THE UNIVERSITY OF KWAZULU-NATAL

Production of high-value dissolving wood pulp (DWP) from sawdust waste

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PREFACE

The research contained in this dissertation was carried out by the candidate while based at the Council for Scientific and Industrial Research (CSIR) Biorefinery Industrial Development Facility (BIDF) based in Durban, South Africa. The work was carried out during the period 2020-2023 under the supervision of Professor Bruce Sithole and Doctor Jerome Andrew. The research was financially supported by the Department of Science and Innovation (DSI) Waste Research, Development, and Innovation (Waste RDI) Roadmap.

The contents of this work have not been submitted in any form to another university and, except where the work of others is acknowledged in the text, the results reported are due to investigations by the candidate.

Signed student: [redacted]

Date: 11 December 2023

As the candidate's Supervisor I agree to the submission of this thesis.

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DECLARATION 1 - PLAGIARISM

I, Simiksha Rajcomar, declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.
2. This thesis has not been submitted for any degree or examination at any other university.
3. This thesis does not contain other persons' data, pictures, graphs or other information unless specifically acknowledged as being sourced from other persons.
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DECLARATION 2 - PUBLICATIONS

Details of contribution to publications that form part and/or include research presented in this thesis (include publications in preparation, submitted, *in press*, and published and give details of the contributions of each author to the experimental work and writing of each publication)

1. Balkissoon S, Andrew J, Sithole B. 2022.Dissolving wood pulp production: a review. Biomass Conversion and Biorefinery. DOI: https://doi.org/10.1007/s13399-022-02442-z. 14 March 2022. PP 1-36.
2. Balkissoon S, Andrew J, Sithole B. 2022. Production of microcrystalline cellulose (MCC) from sawdust waste biomass. 18th International Conference on Renewable Resources and Biorefineries, Bruges, Belgium on 1 -3 June 2022. Work presented by Dr J Andrew.
3. Balkissoon S, Andrew J, Sithole B. 2021.A novel approach to produce a high-purity cellulose product from sawdust waste material. South African Chemical Engineering Conference (SACEC). Virtual conference, 20-22 September 2021. PP 236-246. ISBN 978-1-991213-99-0 (Electronic)
4. Balkissoon S, Andrew J, Sithole B. 2021.Production of dissolving wood from sawdust waste. Poster presentation at the Sustainable Bioenergy and Processes Conference, 13-15 December 2021, Cape Town, presented online.
5. Rajcomar S, Sithole B, Andrew J. 2023. Production of microcrystalline cellulose (MCC) from wood sawdust waste. (In review).

- **Note that the student's surname was changed from Balkissoon to Rajcomar due to a change in marital status.** The **16-digit ORCID identifier is 0000-0002-9600-6188**

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Dedication

To the remarkable women in all facets of my life, spanning generations, who have been a wellspring of inspiration, showed unwavering support, countless moments of encouragement, and most importantly an unshakeable belief in me, your presence has illuminated my path. This thesis is dedicated to you as a testament to the profound impact you have had on my academic and personal growth.

In the words of Diane Mariechild "A woman is a full circle. Within her is the power to create, nurture, and transform." Thank you for making my journey lighter, and more transformative and for being there to lift me every step of the way. I am truly grateful.

Nomenclature

	Units
US dollars	$
Microns	μ
Degrees Celsius	℃
Density	kg/m^3 or g/cm^3
gram	g
hour	h
Intrinsic viscosity	ml/g
Kilogram	kg
Litres	L
Molar concentration	M
Millilitres	ml
Mils per year	my
South African Rands	R
Specific heat capacity	KJ/kg℃

	Units
Q-energy	KJ

Abbreviations

Abbreviations	**Meaning**
AIL	Acid insoluble lignin
APS	Ammonium persulphate
AS	Acid bisulphite
AS	Ammonium sulphate
ASL	Acid soluble lignin
CAGR	Compound annual growth rate
CP	Cellulose protector
CrI	Crystallinity index
DOE	Design of experiments
DP	Degree of polymerisation
DWP	Dissolving wood pulp
FTIR	Fourier transform infrared spectroscopy

Abbreviations	Meaning
FTPP	Forestry, timber, pulp and paper
GDP	Gross domestic product
HAZOP	Hazard and operability
HPLC	High performance liquid chromatography
HW	Hardwood
IRR	Internal rate of return
L: S	Liquid-to-solid ratio
L: W	Liquid-to-wood ratio
LODP	Levelling- off degree of polymerisation
MCC	Microcrystalline cellulose
MHW	Mixed hardwood
n.d.	Not detected
NLT	Not less than
NMT	Not more than
o.d	Oven-dried
PBP	Payback period

Abbreviations	**Meaning**
PHK	Prehydrolysis kraft pulp
ROI	Rate of return
SARS	South African Revenue Services
SEM	Scanning electron microscopy
SW	Softwood
TAPPI	Technical Association of the Pulp and Paper Industry
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
KWh	Kilowatts per hour
mpy	MilS per year
α	Alpha
β	Beta
Δ	Delta
θ	Theta

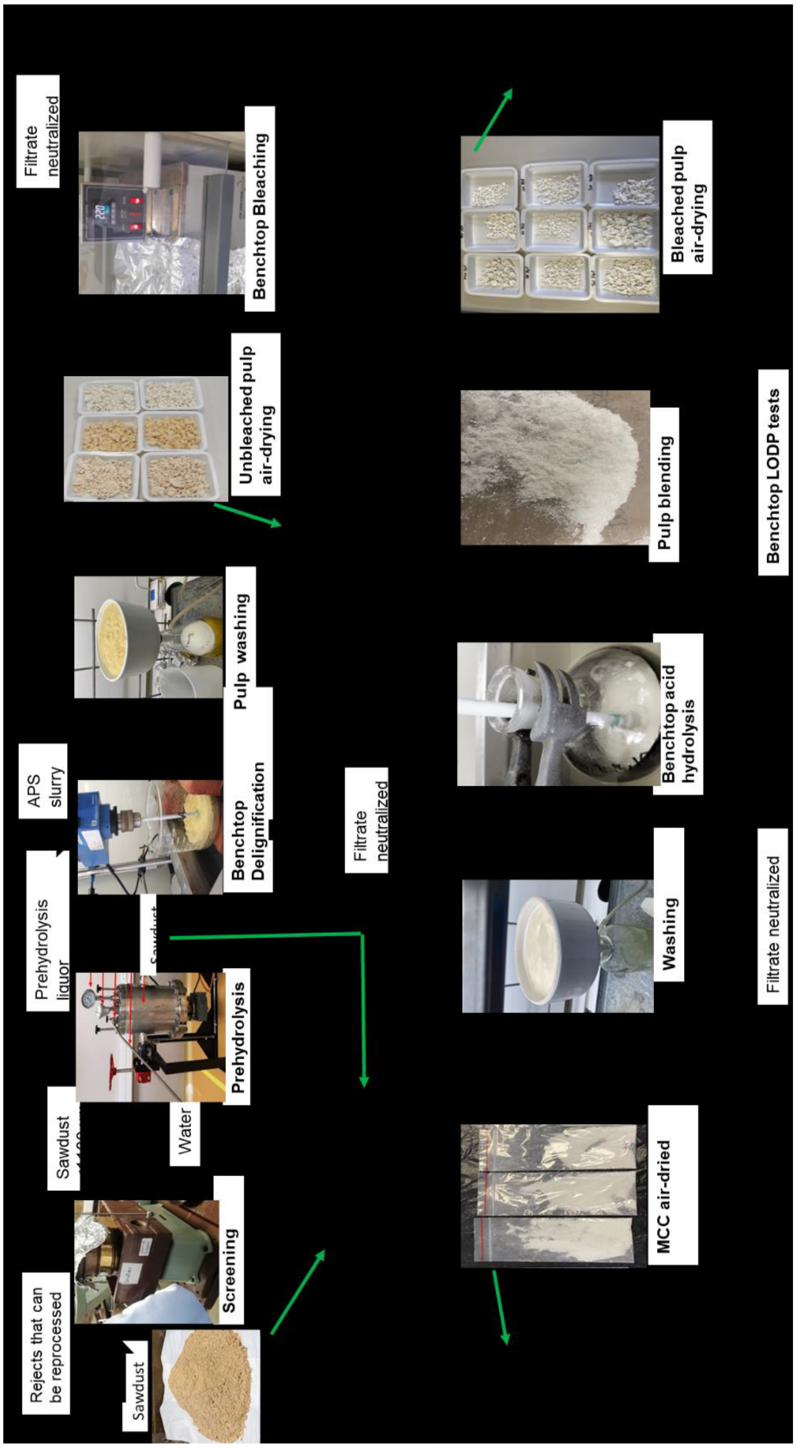
Abstract

This study adopts a circular economy framework, aiming to divert waste from landfills and channel it towards more lucrative value chains. A novel approach for producing dissolving wood pulp from wood sawdust waste, focusing on three sawdust species: hardwood, softwood, and a mixture of hardwood species was undertaken. The two-step low-temperature chemical process (60-80°C) involved delignification using ammonium persulphate and subsequent bleaching to remove residual lignin, and hemicellulose, and enhance pulp brightness. This approach provides a more environmentally friendly alternative with reduced chemical, water, and energy intensity compared to complex traditional processes involving several stages.

