.

### 8.5.2.3. Membrane Filtration of Plug Screw Pressate

Regenerated cellulose membranes showed slightly higher flux than the polyethersulfone membranes. See Figure 8.11. Terpenes are hydrophobic. Plug screw pressate have colloidal materials other than terpenes, which are also hydrophobic. This causes the PES membranes to be fouled than RC membranes. See Figure 8.12. The increasing flux rate in RC membrane with increasing pH could be attributed to decreasing colloid size as observed and discussed in resin acids earlier. However, it is difficult to understand the relationship between fouling and pH.

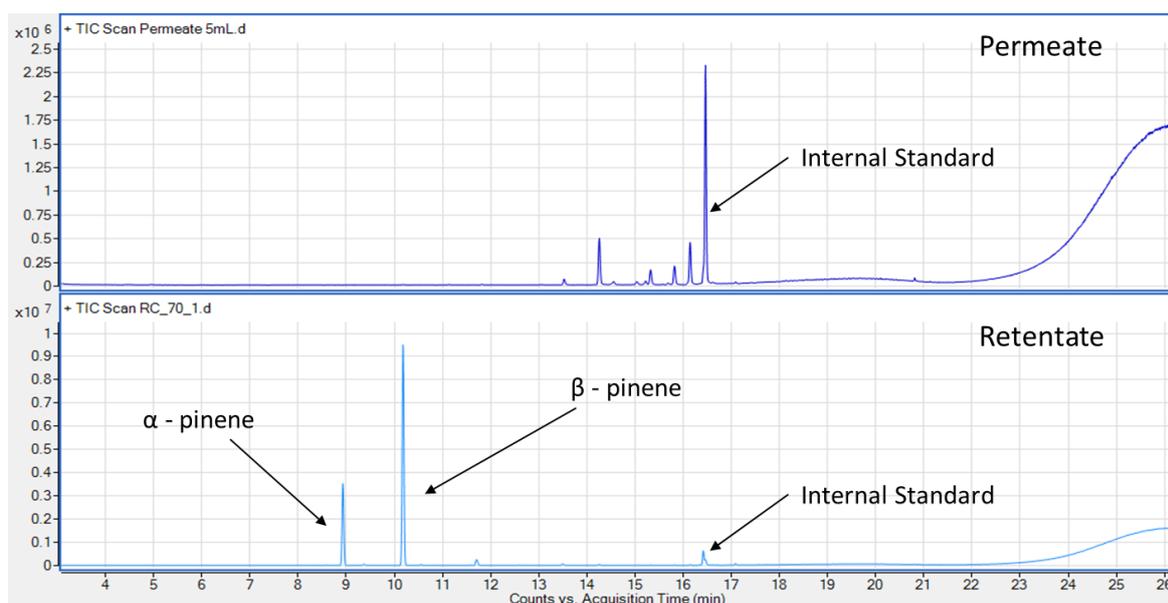


**Figure 8.11.** Flux of Plug Screw Pressate through Ultrafiltration Membranes: Error bars represent values from the two individual runs



**Figure 8.12.** Fouling Intensity in Ultrafiltration Membranes: Error bars represent values from the two individual runs

Headspace analysis of retentate and permeate samples showed that regardless of the pH, permeate did not contain any terpenes or the concentrations were below the lowest sensitivity of the headspace GC method used. The GC chromatographs of the retentate and the permeate at pH 7.0 are shown below in Figure 8.13.



**Figure 8.13.** GC Chromatographs of Retentate and Permeate at pH 7.0

Table 8.4 shows the percentage recoveries of terpenes in retentate under different pH levels. In contrast to what GC chromatographs suggested, the percentage recoveries of terpenes in the retentate was not even close to 100%. This was due to the membrane filtration set up used. The setup was pressurized to 3 bar gauge pressure. The pressure had to be released before opening the setup to collect the retentate. This caused some of the terpenes, which are volatile to evaporate and escape the apparatus. However, this could be avoided in an industrial scale membrane filtration set up with a cold trap.

**Table 8.4. Percentage Recovery of Terpenes in Retentate**

Membrane	pH	Average Percentage Recovery in Retentate (%)		
		$\alpha$ -pinene	$\beta$ -pinene	d-limonene
RC	3.5	40%	48%	57%
	7	63%	68%	76%
	10.5	51%	51%	64%
PES	3.5	69%	69%	76%
	7	77%	74%	81%
	10.5	69%	66%	75%

The maximum yield was achieved pH 7.0 with PES membrane. However, there is no significant difference between yields at pH 3.5 or 10.5 either. It might be even worth not changing the pH at all and processing the plug screw pressate as it is.

Literature suggests that terpenes can damage the regenerated cellulose, polyethersulfone and other common polymeric membrane materials [11]. Some researchers have previously used Teflon membranes to separate process water streams containing terpenes [11]. However, our attempts to use hydrophilized Teflon membranes were not successful as they expanded as they wetted with water or the plug screw pressate. Ceramic ultrafiltration membranes might be the best option for a pilot-scale filtration setup.

The concentrated retentate stream could be processed using existing reboiler-condenser technologies available from Andritz [12-14]. Ultrafiltration of plug screw pressate can help in three different ways rather than directly processing the plug screw pressate in a reboiler-condenser, which needs significant input of energy in the form of heat. Ultrafiltration would produce a purer process water stream as the permeate, which can directly recycled back into the loop. Ultrafiltration also reduces the volume of water, which has to be treated in a reboiler-condenser to recover terpenes, and in turn, it reduces the

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possible energy consumption. Recovery of terpenes also reduces the organic load to the effluent treatment facility.

## 8.6. Conclusions

TMP whitewater clarified using the dissolved air flotation (DAF) unit at Norske Skog – Boyer was evaluated for potential for recovery of resin acids. Microfiltration was not suitable for this application as microfiltration membranes are clogged easily with colloids present in whitewater. On the other hand, ultrafiltration membranes performed better and regenerated cellulose (RC) is a better material than polyethersulfone (PES) for membranes. Two-stage membrane separation process can isolate resin acids and produce a resin acid-rich aqueous stream. The proposed two stage operations are; membrane filtration of TMP whitewater at pH 9.5 through a RC 100-kDa membrane, and membrane filtration of permeate from Stage 1 at pH 4.5 through a 30-kDa membrane. The proposed process can recover 64% of resin acids present in the original whitewater stream with 77% enrichment of resin acids. These recoveries can be improved by increasing the concentration factor and using a more efficient membrane filtration setup. Removal of triglycerides and sterols in Stage 1 and recovery of resin acids in Stage 2 cleans the whitewater which will significantly reduce the pitch formation. This also reduces the organic load to the effluent treatment facility.

Plug screw pressate from TMP2 had significant levels of terpenes while the Primary Refiner Steam Condensate does not contain any detectable amounts of terpenes. Ultrafiltration of the plug screw pressate showed that we could recover and concentrate 100% of the terpenes in the retentate, with an efficient membrane filtration setup with a cold-trap for terpenes. The concentrated terpene rich retentate could be processed in a reboiler-condenser unit to recover terpenes, which could be further processed into fragrances, pharmaceuticals, and polymers. Ultrafiltration of plug screw pressate could help the mill in three other ways as well; recovering water for closing the loop, reducing energy consumption in subsequent reboiler-condenser, and reducing organic load to the effluent treatment facility.

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# Chapter 9

## Conclusions & Recommendations

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# Chapter 9 – Conclusions & Recommendations

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# Chapter 9 – Conclusions & Recommendations

In this project, several biorefinery pathways for the recovery of valuable components from process wastewater streams at Norske Skog – Boyer facility were analysed. This project uncovered valuable insights into how wastewater streams at the mill could be upgraded or utilized to recover valuable phytochemicals. The wastewater was sourced from several locations in the process. Four process streams were investigated and three possible upgraded products or bioproducts were evaluated. The following table summarizes the investigated process streams and bioproducts. See Table 9.1.

**Table 9.1.** Investigated Process Streams and Possible Bioproducts from Norske Skog – Boyer Facility

Process Stream	Product
Whitewater Fines from Dissolved Air Flotation Unit	<ol style="list-style-type: none"> <li>1. Upgraded Whitewater Fines</li> <li>2. Microfibrillated Cellulose</li> <li>3. Extractives</li> </ol>
Subnatant from the Dissolved Air Flotation Unit	<ol style="list-style-type: none"> <li>1. Resin Acids</li> </ol>
Plug Screw Pressate from the TMP2 Mill	<ol style="list-style-type: none"> <li>1. Terpenes</li> </ol>
Primary Refiner Steam Condensate TMP2 Mill	<ol style="list-style-type: none"> <li>1. Evaluated for terpenes, however not suitable for terpene recovery</li> </ol>

## 9.1. Thesis Outcomes

The objectives for this project was set in Chapter 3. All the objectives were addressed and realized at different levels. The following section provides a summary of how each objective was addressed and the key results obtained.