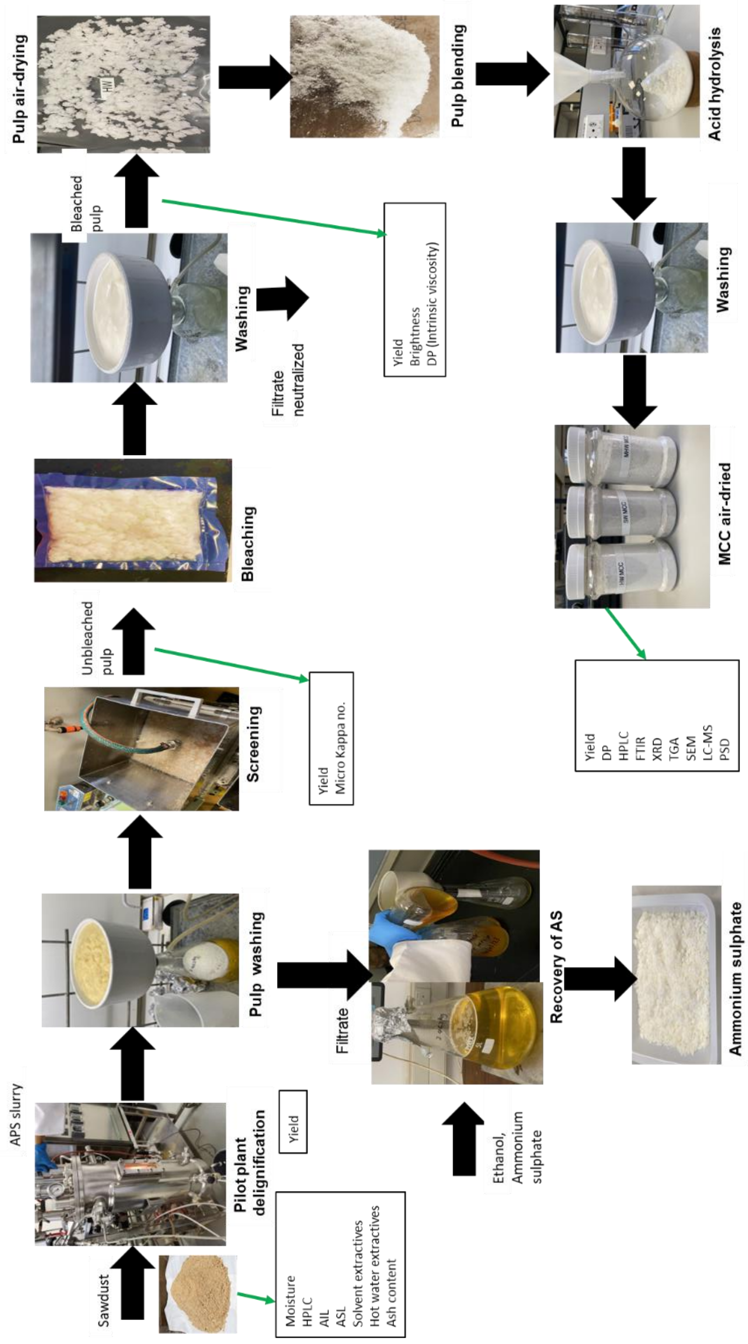
The delignification process was optimised on a benchtop level for reaction time, chemical concentrations, liquid-to-wood ratios, and temperature following respective benchtop bleaching treatments. The resulting bleached sawdust pulp, with yields ranging from 38-46% and an ISO brightness of 86-88%, proved unsuitable for viscose production due to the low intrinsic viscosity (180-310 ml/g). However, microcrystalline cellulose production remained viable requiring a final acid hydrolysis step to modify the degree of polymerization. Scaling up to a pilot-scale operation, the study included characterisation of the final microcrystalline cellulose using various analytical techniques such as wet chemistry, thermogravimetric analysis, microscopic and spectroscopic techniques, chromatographic and mass spectrometry methods, particle size analysis and colourimetric methods of analysis. Characterization using these methods showed some close similarities between the prepared microcrystalline cellulose samples and commercially available microcrystalline cellulose. Microcrystalline cellulose yields varied between 30-42%, the degree of polymerisation ranged between 257-398, brightness ranged between 79-86%, pH between 5-7 and the crystallinity index between 76-84%, with physical attributes like particle size requiring further modification for commercial applications. By-product recovery explored the potential of ammonium sulphate, benefiting both agricultural and non-agricultural applications. A techno-economic assessment, incorporating recovery methods, indicated a return on revenue of 78-84%, an internal rate of return of 67-70%, and a payback period of 1-2 years, with marginal effects from acid (hydrochloric) recovery.

The study highlighted the highest potential in microcrystalline cellulose derived from hardwood, with bleached softwood sawdust showing promise for lyocell production due to its high degree of polymerization. Overall, the methodology not only demonstrated environmental benefits but also economic viability, making it a promising avenue for sustainable wood waste utilization.

Graphical abstract- Benchtop trials



Graphical abstract- Pilot trials



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CHAPTER 1 INTRODUCTION

1.1.Background

The Forestry, Timber, Pulp, and Paper (FTPP) sector faces significant challenges in waste generation and accumulation. As industries strive to adopt the principles of a "circular economy," there is a growing need to explore innovative and transformative technologies that can eliminate waste and establish new value chains. In line with this goal, there has been a notable shift towards the development of sustainable and eco-friendly materials in recent years.

In South Africa, although deforestation is not of concern, approximately half of the wood processed in the FTTP sector goes to waste (Herbst, 2013, Phillips, 2017). Waste biomass generated from sawmills includes tree bark, sawdust, and wood shavings. According to Stafford and Lange (2018), approximately 440 000 tons per annum of sawdust waste is generated by approximately 218 sawmills in South Africa. This poses a significant challenge for waste disposal. Disposal of sawdust by landfilling is not a sustainable option due to the additional costs associated with transportation to landfills, maintaining landfill sites, and opening new landfill sites. In addition, impending regulations may prohibit the disposal of organic waste in landfills (Andrew et al., 2018). The idea surrounding the utilization of materials commonly viewed as waste becoming a resourceful commodity has emerged in the realm of sustainable development. Biomass waste can be classified as renewable material resources or secondary material resources. The necessity for cleaner production technologies as well as the need to hamper rapid global deforestation have stimulated renewed interest in waste beneficiation (Andritz, 2020). Moreover, the overall decline in the FTPP sector due to the decrease in demand for traditional wood, pulp, and paper products and other challenges facing the industry such as energy and water shortages, have propelled the industry, to explore alternative revenue-generating opportunities to sustain the industry.

One such material that has attracted significant attention is dissolving wood pulp (DWP), a high-purity cellulose product that is produced from wood chips (Potgieter, 2018). Such products are valuable for commercial applications for the production of end-user products such as pharmaceuticals, and textiles like viscose, and microcrystalline cellulose (MCC) (Sappi, 2019b). Extensive research has been conducted over the years to produce DWP in alignment with pulping mills' efforts to advance technological innovations aimed at fractionating or converting lignocellulosic materials. The goal is to enhance the utilization of renewable feedstocks by generating a diverse array of products and by-products, as opposed to mere accumulation (Lehto and Alen, 2014). Existing processes used to produce DWP from wood chips are characterised by time-consuming, complex, energy, water, and chemically intensive processes (Chen et al., 2016). The proposed approach offers a promising solution by reducing or eliminating several stages associated with traditional methods, thereby mitigating the environmental impact and resource consumption.

Dissolving pulp has witnessed a surge in demand worldwide, owing to its versatile end-user applications across various industries, including pharmaceuticals, cosmetics, personal care, paints, textiles, and food manufacturing. Its unique properties and functionalities make it an appealing choice for high-value products. However, the limited availability of raw material sources or associated costs of some raw materials, such as cotton, pose a potential hindrance to maximizing revenue generation in the future. This growing market for DWP underscores the importance of research and development in this field. In this context, this PhD study aims to address the challenges of waste generation and sustainability in the FTPP sector by exploring a novel approach for producing MCC from waste sawdust material. The novelty lies in the use of a low-temperature (60 °C) process to delignify the sawdust and to produce a grade of pulp, which can then be further processed into commodities such as viscose and MCC.

Additionally, the proposed approach tackles the challenge of limited raw material sources by redirecting waste materials as potential feedstock for DWP production. By doing so, it addresses the issue of waste accumulation while simultaneously providing an alternative source for MCC manufacturing. This innovative approach holds the potential to enhance the sustainability and economic viability of MCC production, ensuring a reliable and continuous supply of raw materials while reducing the strain on existing resources. By leveraging this approach, the study seeks to contribute to the development of a circular economy model while meeting the increasing demand for sustainable materials.

1.2. Rationale

Sawdust, an abundant lignocellulosic material, is readily available as a by-product from timber processing industries, including sawmilling and papermaking. The production of DWP from sawdust waste offers several significant benefits. Firstly, it provides a sustainable solution for the disposal of sawdust waste, which is typically burned or discarded in landfills. Secondly, it reduces the demand for virgin wood pulp, which helps conserve natural resources. Finally, it offers a cost-effective alternative to traditional production methods, which can be expensive and resource-intensive (time, energy, water, and chemicals).

In this study, the anticipated end products targeted were the production of viscose and MCC. However, preliminary results from the study showed that the sawdust pulps produced were not suitable for the production of viscose but showed characteristics that were suitable for the MCC application.

The high production costs associated with conventional DWP production pose a significant challenge. Moreover, the dependence on plant-based materials for raw material resources threatens sustainability, and particularly expensive and limited raw material resources like cotton, impose constraints on meeting the potential demands and production of MCC.

In this regard, utilizing sawdust waste as a raw material for DWP production offers several compelling advantages. Overall, the utilization of sawdust waste as a raw material for DWP production addresses environmental concerns, conserves natural resources, and provides a cost-effective alternative to conventional methods. These advantages highlight the rationale behind exploring the production of MCC from sawdust waste as a sustainable and viable alternative.

1.3. Aim & objectives

The research undertaken focused on five objectives:

- Demonstration of proof-of-concept using novel technology to produce a grade of DWP from sawdust obtained from three wood processing industries (sawdust from 2 sawmills processing hardwoods (Eucalypts) and softwoods (Pine) and chip screenings (pin chips) from a local pulp mill processing a mixture of hardwoods). This entailed optimising conditions on a benchtop scale for each sawdust type for delignification and bleaching.
- Characterisation of sawdust pulps and the final products, and comparison with commercially available DWP and MCC.
- Scale-up of the process using optimised conditions from benchtop studies
- Evaluation of recovery methods for waste or by-products emanating from the process
- Techno-economic evaluation to determine the economic viability of the proposed process

1.4. Research chapters overview

The summary of each chapter is briefly described below:

Chapter 1: An introductory chapter that provides the foundation for the research conducted by providing the reader with background information relevant to the study, stating the research problem or objectives, and outlining the rationale behind the study.

Chapter 2: Literature review – Highlights key findings from a review of literature that were pertinent to developing a background on the study.

Chapter 3: Experimental methodology**-** Defines the experimental procedures followed and methods employed. Laboratory methods employed for the characterisation of all products from each stage are also outlined in this chapter.

Chapter 4: Results and discussion- Reports on important findings and provides the reasoning behind findings while correlating the findings or drawing comparisons to literature.

Chapter 5: Conclusions and recommendations- Conclude the results and identify if the study aims and objectives were met. Proposes recommendations for further work.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

2.1.1 *State of waste and landfilling*

The South African Department of Environment, Forestry, and Fisheries (DFFE) has reported that the recycling rate for waste generated in the country stands at a mere 10%, with the remaining 90% of waste being directed to landfills (TheConversation, 2020). The remaining 90% of the waste produced ends up in landfills (DFFE, 2020, Regenize, 2023). While specific statistics concerning landfill capacity in the nation are somewhat limited, waste management authorities concur that South Africa finds itself on the precipice of a landfill capacity crisis, with these facilities rapidly approaching their maximum thresholds (InfrastructureNews, 2022, Regenize, 2023). According to InfrastructureNews (2022), the procedural timeline for licensing and construction processes for a new landfill typically spans over three to five years, followed by appeals and possible legal processes. Given the inherent health risks associated with landfill sites, particularly for communities residing in proximity, there is an urgent imperative to mitigate waste generation and bolster waste management by employing more vigorous recycling initiatives (TheConversation, 2020). According to EngineeringNews (2021), major urban centres in South Africa, such as Johannesburg, Tshwane, and Cape Town, currently possess less than a decade's worth of viable landfill capacity remaining. This predicament is primarily a reflection of the low priority assigned to waste management matters within South African municipalities. Landfill closures are at times necessitated by a variety of factors, including adverse environmental consequences such as groundwater contamination and unmanageable air pollution in the form of dust or odours (EngineeringNews, 2021). Geological challenges, including dolomitic ground conditions, may lead to the infiltration of water and the formation of sinkholes, further complicating landfill operations (EngineeringNews, 2021). In many instances, improving the management and operations of existing landfills represents a necessary initial step; however, if such efforts prove unsuccessful, landfill closure becomes an unavoidable course of action (EngineeringNews, 2021).

Mwango and Kambole (2019) highlight the prevalent disposal practices, which typically involve open dumping, open burning, or dumping in landfills. These practices place a significant strain on landfill sites and contribute to greenhouse gas emissions, particularly in the case of open burning (Mwango and Kambole, 2019, Udokpoh and Nnaji, 2023). Despite the accompanying air pollution and associated public health challenges, open burning remains a common recourse among saw millers as a convenient means of sawdust disposal (Mwango and Kambole, 2019, Udokpoh and Nnaji, 2023). Sawdust, when irresponsibly discarded on streams and riverbanks, may be transported by rainwater or wind into surface water, causing adverse effects on aquatic life (Mwango and Kambole, 2019, Udokpoh and Nnaji, 2023). Additionally, indiscriminate sawdust disposal on land poses risks to terrestrial plant life and contributes to the dispersion of airborne wood dust (Mwango and Kambole, 2019, Udokpoh and Nnaji, 2023). Addressing the issue of sawdust waste is not only crucial for the reduction of CO_2 emissions but also aligns with the broader objective of combating global warming (Mwango and Kambole, 2019).

2.1.2 *The waste management hierarchy*

As outlined by Axil (2022), the waste management hierarchy functions as a structured framework that systematically addresses waste management while concurrently advancing environmental sustainability objectives. This hierarchy is underpinned by a conceptual framework designed to offer guidance and establish a hierarchical order for decision-making in waste management, applicable to both individual and organizational contexts (Axil, 2022, ZeroWasteNetwork, 2023). The hierarchy assigns the utmost priority to waste prevention, followed sequentially by reuse, recycling, recovery, and finally, disposal (Axil, 2022, ZeroWasteNetwork, 2023). Typically represented as a five-tier inverted pyramid, the visual depiction underscores the progressive nature of waste management strategies (Axil, 2022, ZeroWasteNetwork, 2023). According to Axil (2022) steps include:

Prevent – The top priority is placed on reducing or preventing waste. Can waste be avoided by not using the material in the first place?

Reduce – Is it possible to reduce the amount of materials utilized in the design and manufacturing phases?

Reuse – Is it feasible to repurpose materials in different sections of your production process or by another party?

Recycle – Is it possible to recycle the materials, either wholly or partially, to transform the waste into a new product?

Recover – When additional recycling is unfeasible or not an option, energy or materials could be reclaimed from waste through processes like anaerobic digestion or incineration.

Dispose – In cases of unsuccessful reuse, recycling, or energy recovery, materials that cannot undergo these processes will be disposed of through landfilling and incineration (without energy recovery). This represents an unsustainable approach to waste management, as landfill-bound waste can perpetuate adverse environmental effects.

The waste management hierarchy represents an evolution beyond the traditional “three Rs” approach (reduce, reuse, and recycle), expanding into a more comprehensive five-step process. This approach prioritizes actions at the top of the hierarchy, gradually moving to less preferred options at the bottom, as depicted in Figure 2-1 (Axil, 2022, ZeroWasteNetwork, 2023). This concept resonates strongly with the principles of "cradle to grave," where the overarching objective is to guide organizations in appraising the potential for waste stream recycling and reusability, with landfill disposal as the last resort. This paradigm shift aims to foster substantial changes towards a sustainable future (ZeroWasteNetwork, 2023).

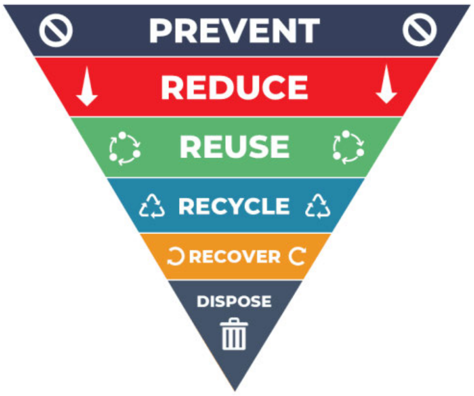


Figure 2-1: The five-step waste management hierarchy (Axil, 2022).

In pursuit of the ambitious goal of achieving zero waste in landfills by 2030, as outlined in South Africa, a comprehensive strategy has been employed. This strategy aims to divert 90% of waste away from landfills through a holistic approach that encompasses recycling, reuse, recovery, and beneficiation technologies (Mail&Guardian, 2021). This multifaceted strategy not only seeks to reduce environmental impact but also possesses the capacity to generate various environmental, social, and economic prospects for the population of South Africa. (Mail&Guardian, 2021). According to Mail&Guardian (2021), for the vision of a zero-waste and sustainable nation to materialize, a fundamental shift is necessary in managing waste at its source, ensuring it is harnessed efficiently, thereby heralding a paradigm shift in waste management practices.

The government of South Africa has taken proactive measures to redirect waste away from landfills, enacting new legislation and rolling out regulations to address the detrimental environmental and health ramifications of waste (Mail&Guardian, 2021). For example, the New Extended Producer Responsibility Act (EPR) is being implemented, mandating that companies assume responsibility for the packaging waste of their products post-sale (Mail&Guardian, 2021).

This approach fosters a proactive strategy where producers, from the outset of product development, institute measures to minimize, reuse, recycle, and recover resources, thereby promoting a mindset that avoids disposability, resilience, and long-term sustainability within the local waste sector (Mail&Guardian, 2021). By advocating for global standards and adopting a long-term perspective, South Africa's waste management industry can transition into a greener and more economically viable future.