### 9.1.1. MFC Production from TMP Whitewater Fines

- **Investigate the feasibility of upgrading whitewater fines back to the desired quality of TMP newsprint**

This objective was addressed in two different ways. In Chapter 6, mechanical refining alone was investigated as an approach towards upgrading the quality of the whitewater fines. It was found that a specific energy input of 3000 kWh/tonne using a

PFI mill could bring the tensile index up from 28 Nm/g to 40.5 Nm/g and fibres could be added back into the TMP newsprint without any detrimental effects. However, the refining action of the PFI mill was not comparable to the industrial scale refiners. Therefore, the experiments were replicated using a lab scale 12" single-disc refiner where the refining action is comparable to the industrial scale refiners. The results achieved by using the lab scale refiner were comparable to those achieved by using the PFI mill, although the energy consumption was high. Modern industrial scale refiners could reduce the energy consumption significantly.

Literature reports suggested that the poor quality of the whitewater fines arise from contamination of extractives on the fibre surface. Mechanical fibrillation techniques could improve the properties of the whitewater fines. However, mechanical fibrillation cannot overcome the negative effects caused by extractives. Therefore, a simple chemical treatment step to upgrade the whitewater fines without any additional mechanical energy input was investigated. A caustic washing of whitewater fines at 0.5 M strength at room temperature was found to be sufficient to improve the tensile index to 48.8 Nm/g, which is ~74% increase in strength. This value is significantly higher than TMP newsprint itself. Extractives can also be recovered from the separated black liquor after centrifugation. However, further experiments and studies are needed to optimize the conditions.

- **Investigate the feasibility of producing MFC or MFC like material from TMP whitewater fines via mechanical fibrillation techniques**

The experiments on whitewater fines using a PFI mill and lab scale refiner were extended to include a high-pressure homogenizer. PFI refining alone could produce lignocellulosic microfibrils with a median diameter of 48 nm after 10,000 kWh/tonne energy addition (50,000 revs in PFI). Homogenization was able to break down the fibres even further and produce better quality lignocellulosic microfibrils. Homogenization of 15,000-rev PFI refined pulp resulted in microfibrils with a median diameter of 19 nm. It was evident that microfibrils with good size distribution could be produced, however, the strength properties were not comparable to the commercially available microfibrillated cellulose produced from chemical pulp. This is due to the contamination by extractives and the presence of lignin. The extractives make the MFC from whitewater fines hydrophobic and this could be advantageous in alternative applications such as a composite material in non-polar matrices.

In Chapter 4, different fines, not only whitewater fines, were investigated. These are fines fractionated from both TMP and Kraft, and could be used to produce MFC by using high-pressure homogenization at a lower energy consumption compared to whole pulp. Consistency of the pulp suspension is the most critical factor and usually the limiting factor when it comes to MFC production by high-pressure homogenization. Typically, when whole pulp is homogenized at consistencies above 0.5 wt%, the homogenizer is often clogged due to the entanglement of longer fibres in certain machine elements. This could lead to significant downtime in operation and even machine failure, causing loss in production and revenue. Most importantly, lower consistencies contribute to higher specific energy consumption. It was found that the fines fractions including TMP whitewater fines, could be homogenized without any clogging issues and machine failures, at higher consistencies up to 1.0 wt%. Specific energy consumption could be reduced by ~ 37% when the consistency was increased from 0.25 wt% to 1.0 wt%.

- **Investigate the feasibility of producing MFC or MFC like material using the existing refining machinery in a TMP mill**

As discussed above, the tensile strength achieved by PFI refining on the whitewater fines could be replicated by using a lab scale 12" single-disc refiner. The energy consumption could be further reduced by using modern industrial scale refiners.

- **Study the potential for enhancement of strength properties by using MFC as a paper additive in newsprint**

Chapter 5 focussed on how the addition of MFC from different sources and of different chemical compositions affected the strength properties of TMP newsprint. It was found that the addition of 10% MFC produced from BEK after refining and high-pressure homogenization, increased the tensile strength of TMP newsprint significantly. This is because the MFC from chemical pulp contains mostly cellulose. Therefore, they are able to form hydrogen bonds quite effectively with TMP newsprint. However, the MFC produced from TMP whitewater fines using homogenization showed only a little improvement in strength after addition to TMP newsprint. This was because of the lower strength of MFC produced from TMP whitewater fines compared to MFC from chemical pulp. The drainage time was negatively affected when MFC from chemical pulp was added. The drainage time was not affected when MFC from TMP whitewater fines were added. This is because of the hydrophobic nature of TMP whitewater fines,

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which aided the water release from fibres during drainage. This suggests that microfibrils with hydrophobic properties could be more applicable and effective as strength additives in newsprint.

### 9.1.2. Extraction of Phytochemicals from TMP Process Water Streams

- **Characterize both qualitatively and quantitatively, the composition of phytochemicals, resin acids and terpenes, in TMP process water streams; whitewater system, plug screw pressate and primary refiner steam condensate.**

The subnatant from the DAF unit was analysed for resin acid content using extraction, followed by gas chromatography (GC) and gas chromatography – mass spectrometry (GCMS). Resin acids were found in significant concentrations (41%), with considerable amounts of fatty acids and triglycerides as well.

Plug screw pressate and primary refiner steam condensate, both from the TMP2 mill, were analysed for terpenes using Headspace GC and Solid Phase Micro-Extraction GC (SPME – GC). The primary refiner steam condensate did not contain any significant levels of terpenes when analysed using Headspace GC. No significant levels of terpenes were found even when the more sensitive SPME-GC was used. The plug screw pressate contained significant amounts of terpenes and it was enriched with  $\beta$ -pinene compared to  $\alpha$ -pinene.

- **Evaluate the potential of membrane filtration to concentrate, extract and separate resin acids and terpenes from the identified process water streams.**

A two-stage membrane filtration process was successfully applied to the DAF subnatant to isolate and concentrate the resin acids via manipulation of pH between the two stages. Ultrafiltration membranes were made from regenerated cellulose (RC). A molecular weight cut-off (MWCO) of 100kDa was found to be the optimum choice for the first stage in which the resin acids were isolated and separated from the complex colloids at pH 9.5. Another RC ultrafiltration membrane with 30kDa MWCO was used for the second stage, in which the resin acids were concentrated at pH 4.5. The final retentate of this membrane filtration process contained 77% of resin acids by concentration, and 64% of the initial resin acids in DAF subnatant were recovered. These numbers could be further improved in a better membrane filtration design with a higher concentration factor.

Plug screw pressate was processed using ultrafiltration membranes with 100 kDa MWCO. The results showed that 100% of the terpenes in the retentate could be recovered with a cold-trap and using an industrial scale membrane. Terpenes could be recovered using a commercially available reboiler-evaporator system. The advantages of processing the plug screw pressate using ultrafiltration are reduced heat load to reboiler-evaporator unit and recovery of a purer water to be readily recirculated in the mill.

## 9.2. Retrofit Biorefinery at Norske Skog – Boyer Facility

Three different bioproducts: MFC, resin acids, and terpenes, were investigated at the start of this project. Four different processes have been proposed as possible pathways to produce these bioproducts. Figure 9.1 summarizes these process options and bioproducts in the form a retrofit biorefinery at Norske Skog – Boyer facility.

TMP whitewater fines could be directly refined to produce lignocellulosic microfibrils and to upgrade the TMP whitewater fines back to the desired quality for TMP newsprint. Lignocellulosic microfibrils could also be used in alternative applications such as a composite material in non-polar matrices. This process has the option to produce lignocellulosic microfibrils with a sheet strength of 40.5 Nm/g with <3000 kWh/tonne energy addition in a refiner.

The second option for processing TMP whitewater fines is to employ a caustic treatment at 0.5 M caustic concentration. No mechanical refining is necessary and this will produce a fibre with sheet tensile index of 48.8 Nm/g. However, treated fibre could be further upgraded using a refiner. This process is capable of producing an extractive stream, which could be recovered by treating the black liquor.

The Table 9.2 summarizes and compares key properties of different grades of MFC from whitewater fines and/or upgraded whitewater fines produced in this research.

The proposed two-stage ultrafiltration process is capable of producing a resin acid-rich retentate from DAF subnatant, which could be further processed downstream to recover resin acids. This process is capable of isolating the resin acids from the complex colloids in whitewater system and concentrating them. The recovery yield of resin acids in this process is 64% and purity of resin acids is 77%. These numbers could definitely be improved in an efficient industrial scale membrane filtration setup and a higher concentration factor between retentate and permeate.