2.1.3 *The future of the circular economy in South Africa*

Amidst the looming landfill crisis and the multifaceted challenges it entails, there is a discernible surge in initiatives aimed at mitigating the adverse and irreparable environmental, human health, and economic repercussions (DFFE, 2020, Mail&Guardian, 2021). One of these pivotal initiatives, continually evolving and gaining prominence, is the concept of a Circular Economy (CE) (Mail&Guardian, 2021, TheConversation, 2020). The concept of the "circular economy" model (Figure 2-2), is a relatively recent idea; nonetheless, as a transformative system, it presents substantial prospects for achieving more inclusive economic growth. This involves creating job opportunities and adopting environmentally friendly practices that are essential for sustainability in the country, as reported by (Mail&Guardian, 2021). This is accomplished by eliminating unnecessary waste materials, minimizing energy and raw material consumption, and facilitating the reintroduction of these materials, energy, and resources into the cycle (DFFE, 2020, Mail&Guardian, 2021). In essence, it embodies a design philosophy that is both restorative and regenerative, with the overarching goal of preserving products, components, and materials at their maximum utility and value throughout their lifecycle, thereby delineating the distinction between technical and biological cycles (DFFE, 2020). The foundational principles of the CE have, indeed, transcended national boundaries to become global agents of transformation, redirecting prevailing production and consumption patterns away from a linear economy that inexorably depletes resources toward a CE paradigm that renews resources, thus fostering sustainability over the medium to long term (DFFE, 2020).

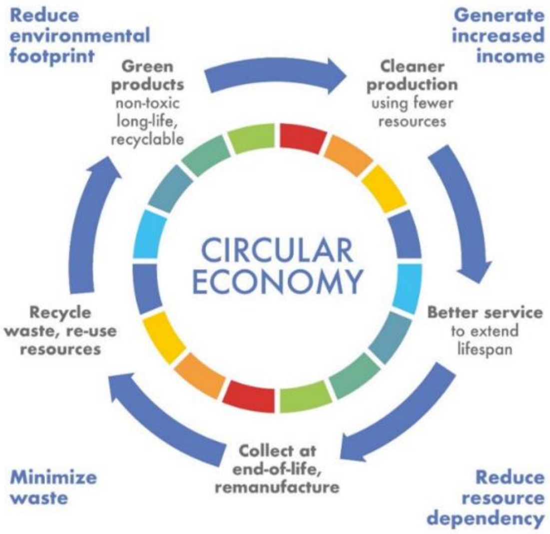


Figure 2-2: Waste minimization activities that occur within a circular economy (DFFE, 2020).

DFFE (2020) mentions that numerous developing nations have, to a notable extent, lagged in the integration and application of CE principles. The SA government has exhibited a keen awareness of the pivotal role that the CE plays in the cultivation of a sustainable, low-carbon, resource-efficient, and globally competitive economic landscape. Concretely, South Africa has embraced the CE as a cornerstone of its sustainable development strategy (GEM, 2021, Mandaha, 2021). Notably, scholarly perspectives endorse the prominence of government leadership in promoting the CE concept through the reformulation of existent legislative frameworks, the enactment of new regulatory measures, the advocacy for innovative environmental technologies, and the organization of public education endeavours designed to elucidate the inherent benefits of this paradigm (DFFE, 2020).

According to DFFE (2020) and Mandaha (2021), South Africa, especially disadvantaged communities, stands to gain substantial economic and environmental advantages by fostering the creation of green jobs within the framework of the circular economy. Opportunities for employment generation manifest in the strategic shift of waste management practices away from conventional landfill approaches and toward alternative waste treatment modalities situated within the comprehensive waste management hierarchy. These prospects materialize through the adoption of cleaner production techniques, industrial efficiency enhancements, measures encompassing disassembly, refurbishment, and reuse, as well as the advent of novel approaches to waste collection, sorting, reprocessing, and manufacturing (DFFE, 2020, Mandaha, 2021). In essence, the CE offers a viable pathway to realizing sustainable patterns of consumption and production. Figure 2-2 illustrates activities that are modelled on the principle of CE and that foster a CE.

DFFE (2020) explains that the positive effects of a CE extend beyond saving materials and leaving a smaller footprint on the environment. A profound transformation in the dynamics between producers and consumers, as well as products and their users, is engendered by novel service paradigms and business models (DFFE, 2020). This paradigm shift yields several advantages, according to DFFE (2020), including the conservation of raw materials, heightened innovation, the development of long-lasting products, the establishment of new avenues for employment, the optimization of resource utilization, and a concomitant reduction in carbon emissions. These multifaceted benefits are depicted in Figure 2-3.

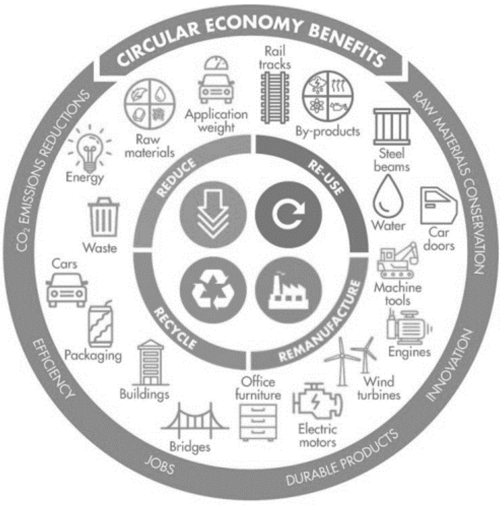


Figure 2-3: The benefits of a circular economy (DFFE, 2020).

A national-level attempt towards waste management and support of the circular economy relating to the forestry sector includes the forestry master plan. The development of the Forestry Sector Master Plan involved utilizing existing research and conducting extensive consultations with industry stakeholders, specialized entities, as well as relevant government departments and agencies (DTIC, 2020). The master plan is tailored to cater to various sub-sectors within the forestry value chain, with a focus on the primary sector: pulp and paper, sawn timber, board products, utility poles, and treated products (DTIC, 2020). Of noteworthy relevance to this study is a specific undertaking within the master plan involving the execution of a techno-economic benchmarking study, designed to pinpoint technological gaps prevailing in the South African sawmilling sector (DTIC, 2020).

The ultimate objective of this benchmarking study is to bolster the adoption of modern technologies in this sector. This initiative will be carried out in collaboration with the incentives provided by the Department of Trade, Industry, and Competition (DTIC) to upscale and modernise mills to be more efficient while elevating the value of their products. Diverting sawdust, a waste by-product from sawmills, steering it away from landfills, and directing it towards more profitable market segments and value chains, aligns with the objective of optimizing the utilization of sawdust and drives a positive momentum towards the CE model.

2.2 Overview of the Forestry, Timber, and Pulp and Paper (FTPP) industry in South Africa.

2.2.1 *The FTPP sectors' role and position in the South African economy*

Understanding the role of the FTPP sector in the SA economy forms the basis for why it is important to sustain the industry in the future by identifying new value chains, most especially from waste. The concept of “One man’s trash is another man’s treasure” has become a focal point amongst many industries to encourage the diversion of waste streams to value chains that generate revenue. The forestry industry plays a key role in the South African economy, making substantial contributions to both the overall GDP and the manufacturing GDP. The industry is estimated to contribute approximately 9.8% to the agricultural GDP, 4.9% to the manufacturing GDP, and 0.6% to the overall GDP (FSA, 2020a). The industry also generates an export value of approximately R29 billion (FSA, 2020a).

The forestry sector is typically categorized into two distinct groups: forestry and forestry products. The forestry segment encompasses the cultivation and management of forests, serving as a vital source of raw materials for various industries, including pulp and sawmills, construction, and industrial markets (DOT-KZN, 2020a). Notably, around 70% of the forestry land in South Africa is actively managed for production (FSA, 2020). In turn, the forestry products industry plays a pivotal role in transforming these raw materials into value-added products. Leveraging advanced technology and innovation, this sector has successfully penetrated a diverse range of markets, thereby enabling the forestry industry to cater to the needs of the automotive, pharmaceutical, chemical, cosmetic, textile, and food industries. These advancements have opened new avenues and brought forth exciting opportunities for the industry.

Despite being a multimillion-rand industry, the SA forestry sector encounters numerous challenges that pose significant threats to its long-term sustainability. Sithole (2017) highlighted several key challenges confronting the industry, including shortages of raw materials resulting from drought conditions, ageing machinery, underdeveloped infrastructure, restricted financial resources for progressing into value-added products through forward integration, unsustainable utilization of waste materials, skills shortages, and the need to keep pace with global technological advancements. Furthermore, a pervasive issue pertains to the low timber utilisation rates, which currently stand at approximately 47% within the South African context, significantly lower than the international recovery rates of over 60% (Sithole, 2017). This discrepancy implies that a staggering 53% of the available timber, which could have been utilized for value-added processes, is being wasted and remains unexploited.

Godsmark and Oberholzer (2018) showed that there is a discernible trend of diminishing demand for forestry and forestry products as the years progress. This decline may be presumed to stem from a reduced need for traditional wood products, particularly paper, which has witnessed a decrease in demand due to changing societal needs and advancements in technology. In today's era, the demand for paper has significantly diminished, reflecting the shift towards digital alternatives and paperless practices.

Furthermore, the diminishing demand for forestry products extends beyond paper. This decline can be attributed to multiple factors, including the emergence of competitive industries that offer alternative products as well as the growing awareness and emphasis on environmental sustainability. The call to reduce the environmental footprint has driven consumers and businesses to seek alternative materials and solutions, thereby further dampening the demand for certain forestry products such as timber, panels, lumber, and poles (Godsmark and Oberholzer, 2018).

Given the aforementioned circumstances, it becomes imperative for the forestry industry to strategically reposition itself for sustainable growth. This entails adopting measures that enable the extraction of greater value from the raw material while simultaneously minimizing waste and processing costs. By focusing on refining processes, the industry can optimize resource utilization, enhance efficiency, and mitigate any adverse environmental impacts associated with its operations.

Furthermore, diversification of the value chain is a key aspect that the forestry industry must embrace. By expanding beyond traditional wood products, such as paper and timber, and exploring new avenues for value creation, the industry can adapt to evolving market demands and seize opportunities in emerging sectors. This diversification allows for a more robust and resilient industry that is less susceptible to market fluctuations.

In addition to economic considerations, prioritizing environmental sustainability is paramount for the long-term viability of the forestry industry. Implementing environmentally friendly practices, such as responsible forest management, sustainable sourcing, and adopting technologies that minimize the industry's ecological footprint, will not only address current challenges but also contribute to the preservation of natural resources for future generations.

By undertaking these adaptations and proactive efforts, the forestry industry can effectively tackle the challenges it faces today while positioning itself as a driving force that sustains the industry for years to come. This forward-looking approach acknowledges the need for continual evolution and innovation, ensuring the industry remains resilient and relevant in the face of changing market dynamics and societal expectations.

2.2.2 *Different tree species planted in South Africa*

Understanding the availability of raw material resources is important in the context of ensuring the sustainability of the natural resources used in production methods and ensuring maximum utilisation of the resources that are currently processed. Approximately 1% of the total land area (1,27 million ha) is afforested in South Africa (DOT-KZN, 2020a). The three tree genera, namely Pine (52.2%), Eucalyptus (38.92%), and Wattle (8.3%) (DOT-KZN, 2020a).

The Eucalyptus species accounts for approximately 51.8% of the total hardwood area and is planted primarily to supply the pulpwood, mining, and timber industries; it is also used for chipping for export (DOT-KZN, 2020a). The species is planted on an 8-12-year rotation, highlighting the need to ensure that it is sourced sustainably (Godsmark and Oberholzer, 2018). Approximately 87.3% of hardwoods planted are used for pulpwood (Godsmark and Oberholzer, 2018). *Eucalyptus grandis* is the main hardwood (DOT-KZN, 2020a, Meadows, 1999). The species is sought after for its broad adaptability, remarkably rapid growth, favourable form, and outstanding wood and fibre characteristics (Rana et al., 2014).

Pinus patula and Pinus elliotti are predominant softwoods in SA (Meadows, 1999). Softwood consists mainly of pinewood species. About 69% of the softwoods are used for saw log production (DOT-KZN, 2020a) and 25% are used for pulpwood (Godsmark and Oberholzer, 2018). Mature pine is generally reserved for sawmilling because of the product's elevated value, approximately R500 000 per hectare (DOT-KZN, 2020a). Due to the scarcity of mature pine locally, the yearly increase in the importation of sawn timber tonnage is on the rise, and it is anticipated that South Africa will rely heavily on imports for the majority of its sawn timber in the next decade (DOT-KZN, 2020a).

It is evident that due to the large contribution of hardwood and softwood being processed, specifically the Eucalyptus and Pine species, for wood chipping and sawmilling, the dependency on these species will result in limited resources in the future. In addition, there is also evidence that, due to the large quantities being processed, a large quantity of wood waste, in the form of sawdust or pin chips, is expected to be generated.

2.2.3 *Significant industries in the FTPP sector and their consumption of wood*

To quantify the amount of wood waste or sawdust waste available for conversion and utilisation, a brief study of the industries and processes that generate the waste must be explored. The three most significant industries have been investigated:

2.2.3.1 Sawmilling process

A formal sawmill's average log intake ranges between 15 000 and 250 000 m^3 (DOT-KZN, 2020b). The sawmilling process relies on timber such as Pine, Eucalyptus, and limited amounts of other species and transforms the best parts into veneer. The straight sections become saw logs, while the offcuts get chipped, flaked, or turned into sawdust (FSA, 2020b).

The chips and flakes vary in size and are used to create several products across an array of industries, such as pulp and paper or dissolving pulp processes (FSA, 2020b). The estimated output of a sawmill ranges between 66 000 and 100 000 tons per annum of sawn timber (Snow, 2014). Eucalyptus timber and Wattle are exported in the form of wood chips (DOT-KZN, 2020a). An estimated 500 000 tons become available as chips to pulp and paper mills per annum (DWAF, 2004). A wood chipping mill facility located in Maydon Wharf Durban yields about 360 000 tons of air-dried hardwood chips per annum. Wood chips are stored in a shed with a capacity of 80 000 tons. The Eucalyptus wood chips are exported to pulp and paper manufacturers in Japan (DOT-KZN, 2020a). According to Stafford and Lange (2018), approximately 440 000 tons of sawdust waste is generated per annum from 218 sawmills in SA. According to Snow (2014), the sawmilling process yields approximately 47% lumber, 18% sawdust, 27% woodchips, and 8% bark. It is evident that sawdust equates to a large contribution. While wood chips are used for pulping for kraft paper production, the traditional disposal practices of sawdust, encompassing landfilling, incineration, and stockpiling, present substantial challenges (Mwango and Kambole, 2019, Udokpoh and Nnaji, 2023).

2.2.3.2 Pulp and paper

In pulp production, South Africa holds the 14th global position and is listed among the top 25 producers of paper and board products worldwide (DWAF, 2004). Mondi and Sappi are the sole entities that utilize virgin wood fibre to manufacture both pulp and subsequent paper and board products. Pulpwood production in SA equates to approximately 10.3 million tons per annum (DOT-KZN, 2020a).

Most of the hardwoods are used to produce pulp (Meadows, 1999). Wattle timber is used for the manufacture of pulp (2020a). The pulping process involves several steps in which several products can be produced, including by-products, with the aim of minimising waste. For example, during the pulping process, wood chips are commonly used as the raw material. Before the wood chips are subjected to a cooking process, the chips are screened to select suitable sizes since large chips hamper the cooking process (Dyunyasheva, 2017). The wood chips left behind go to waste. KZN is home to the largest pulp and paper mill in South Africa (2020a) but in addition, several other companies form the group of pulp and paper producers in South Africa.

Sappi and Mondi produce approximately 90% of the paper in South Africa. Mondi produces most mechanical pulp (286 000 tons) per annum at the Merebank mill, while Sappi Ngodwana mill produces approximately 100 000 tons per annum. Most of the pulp produced in the country is used for paper manufacture however, the chemical pulp is used in the cellulose industry to produce textile fibres, cellulose acetate film, and explosives.

2.2.3.3 Dissolving wood pulp (DWP)

Sappi is ranked as the world’s largest producer of its umbrella brand DWP, known as Verve (Sappi, 2019b). Sappi owns a 16% share of the global dissolving pulp market and produces approximately 1.4 million tons per annum of DWP (Sappi, 2019a). In this DWP process, wood chips are also used as the raw material and undergo a screening process, therefore resulting in pin chip wood waste, as with the kraft pulping processes.

While the quantification of the pin chips generated is difficult to determine, Sappi indicates that their wood waste (knots, sawdust, slivers, fines oversize, pallets, and other wood) accounts for 10.1% (Sappi, 2022). To understand approximately how much waste is generated from these processes, the SA Saicorr mill has been employing the sulphite process since 1955 to produce 780 000 tons of DWP annually, while the Ngodwana mill, also located in South Africa, has a DWP capacity of 250 000 tons per year through the Kraft process since 2013 (Sappi, 2020). One can conservatively assume that with a typical PHK or AS process yield of about 40-50% (Dyunyasheva, 2017), almost double the amount of wood is processed, and hence large quantities of wood waste are generated in the various forms mentioned which are pin chips (oversized fines) and sawdust. Both of the abovementioned sites utilise Eucalyptus hardwood fibre obtained from plantations located near the mills (Sappi, 2019a). Sappi Ngodwana uses 100% Eucalyptus hardwood, while Sappi Saicorr uses hardwood fibre (Eucalyptus and Acacia).

2.3 The chemistry of wood

The chemical composition of the raw material is identified as a decisive factor, and its attributes should be taken into account when choosing a suitable pulping process for the production of dissolving pulp (Chen et al., 2016, Jahan et al., 2008, Jardim et al., 2018, Liu et al., 2016, Shahzad, 2012). Through specific processing techniques, certain components of wood can be selectively extracted and utilized in the production of other materials like textiles and pharmaceuticals (Riki et al., 2019).

According to Woodford (2020), wood can be categorized into two primary types: hardwood and softwood. However, it should be noted that these terms do not always directly correlate with the actual hardness or softness of the wood. Hardwoods are derived from broad-leaved trees, also known as deciduous trees, which shed their leaves annually. They are often referred to as angiosperms because their seeds are enclosed within fruits or pods. Examples of hardwood species include ash, eucalypts, beech, birch, mahogany, maple, oak, teak, and walnut (Woodford, 2020). On the other hand, softwoods are typically obtained from evergreen trees, known as coniferous trees, which retain their needle-like leaves and cones throughout the year. They are also referred to as gymnosperms. Common softwood varieties include cedar, cypress, fir, pine, spruce, and redwood (Woodford, 2020). Both hardwood and softwood groups exhibit significant variations in their fibre structure and wood chemistry, leading to diverse properties of the pulp obtained through specific conversion processes (NumeraAnalytics, 2020).

According to SWST (2017), wood consists primarily of three fundamental elements: carbon, oxygen, and hydrogen. These elements combine to form intricate molecules, which then assemble into polymers. The polymers present in wood can be categorized into three main types: cellulose, hemicellulose, and lignin. In addition, the remainder consists of other components called extractives (Woodford, 2020). The relative proportions of these polymers vary across different wood species, and they provide the structural integrity of wood (SWST, 2017).