**Table 9.2.** Summary Comparison of MFC and Upgraded Products from Whitewater Fines

Treatment	Energy Consumption	Chemicals Needed	MFC Surface Characteristics	Potential for Strength Improvement	Impact on Drainage Time
Refining Only	Moderate	None	Hydrophobic	Low	Low
Refining + Homogenization	High	None	Hydrophobic	Moderate	Moderate
Caustic Treatment	No refining energy needed	NaOH	Less hydrophobic	Moderate - High	Moderate - High

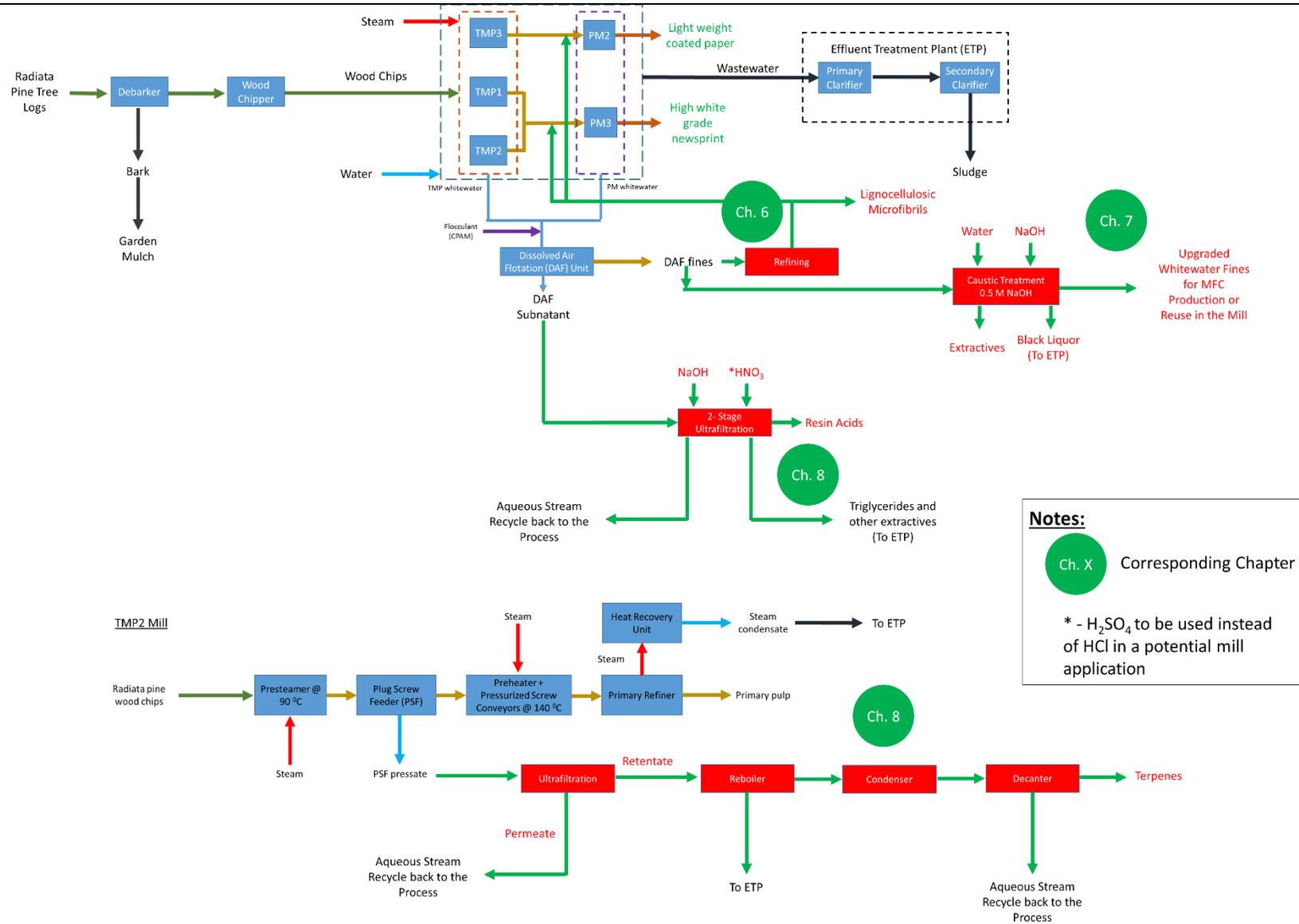
Plug screw pressate is also processed with another ultrafiltration unit. Terpenes can be 100% recovered and concentrated in the retentate with the use of a cold-trap in an industrial setting. The permeate is free from colloidal extractives and terpenes and can be recycled back to the mill directly. The retentate can be processed in a commercially available reboiler-evaporator system to recover terpenes. The advantages of concentrating the terpenes prior to the reboiler-evaporator are twofold: reduced heat energy consumption in the reboiler-evaporator and production of a readily recyclable process water stream.

### 9.3. Economic Considerations

The Table 9.4 summarizes the basic economic analysis performed for each biorefinery option with the level of recommendation for further analysis and implementation in the mill. This analysis only considers the approximate value of the product. This analysis doesn't incorporate indirect benefits achieved by reducing the waste such as reduce organic load to effluent treatment unit.

The Table 9.3 summarizes the estimated price for each product. Commercial suppliers such as Alibaba has been reviewed when recorded data is not available through organizations. US Dollar values were converted by the current exchange rates, 1 AUD = 0.70 USD, February 2019 [1].

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**Figure 9.1.** Simplified Norske Skog – Boyer Process Flow Diagram with Retrofit Biorefinery

**Table 9.3.** *Estimated values of products*

<b>Product</b>	<b>Assumption Criteria</b>	<b>Price</b>	<b>Source</b>
Upgraded whitewater fines through mechanical refining only	Price was assumed as same price as thermomechanical pulp	USD 600/tonne	National Resources Canada [2]
Upgraded whitewater fines through caustic treatment	Price was assumed as same price as unbleached Kraft pulp	USD 1000/tonne	National Resources Canada [2]
Resin acids	Price was assumed as same price as Tall oil rosin	USD 1000/tonne	Alibaba [3]
Terpenes	Price was assumed as the same price as Kraft/Gum turpentine	USD 2000/tonne	Alibaba [3]

It is recommended that the highest priority should be given to the process option of upgrading whitewater fines via caustic treatment. The current recovery of floated fines in the DAF unit is 10 tonnes per day; however, it is estimated that additional 30 tonnes per day could be recovered if needed. Therefore, it is estimated that up to 15000 tonnes of whitewater fines could be recovered. Caustic treated whitewater fines are of higher quality and could be estimated to have the quality of unrefined Softwood Kraft pulp. This values this upgraded whitewater fines as \$ 17 million annually. Additionally, 825 tonnes of caustic floated extractives could be recovered which has an annual value of \$ 1.5 million; caustic floated extractives were assumed to have the same price as tall oil rosin from chemical pulping processes. The total estimated value of this biorefinery option is \$ 18.5 million. The indirect benefits of this process such as avoided burden to the effluent treatment unit would place the value over \$ 20 million annually. The proposed process is a relatively simple process and there is a plethora of knowledge on chemical digesters in chemical pulping industry which could be easily transferred to a TMP mill. Therefore, the level of

further research and development is minimal, and the unit operations needed, digesters and washers, are not high capital intensive. Therefore, this option is highly recommended.

The second option is to mechanically treat whitewater fines in a refiner without any chemical treatment. This would produce a pulp stream which is equivalent to TMP pulp in quality as shown in Chapter 6. The annual value of this stream could be estimated as \$ 12.5 million. The costs for mechanical energy should be considered in a detailed economic analysis. It was shown that at least 2000 kWh/tonne should be expended to bring the whitewater fines to the quality of TMP pulp, in Chapter 6. The capital investments would be minimal as existing secondary refiners could be used. However, this is only recommended only if the 1<sup>st</sup> option is not pursued.

The third option is the medium priority terpene recovery process. Approximately, 70 tonnes of terpenes could be recovered from the plug screw pressate of TMP2 mill. This would produce a value of \$ 200,000. The low concentration of terpenes in plug screw presage might transform the process undesirable. However, the pharmaceutical grade of the recovered terpenes in this process might demand a higher price than USD 2000 per year. However, this value is difficult to estimate without a through supply-demand analysis. The annual production of terpenes could be improved by recovering terpenes from TMP 1 and TMP 3 mills. Membrane separation processes could be capital intensive, especially with chemical resistant ceramic ultrafiltration membranes. A thorough techno-economic analysis needed after a pilot scale study to determine the financial viability of this process.