Petterson (1984) states that the chemical composition of wood cannot be accurately defined for a given tree species or tree. The chemical composition varies according to the parts of the tree (root, stem, or branch), type of wood (i.e., normal, tension, or compression), geographic location, climate, and soil conditions (Petterson, 1984). An accumulation of analytical data collected from various laboratories over several years provides a generalised reference for the chemical composition of wood.

According to Petterson (1984), there are two major chemical components in wood: lignin (18–35%) and carbohydrate (65–75%). Both are described as complex, polymeric materials. In addition, small amounts of extraneous materials, mostly in the form of organic extractives and inorganic minerals (ash), are also present in wood (usually 4–10%).

Gladyshko (2011) states that the chemical composition of wood exhibits quantitative variations across different tree species. However, it is possible to establish a general representation of wood's content. The overall chemical composition of wood is comprised of cellulose accounting for 38-50%, hemicelluloses, ranging from 23-32% and lignin ranging from 15-25%.

Similarly, SWST (2017) indicates that the chemical composition of wood comprises cellulose (about 40-50%), hemicellulose (20-35%) and lignin (15-35%). The majority of wood primarily comprises organic matter, constituting approximately 99% of its composition, while only around 1% is composed of mineral compounds (Gladyshko, 2011). The mineral compounds can be obtained by subjecting the wood to incineration in the oven at temperatures of 600-800 °C (Gladyshko, 2011). The carbohydrate component of wood (holocellulose) is composed of cellulose and hemicelluloses.

As can be noted from the various studies of wood composition, it is evident that the cellulose content in both hardwood and softwood is relatively similar, ranging from 40-45%. However, Gladyshko (2011) suggests that there are notable differences in hemicellulose composition in softwood and hardwood. Hemicelluloses of softwoods are mostly presented by hexosanes (hexatomic carbohydrates), while hemicelluloses of hardwoods are presented mostly by pentosans (pentatomic carbohydrates) (Gladyshko, 2011).

Generally, hardwoods possess a higher content of cellulose along with lower levels of lignin and extractives, compared to softwoods. Hardwoods also tend to possess a higher initial brightness. In terms of pulp, softwood fibres are, on average, more than three times the length of those contained in hardwoods (Gladyshko, 2011). Increasing fibre length typically results in enhanced inter-fibre bonding, and products produced from softwood pulps through the same process tend to exhibit greater strength compared to those made from hardwood pulps (Gladyshko, 2011).

Softwood species are also believed to contain more lignin and fewer hemicelluloses than hardwoods. The lignin content of hardwoods is approximately 20-25%, while the amount of lignin in softwoods is around 25-30% of the wood dry solids (Gladyshko, 2011). In temperate tree species, the extractive content is between 5 and 10%.

Ultimately, wood contains minute quantities of inorganic components that play a crucial role in the well-being of the tree. The amount of these minerals also varies according to the tree species and environment. There is a consensus among multiple authors regarding the overall chemical composition of wood polymers. However, notable distinctions exist in the chemical composition of specific substances found in hardwood and softwood. These substances exhibit unique characteristics and properties that vary depending on the wood type, which plays an eminent role in their processing steps and the quality of their end-user products.

2.3.1. *Cellulose*

Cellulose is the most abundant natural polymer worldwide and forms the primary structural component of a plant's cell wall (Gladyshko, 2011, SWST, 2017). Cellulose is a fibrous, white material composed of carbon, hydrogen, and oxygen. In its most basic chemical representation, it is expressed as $(C_6H_{10}O_5)n$, where 'n' denotes the number of cellulose units (Subrahmanyam et al., 2004).

Cellulose is produced through the process of photosynthesis. During photosynthesis, water and carbon dioxide combine to generate glucose and other sugars (SWST, 2017). Initially, glucose undergoes chemical changes to form glucose anhydride by removing a water molecule from each glucose unit (SWST, 2017). These glucose anhydride units subsequently polymerize to create long-chain cellulose molecules, which contain approximately 5 000-10 000 glucose units (SWST, 2017). The number of glucose units within a cellulose molecule is referred to as the degree of polymerization (DP), which exceeds 10 000 in native wood but is less than 1 000 for highly bleached kraft pulp (Riki et al., 2019).

The function of cellulose in wood is to provide strength. Hydrogen bonding among cellulose molecules contributes to the elevated strength of cellulose fibre, leading to enhanced fibre strength. The fundamental repeating unit of the cellulose polymer are glucose residues linked β (1→ 4) (Figure 2-4).

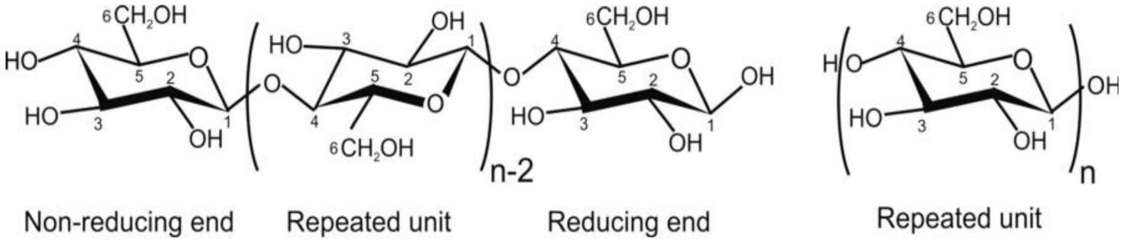


Figure 2-4: Structure of a cellulose polymer (French, 2017).

Cellulose exhibits insolubility in water and the majority of organic solvents (Gladyshko, 2011). However, cellulose can be degraded into glucose units by treatment with concentrated acid at high temperatures because it is composed of β-D-glucopyranose units (Gladyshko, 2011). The close association between cellulose and glucose is evident, as mild acid hydrolysis of cellulose results in its transformation into glucose with the addition of a single water molecule (Subrahmanyam et al., 2004).

As the primary component in papermaking, cellulose is anticipated to possess high quality, with its quality contingent on both the raw material and pulping methods (Riki et al., 2019). Cellulose exists in three forms, which vary based on the degree of polymerization (DP), namely, alpha-cellulose, beta-cellulose, and gamma-cellulose. Wood from softwoods and hardwoods contains about 65 to 75% cellulose of which α-cellulose accounts for 45% to 55%. Alpha (α) cellulose represents the most refined state of cellulose, exhibiting resistance to degradation and the ability to endure alkaline and acid treatments applied to wood in the fibre extraction process, known as pulping. This form is insoluble and can be separated from the solution, washed, and subsequently utilized in the production of paper or cellulosic polymers (Riki et al., 2019).

2.3.2. *Hemicelluloses*

Hemicelluloses are a group of compounds similar to cellulose but with a reduced molecular weight; specifically, they feature a shorter chain of polysaccharides (with a degree of polymerization typically ranging from 50 to 300) compared to cellulose (Riki et al., 2019, SWST, 2017). Hemicelluloses, characterized by a non-fibrous nature and an average DP of 150±30, become soluble in diluted caustic soda after wood hydrolysis, forming mannose, glucose, galactose, arabinose, and aldobiuronic acids. The content of hemicelluloses ranges from 10 to 30%, contingent on the source of the fibres, with the highest quantities typically found in agricultural residues, followed by hardwoods and then softwoods (Riki et al., 2019, Subrahmanyam et al., 2004).

Hemicelluloses originate from glucose and other sugars (including galactose, mannose, xylose, and arabinose) generated through photosynthesis. Consequently, hemicelluloses constitute a blend of assorted polymerized sugar molecules. While some of these polymers are straight-chained akin to cellulose, polymers featuring short side chains are also prevalent in certain instances (SWST, 2017).

Maintaining hemicellulose throughout the pulping process is crucial as it enhances pulp yield and adds to the bonding strength of fibres. Nevertheless, the presence of hemicellulose is undesirable in the production of dissolving grade pulps. Consequently, the quantity of hemicellulose is minimized in the raw material before pulping through a prehydrolysis stage (Subrahmanyam et al., 2004).

Hemicelluloses exhibit notable distinctions between hardwoods and softwoods, influenced by the composition and content of the wood cell walls. Typically, hardwoods feature a substantial percentage of xylose units and a greater number of acetyl groups compared to softwoods. In contrast, softwoods display a higher proportion of mannose units and an increased presence of galactose units (Gladyshko, 2011).

The arabinogalactan content is less than 1% in most softwood species (Gladyshko, 2011). Arabinogalactan is a carbohydrate comprised of arabinose and galactose monosaccharides. Due to its water-soluble nature, larch arabinogalactan can be extracted from untreated heartwood using hot water (Gladyshko, 2011). Another minor compound of softwoods is xyloglucan. Side branches consist of either single xylose units or units of galactose, arabinose, or fructose bonded to xylose in a (1→2) linkage (Gladyshko, 2011).

Xylan denotes the xylose-based hemicelluloses found in both softwoods and hardwoods. Hardwood species typically contain 15-30% xylan (Gladyshko, 2011). The content of glucomannan in hardwood typically falls within the range of 3 to 5%. The ratio between glucose and mannose varies among wood species, ranging from 1:2 to 1:1, respectively (Gladyshko, 2011).