The least recommended option is recovering resin acids via ultrafiltration. The concentration of resin acids in the DAF subnatant is low, 259 mg/L. However, the sheer volume of DAF subnatant, 10 mega litres/day, means that we could recover 600 tonnes for resin acids at 64% recovery efficiency. This values this stream at \$ 1.2 million annually. However, further research is needed to isolate resin acids from the aqueous stream. The low concentration of resin acids might render ultrafiltration financially unviable. The capital investment would be high for a large ultrafiltration system. However, potential value could be if process to purify individual resin acids are developed. The value of purified individual resin acids could be much greater than the value of crude resin acids, USD 1000/tonne. Refer to Section 1.2.5.3. Resin acids for the price of individual resin acids. However, this option is ranked the lowest due to the high level of further research & development needed and the high level of anticipated capital investment.

## 9.4. Key Learnings

- TMP whitewater fines can be upgraded back to the desired quality of TMP newsprint with <3000 kWh/tonne energy addition.
- Lignocellulosic microfibrils can be produced from TMP whitewater fines using refining and/or homogenization with median diameter below 20 nm. These lignocellulosic microfibrils show hydrophobic properties. They could be useful in alternative applications such as a composite material in non-polar matrices.
- TMP whitewater fines can be upgraded directly without any further mechanical energy input, via a simple caustic washing process at room temperature. Extractives could also be recovered from the black liquor of the caustic process.
- Resin acids can be successfully isolated from complex colloids, concentrated using ultrafiltration and pH adjustment.
- Terpenes can be completely recovered from plug screw pressate using ultrafiltration, increasing the efficiency in downstream processing and closing the water loop in the mill.

## 9.5. Future work & Recommendations

The focus of this thesis was to identify the biorefinery opportunities in the thermomechanical pulping mills of the Norske Skog – Boyer Facility. Four key processes were proposed to isolate three main products from waste streams in the mill. The application of proposed processes is not exclusive to the Norske Skog – Boyer Facility, and could be applied to any of the softwood thermomechanical pulping mills in the world. However, further research is needed to optimize the proposed processes.

Lignocellulosic microfibrils can be produced from whitewater fines using mechanical refining and homogenization. The application of these lignocellulosic microfibrils in paper industry or in alternative applications were not investigated. Whitewater fines can be upgraded to the quality of the TMP newsprint. These whitewater fines could be added to the TMP newsprint without any detrimental effects. This needs further investigation to understand the effect of this addition. Lignocellulosic microfibrils show hydrophobic properties and could be applied as a composite material in non-polar matrices. Future research could be undertaken on how these microfibrils would behave in different polymer composites made by different technologies, more importantly by 3D printing.

Table 9.5. Estimated value of biorefinery products sorted according to the recommended prioritisation

Biorefinery Option	Product and/or By-Product	Amount/year	Unit Value	Value/year	Level of Further Research & Development Needed	Level of Capital Investment Needed	Recommended Prioritisation
Upgraded Whitewater Fines via Caustic Treatment	Upgraded whitewater fines	~ 12000 tonnes (at 80% yield of the annual whitewater fines flow rate)	\$ 1400/tonne	~ \$ 17 Million	Low-Medium	Low – No refiners are needed unless further refining is demanded	High (1 <sup>st</sup> )
	Resin Acids	~ 825 tonnes (5.5% recovery of caustic floated extractives)	\$ 1400/tonne	~ \$ 1.5 Million			
Upgraded Whitewater Fines via Refining	Upgraded whitewater fines	~ 15000 tonnes (at 40 tonnes per day)	\$ 850/tonne	~ \$ 12.5 Million	Low	Low – Existing refiners could be utilized	High (2 <sup>nd</sup> ) – recommended only if 1 <sup>st</sup> option is not pursued

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Terpenes from the Plug Screw Pressate via Ultrafiltration	$\alpha$ -pinene and $\beta$ -pinene	~ 70 tonnes/year (at 401 mg/L at 500000 litres per day flow rate)	\$ 2000/tonne	~ \$ 200,000	Medium as only one membrane filtration system has to be developed and it is independent of pH	Medium – High as ceramic ultrafiltration systems will be costly	Medium (3 <sup>rd</sup> )
Resin Acids from Whitewater via Ultrafiltration	Resin Acids	~ 600 tonnes (at 259 mg/L in 10 mega litres per day flow rate of DAF subnatant with 64% recovery efficiency)	\$ 1400/tonne	~ \$ 1.2 Million	High as pilot scale membrane separations must be carried out and investigations are required for further purifying resin acids	High as ultrafiltration systems will be costly to build	Low(4 <sup>th</sup> )

Caustic treatment (NaOH) can be used to upgrade the whitewater fines with no additional input of mechanical energy. These fibres were superior in strength to lignocellulosic microfibrils produced by mechanical refining. These fibres could be further processed to produce better quality microfibrils. The effects of chemical treatment on the fibrillation and the hydrophobic properties also need further investigation.

Ultrafiltration can isolate and concentrate resin acids from TMP whitewater. This could be used to treat any process water stream that contain colloidal extractives. However, this process has to be further optimized with the use of a more efficient membrane filtration setup such as cross filter with a vibrating membrane. It could further improve the recovery yield and the purity of the resin acids. Further research is required on how to obtain a purer resin acid fraction from the concentrated retentate. In addition, research is needed to understand how to separate the mixture of resin acids to isolate valuable individual resin acids. Recovery of terpenes is possible with ultrafiltration. A pilot scale study is warranted, incorporating an efficient ultrafiltration design with a ceramic membrane.

The feasibility of the proposed biorefinery ideas depends on the arrangement of the each mill. A customised techno-economic feasibility should be carried out after optimizing the proposed biorefinery processes, based on the real-life process and economic data from the mill.

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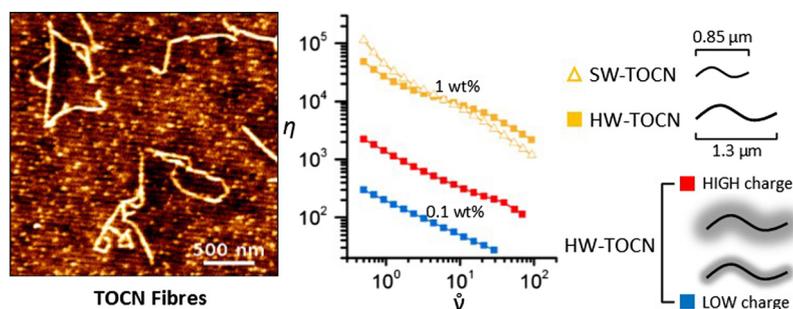
## Effects of fibre dimension and charge density on nanocellulose gels

Llyza Mendoza, Thilina Gunawardhana, Warren Batchelor, Gil Garnier\*



Bioresource Processing Research Institute of Australia (BioPRIA), Department of Chemical Engineering, Monash University, VIC 3800, Australia

## GRAPHICAL ABSTRACT



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## ABSTRACT

**Hypothesis:** Carboxylated cellulose nanofibres can produce gels at low concentrations. The effect of pulp source on the nanocellulose fibre dimension and gel rheology are studied. It is hypothesised that fibre length and surface charge influence aspects of the gel rheological properties.

**Experiments:** TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)- mediated oxidised cellulose nanofibres from never-dried hardwood and softwood pulp and containing different charge levels were produced and characterized. Steady-state and dynamic rheological studies were performed to ascertain the effects of pulp type on gel behavior and properties.

**Findings:** Nanocellulose fibres extracted from softwood (SW-TOCN) and hardwood (HW-TOCN) pulp exhibit similar widths but different length dimensions as shown via AFM analysis. Rheological measurements show that the dynamic moduli ( $G'$  and  $G''$ ) of nanocellulose gels are independent of pulp source and are mostly influenced by fibre concentration. Differences in the steady-state behavior (i.e. viscosity) at constant surface charge can be attributed to differences in fibre length. Increasing the surface charge density influences the critical strain and the viscosity at the percolation concentration (0.1 wt%) due to higher electrostatic interactions.

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## 1. Introduction

Cellulose nanofibres are long semi-flexible fibrils derived from the disintegration of wood pulp via various chemical and mechanical treatments [1]. Chemical methods, such as TEMPO-mediated oxidation, selectively introduce carboxylate moieties on the

cellulose fibril surface. The high electrostatic repulsion between the individual fibrils assists in the liberation of TEMPO-oxidised cellulose nanofibres (TOCNs) upon mechanical disintegration [2]. The ease of scale-up of TEMPO-mediated oxidation has led to the establishment of pilot-scale production and its availability as a commercial product [3]. Applications of TOCNs extend far beyond pulp and paper. TOCNs have shown great performance as reinforcing agent in plastics, [4,5], in biomedical applications [6–11], pharmaceuticals [12], catalysis [13], superabsorbents [14,15], and flexible electronics [16].

\* Corresponding author.

E-mail address: [gil.garnier@monash.edu](mailto:gil.garnier@monash.edu) (G. Garnier).

Nanocellulose is typically found as a suspension or a gel with water as continuous phase. Rheology is the technique of choice to quantify nanocellulose behavior and properties. For instance, the flow behavior of semi-flexible nanocellulose fibrils can be related to the length and width of the fibrils. The studies of Tanaka et al. [17] and Jowkarderis and van de Ven [18], related shear and intrinsic viscosities of dilute TOCN suspensions to equations of flow for rigid rod-like particles to determine fibre aspect ratio. Varanasi et al. [19], on the other hand, utilised yield stress measurements to determine the fibre gel point and correlate it to the aspect ratio via the crowding factor theory.

The bulk properties of nanocellulose gels and suspensions have been investigated in several rheological studies. In particular, TOCNs possess high aspect ratio [2] which form percolated networks even at low solid concentrations [20]. TOCNs and similarly surface-charged nanocellulose suspensions form gels which exhibit pseudoplastic and thixotropic behavior due to their inherent fibril assembly and restructuring which occurs during material deformation [20–22]. The presence of high surface charges leading to their colloidal stability was also investigated in several studies [20,23–25]. Local flow phenomenon in nanocellulose such as wall slip, shear-banding, and other flow instabilities which may affect the accuracy of rheological measurements were analysed [12,21]. Simulation and numerical modelling have mainly focused on understanding the mechanism of shear-thinning in nanocellulose [26,27]. However, studies on the effects of fibre dimensions and surface charges, on the nanocellulose gel rheological properties are very limited. Only one known study has related nanocellulose aspect ratio to the changes in the fibre percolation as observed by changes in viscosity [28].

This study aims at quantifying the effect of fibre dimension and surface charge on the rheological properties of nanocellulose gels. Fibre dimension was varied with the pulp source by oxidising softwood and hardwood kraft pulp from *Pinus Radiata* and *Eucalyptus* sp. respectively. The objectives are two-fold. First, to understand the relationship between the initial fibre size on the dimensions of the resulting nanocellulose; second to quantify the effect of nanocellulose fibre dimension on gel rheology. Differences are analysed through steady-state shear and oscillatory rheological measurements via cone and plate geometry. In steady-state shear, changes in the signature double yielding-behavior and zero-shear viscosity will be observed, whereas in oscillatory measurements variations in the key parameters such as the dynamic ( $G'$  and  $G''$ ) moduli and the critical strain  $\gamma_c$  are examined.

## 2. Methodology

### 2.1. Materials

Hardwood (*Eucalyptus* sp.) kraft pulp of approximately 10 wt% solids was supplied by Australian Paper, Maryvale, Australia. Softwood (*Pinus Radiata*) kraft pulp containing 17.7 wt% solids was supplied by Oji Fibre Solutions, Kinleith, New Zealand. 2,2,6,6-tetra methylpiperidine-1-oxyl (TEMPO) and sodium bromide (NaBr) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl) and Sodium Hydroxide (NaOH) were diluted for solutions as required and were purchased from ACL Laboratories and Merck, respectively. 12 w/v% Sodium Hypochlorite (NaClO) was purchased from Thermo Fisher Scientific and used as received. All chemicals were analytical grade.

### 2.2. TEMPO-mediated oxidation

The TEMPO-mediated oxidation process employed is based on the method of Isogai et al. [2]. Wood pulp containing 10 dry g fibre

was suspended in 2500 mL water containing 0.4 g TEMPO and 2.5 g NaBr. The 12 w/v% NaClO solution was initially adjusted to pH 10 via addition of 36% HCl before the reaction. To initiate the oxidation process, NaClO was added drop-wise to the suspension whilst stirred. Varying amounts of NaClO was added depending on the desired carboxylate group density. The primary oxidant content was varied between 3.3 mmol NaClO·g<sup>-1</sup> fibre to 12.5 mmol NaClO·g<sup>-1</sup> fibre for hardwood and constant 6.5 mmol NaClO·g<sup>-1</sup> fibre for softwood. The pH of the reaction was maintained at 10 through the addition of 0.5 M NaOH. The oxidation process was maintained until no pH change was observed. The oxidised fibres were recovered through filtration and stored refrigerated (4 °C). The oxidised pulp was then dispersed in deionised water to a desired concentration (0.1–1 wt%). Fibrillation was accomplished through a high-pressure homogeniser (GEA Niro Soavi Homogener Panda) at 1000 bar for two passes.

### 2.3. Determining solids concentration

The solids concentration of all samples (i.e. gel or pulp) were determined through drying. The sample was weighed before ( $w_i$ ) and after ( $w_d$ ) drying. Sample moisture was evaporated by drying in an oven at 105° for at least 6 h. The solids content was calculated as:

$$\text{solidscontent}(\%) = \frac{w_d}{w_i} \times 100\% \quad (1)$$

### 2.4. Conductometric titration

The carboxylate group content was measured by conductometric titration as reported in [29]. Oxidised pulp samples (approx. 30 mg dry weight) were suspended in 40 mL deionised water. 40 μL 1% NaCl was added to the suspended sample. The pH of the suspended sample was adjusted between 2.5 and 3 prior to titration with 0.5 M HCl. Titration was accomplished by controlled addition of 0.1 M NaOH using a Mettler Toledo T5 titrator. The conductivity of the sample was monitored throughout the titration progress. The carboxyl group content (mmol COO<sup>-</sup>Na<sup>+</sup>·g<sup>-1</sup> fibre) was determined with:

$$CC = \frac{c(V_2 - V_1)}{w} \times 1000 \quad (2)$$

where  $V_1$  and  $V_2$  pertain to the amount of titrant required to neutralise the carboxylic groups (in L),  $c$  is the NaOH concentration (mol/L), and  $w$  is the sample weight (g).

### 2.5. Rheological measurement

Rheological testing was performed with an Anton Paar MCR302 rheometer. A cone (0.997°) and plate (49.975 mm) geometry were selected. Testing was done at ambient temperature (25 °C). A solvent trap was used to ensure stable temperature during measurements. Viscosity was measured at shear rate ranging from 0.5 to 100 s<sup>-1</sup>. Oscillatory strain sweep was performed from 0.01 to 100% at a constant 1 Hz frequency. Frequency sweep was measured from 0.1 to 100 rad/s and at various suitable shear stresses at the linear viscoelastic region (LVR) wherein the dynamic moduli ( $G'$  and  $G''$ ) are independent of the shear stress. All measurements were done in triplicates and the most representative result is presented.

### 2.6. Atomic force microscopy (AFM)

AFM imaging was performed using a JPK Nanowizard 3 to determine fibre length and width. A 0.001 wt% nanocellulose dispersion

was spin coated (Laurell technologies, WS-400BZ-6NPP/LITE) at 2500 rpm onto a plasma coated glass slide. Images were obtained in intermittent contact mode using Brüker NCHV model cantilevers. Fibre widths were obtained from the reported height of single fibres on the surface due to convolution effects. Fibre lengths were estimated by placing segmented lines on the AFM images through an imaging software (Fiji).

### 2.7. Fibrelab

Fibre dimensions (length and width) of the unrefined and unoxidised hardwood and softwood samples have been obtained via the Kajaani Fibre Lab (Valmet). Dilute suspensions ( $\sim 0.05$  wt%) were utilised for size analysis. Image analysis from the Fibrelab software is primarily capable of detecting large fibres more than fines.

## 3. Results

The effect of fibre dimensions, using never-dried bleached kraft pulp of softwood and hardwood, on the dimensions and charge density of cellulose nanofibres resulting from TEMPO-mediated oxidation pre-treatment and homogenization is first studied. Secondly, the rheological properties of the gel formed are quantified to understand the effect of nanocellulose dimensions and surface charge (i.e. extent of oxidation).

### 3.1. Fibre dimensions

The distributions of fibre length and width of never-dried unrefined softwood and hardwood kraft pulps are shown in Fig. 1. On average, hardwood pulp has shorter and narrower fibres than softwood; length and width distributions are also much narrower (Tables 1 and 2). However, the fibre average aspect ratio ( $L/W$ ) are nearly identical for both fibres, with hardwood  $L/W = 36$  and softwood  $L/W = 42$ .