2.3.3. *Lignin*

Lignin is characterized as a category of intricate, high molecular weight polymers with a variable structure (SWST, 2017). It is an amorphous, aromatic polymer serving as a binding agent, binding cells together. Lignin consolidates cellulose microfibrils and hemicellulose, securing them to each other (Gladyshko, 2011). Lignin is also present in cell walls to provide structural strength. Similar to cellulose and hemicellulose, lignin consists of carbon, oxygen, and hydrogen. However, their arrangement is distinct, leading them to be categorized differently, not as carbohydrates but as phenolics. The polymer is constructed based on the phenylpropane unit (SWST, 2017). The position of lignin within the lignocellulosic matrix can be seen in Figure 2-5.

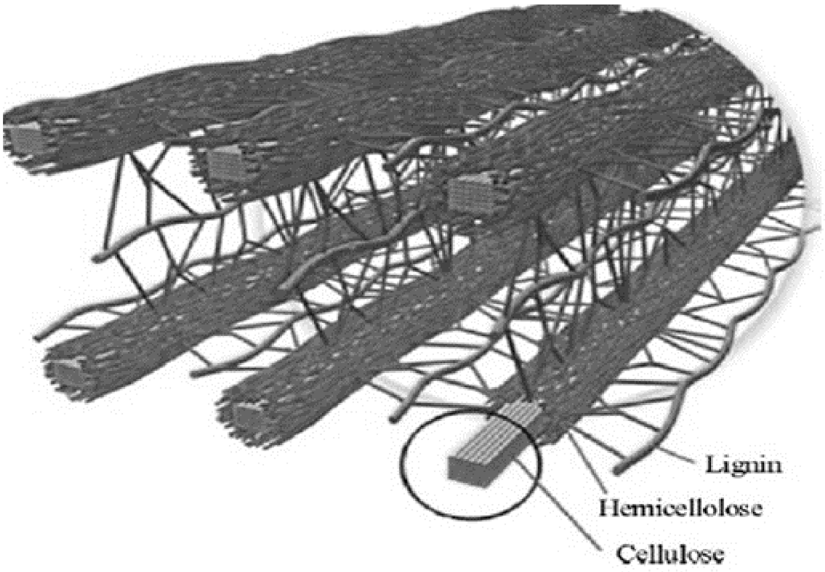


Figure 2-5: The position of lignin within the lignocellulosic matrix (Gladyshko, 2011).

Figure 2-5 illustrates how cellulose serves as reinforcing fibres, while lignin functions as the "glue" binding them together. This property makes it challenging to extract lignin in its original form without disrupting the entire matrix (Gladyshko, 2011). It is suggested that wood lignin has a DP of several thousand (Gladyshko, 2011).

Lignin is considered to have the most intricate structure among other wood compounds. However, the exact structure of native lignin remains uncertain (Gladyshko, 2011). According to Subrahmanyam et al. (2004), the lignin content ranges from 30% in softwoods, 22-27% in hardwoods, and 15-22% in agricultural residues. Various pulping processes aim to selectively remove lignin to facilitate the liberation of fibres (Subrahmanyam et al., 2004).

2.3.4. *Extractives*

In addition to the aforementioned compounds found in wood, there are several other chemical compounds present, constituting a relatively small proportion of the overall wood composition. However, in certain cases, these compounds can be more significant in quantity. Typically, these compounds do not form an integral part of the wood structure.

Extractives are an external plant component and constitute less than 10% of the dry weight of wood (Riki et al., 2019). Extractives are soluble compounds soluble in neutral solvents such as water, diethyl ester, toluene, methanol, ethanol, acetone, etc. (Gladyshko, 2011). The composition of extractives is contingent on the tree species and the environmental factors influencing it. Chemically, extractives are categorized into hydrocarbons (primarily terpenes), alcohols, aldehydes and ketones, acids, resin acids, carbohydrates, phenolic compounds, and nitrogen compounds.

Extractives are classified according to their separation methods, namely volatile oils and resins and water soluble compounds (Gladyshko, 2011). Generally, the amount of resin acids in the heartwood of hardwoods ranges from 0.2 to 0.8%, whereas it ranges from 2.4 to 4.8% in the heartwood of softwoods such as pine (Gladyshko, 2011). There are almost no resin acids present in hardwood (Gladyshko, 2011).

Water-soluble compounds can be extracted by cold or hot water. They consist of various phenol compounds (tannins, colouring compounds), carbohydrates, glycosides, and soluble salts (Gladyshko, 2011). Another group of extractives is polyphenols, which include tannins, flavones, kinos, and lignins. Other organic compounds include gums, tropolones, fats, fatty acids, and waxes.

Wood extractives contribute to wood properties such as colour, odour, and decay resistance (Gladyshko, 2011). Extractives may interfere with the pulping process, causing foaming and sometimes corrosion (Subrahmanyam et al., 2004). Elevated extractive content diminishes pulp yield, influences the brightness of unbleached pulp, and escalates the chemical requirement for pulping and bleaching agents. In general, the existence of extractives in woody materials amplifies the consumption of pulp reagents and diminishes yields. Consequently, materials with minimal or no extractive content are preferred for the reasons stated above (Riki et al., 2019).

2.3.5. *Inorganic compounds*

The inorganic component of lignocellulosic material is commonly known as ash content, denoting the residue that persists following the combustion of organic matter at a temperature of 525±25 ºC. (Riki et al., 2019). Thus, the presence of inorganic substances is indicated by the ash content of the fibrous raw materials (Subrahmanyam et al., 2004).

Some common elements found in wood include calcium, potassium, magnesium, manganese, and silicon (SWST, 2017). The inorganic content falls within the range of 0.5 to 1.0% for softwoods and hardwoods, respectively. Elevated inorganic content in the non-woody fibrous raw material is attributed to the presence of silica, which poses significant challenges, particularly in the chemical recovery process.

Elevated ash content is unfavourable in the processes of refining and recovering cooking liquor. For instance, a high silica content can complicate the retrieval of chemicals during pulping. Nitrogen present in the spent liquor may result in the production of NOx in the chemical recovery furnace, and potassium in the fibre can combine with chlorine to form KCl, causing corrosive effects on metal components in the furnace and boiler (Riki et al., 2019).

2.4 Dissolving pulp

Dissolving pulp of high purity is obtained from plant and wood fibres like wood, bagasse, sugar beet, corn stalk, and cotton. Wood remains a prevalent raw material for dissolving pulp production, as highlighted by Li (2016). Despite cotton's superior purity, its cost hinders widespread use (Kumar and Christopher, 2017).

Extensive research has been conducted to align dissolving pulp production with pulping mills' endeavours for technological innovations. These innovations aim to fractionate or convert lignocellulosic materials into various products and by-products in a cost-effective manner. The goal is to enhance the utilization of renewable feedstocks, avoiding waste accumulation (Lehto and Alen, 2014).

Chemical pulp processing primarily focuses on two areas: the removal of hemicelluloses and lignin. Hemicellulose removal often involves pre-treatment to target the lignin-hemicellulose matrix, improving cellulose accessibility. Lignin removal typically occurs during pulping or cooking processes (Trevorah and Othman, 2015).

The pre-treatment stage aims to disrupt the rigid crystalline structure of cellulose, increasing its structural accessibility and chemical reactivity (Ocwelwang, 2017). Lignin removal is crucial because lignin imparts an undesirable yellowish-brown colour to dissolving pulp. High brightness and cellulose purity are essential for producing cellulose-based products like viscose, cellulose acetate, and microcrystalline cellulose (MCC) (Bodhlyera et al., 2015). The waste liquor extracted, containing a higher concentration of impurities such as lignin and hemicelluloses, and at an elevated temperature, is directed to the chemical recovery station. This station aims to recover the organic or inorganic matter in the waste liquid through acid and alkali recovery processes.

2.4.1. *Dissolving wood pulp (DWP) market and production*

The DWP industry has shown promising growth in developing nations in recent years, with global distribution of production (Chen et al., 2019). According to MarketWatch (2023), the DWP market price stood at USD 5377 million in 2022 and is forecasted to reach USD 6721.1 million by 2029, with a CAGR of 3.2% during the forecast period 2023-2029.

China is one of the world’s largest producers, exporters, and consumers of DWP in the world (Globenewswire, 2020a). In hierarchical order, the United States and South Africa are among the largest producers of DWP, contributing to 48% of global production, as indicated by Globenewswire (2020a). The remaining 41% is distributed among other countries, including Brazil, Canada, Sweden, Finland, India, the Czech Republic, Japan, and Norway (Globenewswire, 2020a).

Globally, dissolving wood pulps are manufactured for various end-user applications, each with its distinct markets, as illustrated in Figure 2-6. The production of dissolving wood pulp involves diverse manufacturing processes, such as nitration, acetylation, xanthation (also known as the viscose process), and other methods used for creating a range of cellulose-based end-products (Christopher, 2017, Ocwelwang, 2017, Schwaiger, 2019).