The fibre size distributions of TEMPO-oxidised cellulose nanofibres produced from hardwood (HW-TOCN) and softwood (SW-TOCN) pulp containing different surface charges are shown in Fig. 2. The nanocellulose produced in all cases have the width distribution in the nano-scale- as expected from TEMPO-mediated oxidation. Length distributions, on the other hand, have changed post- chemical oxidation and mechanical fibrillation. For both fibre types and their varying surface charge levels, the mean length decreased drastically as shown in Tables 1 and 2. On average, hardwood-nanocellulose (HW-TOCN) are wider and longer than softwood-nanocellulose (SW-TOCN) at similar surface charge ( $1 \text{ mmol COO}^- \cdot \text{g}^{-1}$  fibre) as shown in Tables 1 and 2. Moreover,

length and width distributions for HW-TOCNs are slightly broader than for SW-TOCNs. When surface charge is modified in HW-TOCNs, length and width dimension distributions and mean values are very similar.

### 3.2. Rheological measurements

Oscillatory rheology is an ideal technique to characterize the elastic and viscous behavior of nanocellulose gels at varying conditions. For instance, the rheology of nanocellulose gels produced from softwood pulp at increasing fibre concentration is shown in Fig. 3. The elastic modulus  $G'$  pertains to the solid-like behavior whereas the viscous modulus  $G''$  characterizes the liquid-like behavior of the gel. At the linear viscoelastic region (LVR),  $G'$  and  $G''$  are independent of the shear strain. When  $G' > G''$ , the elastic behavior of the nanocellulose gel is dominant at a particular strain. At the critical strain  $\gamma_c$ , the gel moduli ( $G'$  and  $G''$ ) deviates from the LVR and is at the onset of yielding. Consequently, at even higher strains when  $G'' > G'$ , the gel possesses a viscous dominant behavior.

#### 3.2.1. Effect of pulp source

The effect of initial pulp source on the dynamic moduli ( $G'$  and  $G''$ ) at various solid concentrations is shown in Fig. 4A. At constant charge density ( $1 \text{ mmol COO}^- \cdot \text{g}^{-1}$  fibre), the elastic moduli ( $G'$ ) of nanocellulose gels derived from hardwood and softwood sources are very similar. The differences in the viscous moduli ( $G''$ ) observed between HW-TOCN and SW-TOCN are within the error margins. Moreover, for both types of pulp,  $\gamma_c$  is constant across all solids contents as shown in Fig. 4B. However, SW-TOCN possess consistently higher  $\gamma_c$  at all tested concentrations.

The difference of pulp source on the resultant nanocellulose gels viscosity profile is highlighted in Fig. 5. SW-TOCN and HW-TOCN both display similar viscosity values and linear shear-thinning behavior at 0.1 wt%. On the other hand, the double yielding behavior is observed for HW-TOCN and SW-TOCN at concentrations equal or greater than 0.3 wt%. The major difference in nanocellulose produced from hardwood and softwood pulp sources is emphasized at the semi-dilute concentrations (0.3–1 wt%) wherein SW-TOCN viscosity decreases at a steeper gradient at both double yielding regions than HW-TOCNs.

#### 3.2.2. Effect of charge density

The effect of charge density on the dynamic rheological properties of nanocellulose gels produced from hardwood is shown in Fig. 6. Gels with the lowest carboxylate content ( $0.65 \text{ mmol} \cdot \text{g}^{-1}$ ) consistently report the lowest  $G'$  and  $G''$  values. However, gels

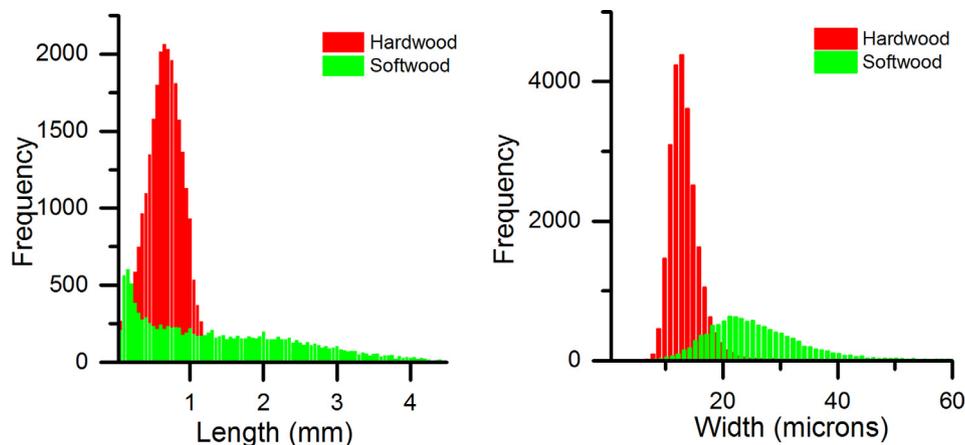


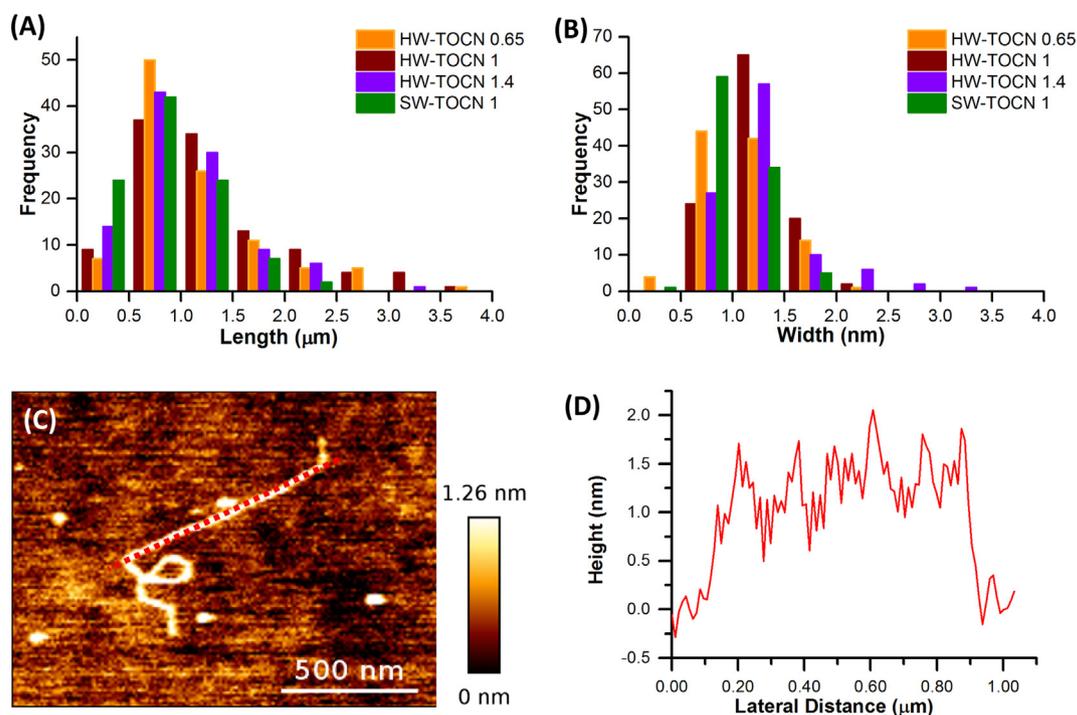
Fig. 1. Population Length and width distributions for hardwood and softwood bleached kraft pulp fibres.

**Table 1**  
Fibre length statistics of hardwood and softwood kraft pulp and the nanocellulose fibres produced from those.

Pulp type	Surface charge (mmol COO <sup>-</sup> .g <sup>-1</sup> )	Mean length (μm)	Standard deviation (μm)	Population (# of fibres)
Hardwood	0	620	260	26,327
HW – TOCN	0.65	1.16	0.62	105
	1.00	1.30	0.73	111
	1.40	1.02	0.53	103
Softwood	0	1420	1130	13,070
SW-TOCN	1.00	0.85	0.42	99

**Table 2**  
Fibre width statistics of hardwood and softwood bleached kraft pulp and the nanocellulose fibres produced from those.

Pulp source	Surface charge (mmol COO <sup>-</sup> .g <sup>-1</sup> )	Mean width (nm)	Standard deviation (nm)	Population (# of fibres)
Hardwood	0	17,240	4253	24,441
HW – TOCN	0.65	1.06	0.37	105
	1.00	1.24	0.33	111
	1.40	1.29	0.47	103
Softwood	0	34,060	9028	10,799
SW-TOCN	1.00	0.97	0.30	99



**Fig. 2.** Nanocellulose fibres produced from softwood and hardwood bleached kraft pulp. Width (A) and length (B) distributions for nanocellulose produced from softwood (1 mmol COO<sup>-</sup>.g<sup>-1</sup>) and hardwood (0.65, 1, and 1.4 mmol.g<sup>-1</sup>) at various surface charges. (C) and (D) AFM image of a single HW-TOCN fibre with surface topology shown.

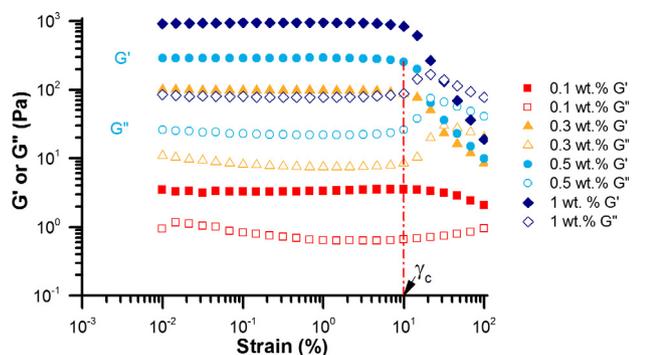
containing either 1 or 1.4 mmol.g<sup>-1</sup> show similar  $G'$ . On the other hand,  $G''$  values were also observed to increase with increasing carboxylate content at all solids concentrations. Critical strain  $\gamma_c$  does not vary significantly up to a charge density of 1 mmol.g<sup>-1</sup>. At the highest surface charge tested (1.4 mmol.g<sup>-1</sup>),  $\gamma_c$  decreases linearly with increasing fibre content.

The viscosity profile of nanocellulose gels produced from hardwood at different surface charges is shown in Fig. 7. All HW-TOCN gels containing at least 0.3 wt% possess a double yielding behavior. At a given concentration past 0.3 wt%, the differences in the absolute viscosity values are minimal and could be attributed to small variations in actual nanocellulose content in the tested samples. However, at 0.1 wt%, the gel containing the lowest surface charge at 0.65 mmol.g<sup>-1</sup> is significantly less viscous than at 1 and 1.4 mmol.g<sup>-1</sup>.

## 4. Discussion

### 4.1. Effect of pulp fibres on nanocellulose fibre dimensions

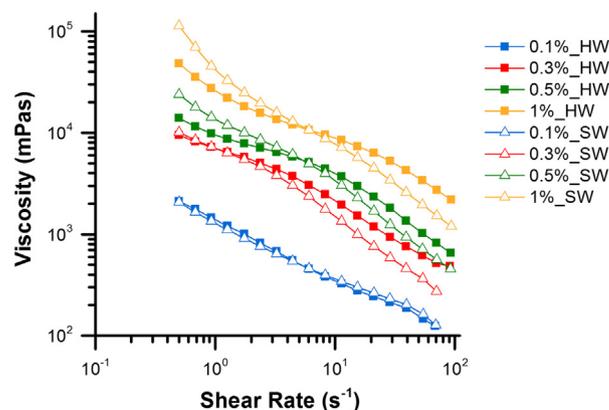
Cellulose fibres vary in fibre dimension and chemical composition depending on the original wood source and the pulping process used. The most widely-used process to produce cellulosic fibres is through a combination of kraft chemical pulping followed by bleaching. This process removes most of the lignin and hemicellulose that occur in different amounts and compositions in softwood (*Pinus Radiata*), and hardwood (*Eucalyptus* sp.) [30,31]. However, traces of lignin and hemicellulose still remain within the bleached cellulose pulp which impact the TEMPO-mediated oxidation process. The softwood pulp used in this study required a higher primary oxidant content (6.5 mmol NaClO.g<sup>-1</sup> fibre) than



**Fig. 3.** Oscillatory strain measurement for nanocellulose gels made from bleached softwood fibres ( $1 \text{ mmol}\cdot\text{g}^{-1}$ ) as a function of solids concentration. Important spectral rheological data including the  $G'$  and  $G''$  at the linear viscoelastic region (LVR), and the critical strain  $\gamma_c$  are identified for the 0.5 wt% gel used as example. Measurements were done at  $25^\circ\text{C}$ , 1 Hz.

the hardwood pulp ( $5 \text{ mmol NaClO}\cdot\text{g}^{-1}$  fibre) to achieve the same surface charge ( $1 \text{ mmol COO}^-\cdot\text{g}^{-1}$  fibre).

The original width and length of the never-dried bleached hardwood and softwood fibres are vastly different (Fig. 1) – softwood fibres are approximately twice as long and thick on average compared to hardwood fibres (Tables 1 and 2). The combination of TEMPO-mediated oxidation and high-pressure homogenisation results in nanocellulose fibres with dimensions multiple orders of magnitude smaller. This chemical and mechanical treatment has effectively liberated elementary fibrils from both hardwood and softwood pulp sources, evident by the similar widths of the HW-TOCN and SW-TOCN fibres in the order of nanometers [15]. Due to the high energy required for mechanical fibrillation (i.e. 1000 bar pressure), it is possible that further delamination occurred resulting in a fibre mean width less than the currently accepted elementary fibril dimensions consisting a  $6 \times 6$  chain array. Since individual cellulose chains are assembled into fibrils by H-bonding along their length, the high-pressure homogenisation could have created shear forces strong enough to liberate thinner fibrils. The widths measured support previous studies. For instance, Usov et al. [32] reported AFM measurements visualising single cellulose chains and  $2 \times 2$  cellulose nanofibrils with average widths of 0.44 and 0.84 nm, respectively. In addition, Geng et al. [33] described a mean width value of 2.35 nm (at a surface charge of  $980 \mu\text{mol}\cdot\text{g}^{-1}$ ); however, width distributions showed a large proportion of fibres thinner than 2 nm. When comparing lengths of the HW-TOCN and SW-TOCN fibres, cleavage is evident for both

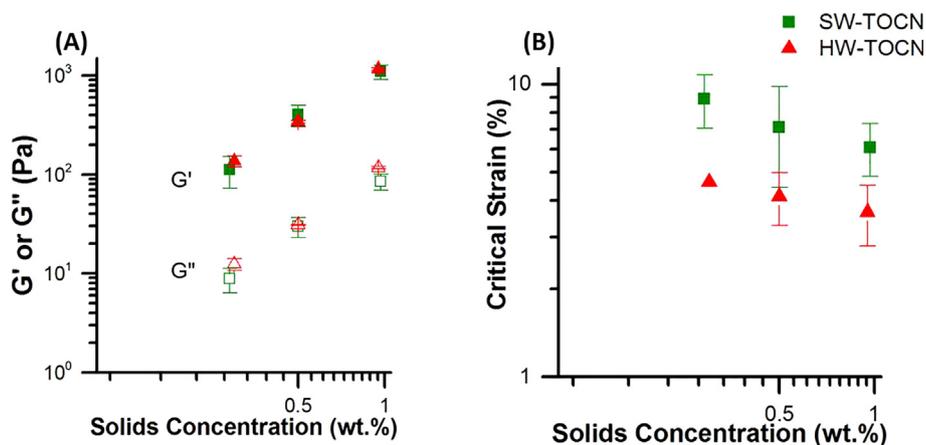


**Fig. 5.** Viscosity Profile of TOCNs from hardwood (solid symbol) and softwood (open symbol) as a function of concentration for constant charge density ( $1 \text{ mmol}\cdot\text{g}^{-1}$ ). Measurements were done at  $25^\circ\text{C}$ .

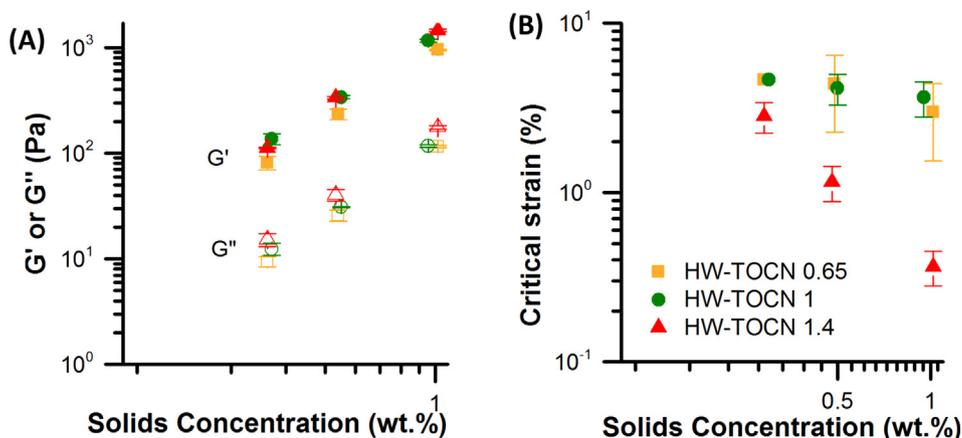
pulp sources, attributed to the preferential oxidation of the weak amorphous regions subsequently cleaved under intense mechanical fibrillation [34]. This is evident in the XRD spectra (Supporting Information) as the small reduction in the crystalline index (CI) could not account for the large degree of fibrillation which we have observed. On average, the resulting HW-TOCNs are longer than SW-TOCNs ( $1.30 \mu\text{m}$  versus  $0.85 \mu\text{m}$ ) for a surface charge of  $1 \text{ mmol COO}^-\cdot\text{g}^{-1}$ .

#### 4.2. Effect of nanofibre dimensions and surface charge on gel rheology

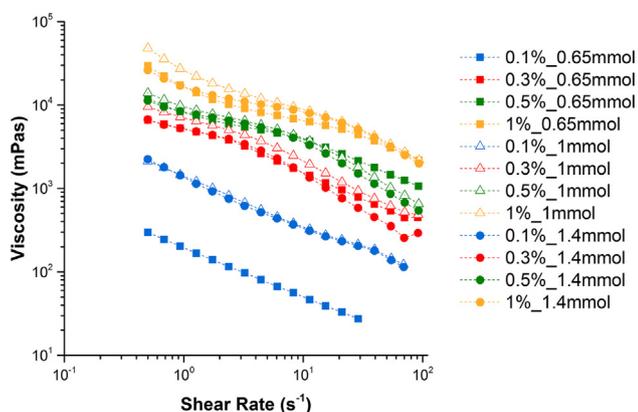
TEMPO-oxidised nanocellulose are characterized by two key parameters: physical dimensions (length and width) and surface charge. For TOCNs, provided sufficient electrostatic repulsion and mechanical fibrillation, width is determined by the elementary fibril width which is similar for hardwood and softwood pulp [35]. Length, on the other hand, can vary depending on the processing conditions [2]. The change in length of a semi-flexible fibre affects the extent and ability of entanglement. For SW-TOCN and HW-TOCN, the difference in fibre lengths is most evident at the onset (i.e. critical strain values) of yielding and steady-state shear (i.e. viscosity) behavior. Across all concentrations, the shorter SW-TOCNs consistently yielded at higher strains than HW-TOCNs. This might be due to a longer persistence length, related to the flexibility and stiffness of the crystalline domains of softwood, affecting nanofibre conformation upon shear [32].



**Fig. 4.** (A) Dynamic Moduli ( $G'$  and  $G''$ ) of nanocellulose gels produced from unrefined softwood and hardwood as a function of solids concentration at constant charge density ( $1 \text{ mmol}\cdot\text{g}^{-1}$ ). (B) Critical Strain of SW-TOCN and HW-TOCN as a function of solids concentration.



**Fig. 6.** The effect of charge density on the (A) dynamic moduli at LVR and (B) critical strain of HW-TOCN nanocellulose gels at different solids concentrations. Yellow symbols for 0.65 mmol.g<sup>-1</sup>, green symbols for 1 mmol.g<sup>-1</sup> and red symbols for 1.4 mmol.g<sup>-1</sup>. Measurements were done at 25 °C, 1 Hz.



**Fig. 7.** Viscosity Profile for HW-TOCNs at three levels of charge density (0.65, 1, and 1.4 mmol.g<sup>-1</sup>) and different solids content. Measurements were done at 25 °C.

Nanocellulose gels exhibit shear-thinning response which is generally understood to be due to the alignment of fibres along the shear direction. As seen in Fig. 5, for concentrations ranging between 0.3 and 1 wt%, SW-TOCNs have steeper viscosity gradients than HW-TOCNs due to easier alignment of the shorter fibres. However, this difference does not seem to affect the percolation threshold which is identified as the concentration wherein there is no double yielding behavior [20]. The double-yielding phenomenon in nanocellulose is attributed to the reorientation of fibres from an isotropic (i.e. randomly oriented) state to partial alignment in the direction of flow. At high fibre concentrations, higher shear rates are required to disrupt any remaining isotropic micro-domains, which leads to a further decrease in viscosity [36]. For both softwood and hardwood-based nanocellulose, the percolation concentration is 0.1 wt%. Moreover, the dynamic moduli in the LVR region are not significantly different from both pulp types and are primarily concentration-dependent (Fig. 4A).

Effective surface charge arising from the nanocellulose carboxylate groups dictates the colloidal stability of the gels [20]. HW-TOCN gel with the lowest charge density (0.65 mmol.g<sup>-1</sup>) has lower moduli than HW-TOCN gels of higher charge density (Fig. 6A). A higher surface charge creates stronger and more stable gels due to higher electrostatic repulsion. The gel critical strain is affected by the variation in the surface charges (Fig. 6B). At 1.4 mmol.g<sup>-1</sup>, the critical strain decreases at increasing concentration. This is not a direct effect of the fibre dimensions as we should observe some differences between 0.65 mmol.g<sup>-1</sup> and 1 mmol.g<sup>-1</sup>.

The observations at 1.4 mmol.g<sup>-1</sup> can be attributed to the repulsive charges among fibres which act as lubricant allowing fibres to slide past each other [37]. Hence, the combination of high surface charge and high fibre concentration results in stronger repelling, partially hydrated fibres per unit volume, which reduces the required minimum strain for yielding. Comparing three levels of carboxylation (Fig. 7) reveals a significant impact on viscosity at the percolation threshold. At 0.1 wt% concentration, the reduction in the surface charge to 0.65 mmol.g<sup>-1</sup> results in an order of magnitude reduction in gel viscosity, possibly due to the less constrained nature of the fibre interactions. A fibre containing low surface charge is expected to have less interactions with other neighbouring fibres as it has a lower effective electrical double layer.

## 5. Conclusion

TEMPO-oxidised cellulose nanofibres (TOCNs) are semi-flexible fibrils derived from the primary alcohol oxidation of cellulose-based sources. Previous studies have primarily focussed on integrating TOCNs into other compatible materials to improve their bulk properties [4,5,10,14]. Some fundamental studies have been conducted, aiming to understand the colloidal stability [20,23], local flow phenomenon [12,21], and model rheological behavior [26,27]. The effect of different process conditions (i.e. bleach content and pH, primary oxidant) have been explored previously [2,38,39], however little is known on how the fibre source and its dimensions affect the rheological properties of nanocellulose gels. This study analysed the effect of wood pulp source and the resulting nanocellulose fibre dimensions on the rheology of nanocellulose gels. Kraft pulped and bleached hardwood (*Eucalyptus* sp.) and softwood (*Pinus Radiata*) contained fibres with significantly different dimensions ( $L = 0.6$  mm,  $W = 17$   $\mu$ m and  $L = 1.4$  mm,  $W = 34$   $\mu$ m, respectively) but similar aspect ratios (36 and 42 respectively). However, the initial fibre size has minimal effect on the degree of fibrillation, resulting in hardwood and softwood nanocellulose fibers (HW-TOCN and SW-TOCN) with similar widths in the order of nanometers, indicating elementary fibrils. In terms of length, HW-TOCN fibres are longer than SW-TOCN ( $L = 1.3$   $\mu$ m and  $L = 0.9$   $\mu$ m, respectively). The decrease in length from initial macro-fibres for both pulp sources is attributed to the preferential oxidation at weak amorphous regions cleaved under intense mechanical fibrillation. This difference in length affects the onset of yielding (i.e. critical strain) and the evolution of the viscosity curves at increasing solids content. This is particularly evident via rheology at the semi-dilute concentrations (0.3–1 wt%) – shorter SW-TOCN fibres display a steeper viscosity gradient in con-

trast to HW-TOCNs. Surface charge also impacts the rheological properties at the percolation threshold – for 0.1 wt% HW-TOCN, increasing the surface charge from 0.65 to at least 1 mmol·g<sup>-1</sup> results in higher viscosity due to greater electrostatic interactions. However, at higher concentrations, fibre length and surface charge have minimal effect, and instead the gel dynamic rheological properties ( $G'$  and  $G''$ ) are primarily affected by fibre concentration. These results indicate that, at fibre concentrations greater than the percolation threshold, nanocellulose gels can be produced with similar properties regardless of pulp source and minimal surface charge. This is a key finding beneficial for engineering nanocellulose gels for any specific biomedical or rheology application.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcis.2018.04.077>.

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