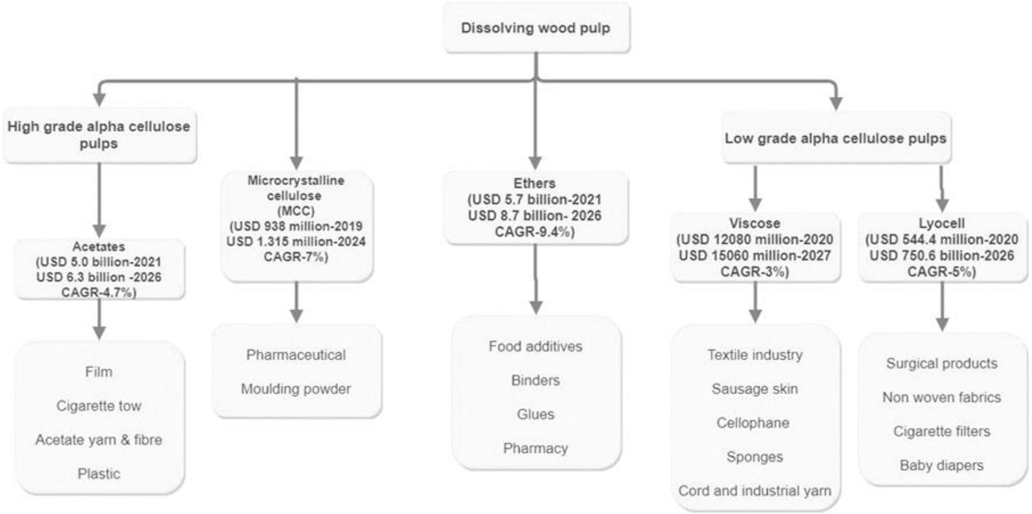


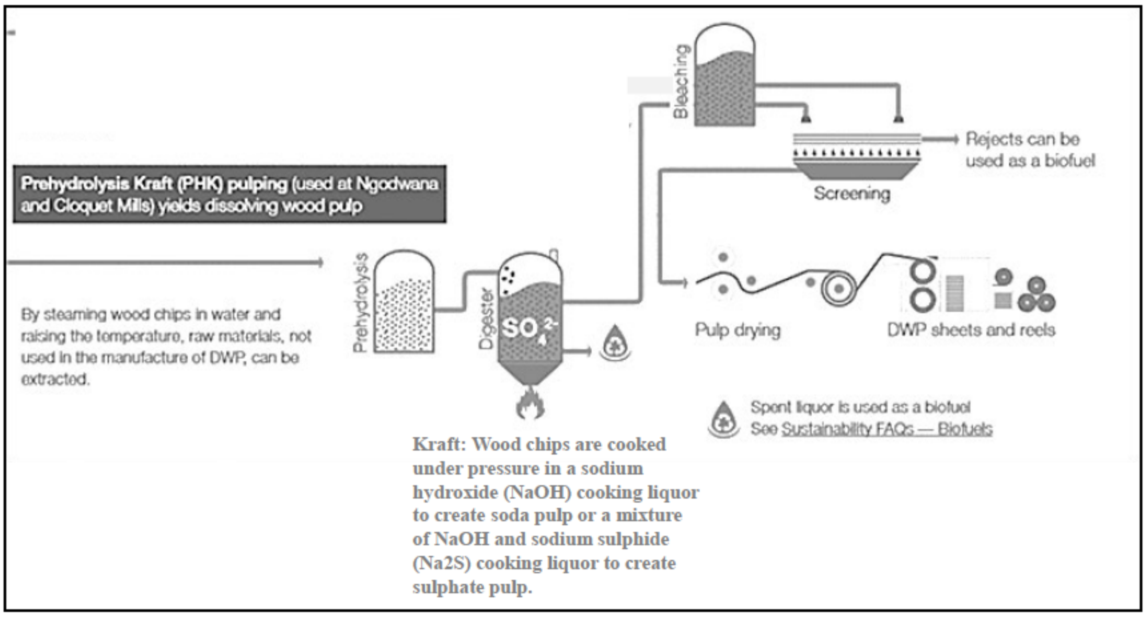
Figure 2-6: Flow chart showing the various applications of DWP-derived products, their current or projected markets and the compound annual growth rate (CAGR) (Balkissoon et al., 2022).

Dissolving wood pulp is produced by two conventional processes: the acid sulphite (AS) process and the prehydrolysis kraft (PHK) process (Astuy, 2016, Strunk, 2012, Yang et al., 2018). Distinct reaction mechanisms characterize each of these chemical pulping processes, yet they share a commonality in selectively removing lignin without significantly degrading carbohydrates. Additionally, they eliminate extractives and other chromophoric structures from residual lignin. The resulting DWP from both processes possesses varying qualities, influencing its suitability for different industries (Christoffersson, 2005, Jahan et al., 2008). The PHK process holds a dominant position, contributing to approximately 56% of the global production of DWP, while the AS process accounts for 42% (Chen et al., 2016). These two processes involve several steps that are time-consuming, complex, energy, water, and chemically intensive (Liu et al., 2016).

2.4.1.1 Prehydrolysis kraft pulp (PHK) process

According to Chen et al. (2016), the PHK process follows a combined process of acid (prehydrolysis) and alkali (Kraft cooking) conditions. The hemicelluloses are removed during the prehydrolysis stage, followed by Kraft cooking, and then a multi-stage bleaching process is applied to achieve high purity and high brightness in dissolving pulp.

In the prehydrolysis stage, a significant portion of the hemicelluloses and some of the lignin are eliminated from the wood chips through auto-hydrolysis induced by the production of acetic acid (Chen et al., 2016). The Kraft cooking stage further eliminates additional hemicelluloses and the majority of the remaining lignin, albeit with some cellulose dissolution. Subsequent bleaching stages are employed to eliminate the remaining lignin. Figure 2-7 shows the PHK process followed by the Sappi Ngodwana and Cloquet Mills.



Prehydrolysis Kraft (PHK) pulping (used at Ngodwana and Cloquet Mills) yields dissolving wood pulp

By steaming wood chips in water and raising the temperature, raw materials, not used in the manufacture of DWP, can be extracted.

Kraft: Wood chips are cooked under pressure in a sodium hydroxide (NaOH) cooking liquor to create soda pulp or a mixture of NaOH and sodium sulphide (Na2S) cooking liquor to create sulphate pulp.

Rejects can be used as a biofuel

Spent liquor is used as a biofuel
See Sustainability FAQs — Biofuels

Figure 2-7: Prehydrolysis Kraft (PHK) pulping (used at Ngodwana and Cloquet Mills) for DWP production (Sappi, 2019b).

According to Saska and Matsumara (2004), conventional Kraft pulps typically include carbohydrates, primarily pentosans, known to impact the cellulose-to-cellulose acetate conversion. To address this issue, the prehydrolysis step was introduced to decrease pentosan content while increasing the quantity of α-cellulose. In the prehydrolysis Kraft pulping process, wood chips undergo pre-treatment at temperatures ranging from 160 to 170°C for 1-3 hours with direct steaming. The steam causes organic acids, such as formic and acetic acids to be released, resulting in the selective hydrolysis of hemicelluloses into soluble sugars.

After this step, the wood chips are cooked with sodium hydroxide and sodium sulphide to produce pulps suitable for raw material production of viscose, cellulose acetate, and MCC (Saska and Matsumara, 2004). The pulp yield of the PHK process is approximately 5-7% lower on a dried wood basis compared to the standard Kraft pulping process. The total cycle cooking time is around 8 hours, encompassing 120 minutes of prehydrolysis at 170°C (maximum hydrolysis temperature) and 70 minutes at the maximum Kraft cooking temperature (160-170°C). The pulp then undergoes a bleaching process that can result in a pulp with an α-cellulose content of up to 95%.

Dyunyasheva (2017) relays that the prehydrolysis treatment step is adopted since alkaline sulphate cooking is unable to remove enough hemicellulose. Prehydrolysis can be carried out in two common ways:

- Acidic hydrolysis: Treatment with HCl or H_2SO_4.
- Auto-hydrolysis: Treatment with hot water.

Auto-hydrolysis is the most preferred method (Dyunyasheva, 2017). The yield from acid prehydrolysis is lower compared to auto-hydrolysis. Hence, the resultant yield of the unbleached pulp is also expected to be lower (Gladyshko, 2011). Acid hydrolysis can be broken down into concentrated and dilute acid hydrolysis. Both methods of prehydrolysis can obtain dissolving pulp of high quality, in terms of the content of a-cellulose and pentosanes. According to Dyunyasheva (2017), lengthening the duration and elevating the temperature of hydrolysis leads to a reduction in pulp yield and, to some degree, the degradation of α-cellulose. For these reasons, it is recommended that the technological process of cooking prehydrolysis cellulose be carefully selected to ensure that the conditions do not negatively impact the downstream cooking process. According to Gladyshko (2011), Prehydrolysis additionally facilitates the selective dissolution of carbohydrates, giving rise to valuable by-products like furfural, HMF, acetic acid, levulinic acid, and others (Gladyshko, 2011).

Following the completion of the prehydrolysis stage, the sulphate cooking process is initiated, wherein the primary constituents of the cooking liquor are NaOH and Na_2S (Dyunyasheva, 2017). This phase involves pressurized cooking of wood at temperatures ranging from 160 to 170 °C for 5-6 hours. The specific cooking conditions vary based on the composition of the raw material, mill facilities available and the composition of the cooking liquor and are determined by the intended use of the pulp. Throughout the cooking process, all wood components react with the cooking agents, leading to the release of a significant portion of lignin, some carbohydrates, and degradation products into the solution, forming waste (black) liquor which is recovered (Dyunyasheva, 2017).

It is recognized that cellulose with a high degree of polymerization (DP) is most suitable for production. Elevating the cooking temperature beyond 170 °C results in lignin dissolution but may lead to the breakdown of cellulose. An increase in alkali content causes a decrease in the intrinsic viscosity and consequently negatively impacts the DP of the pulp (Dyunyasheva, 2017). An increase in sulphidity slightly increases yield and significantly raises intrinsic viscosity. Prolonged cooking time reduces pentosan content, enhancing the filterability of pulp solutions. However, this also results in decreased pulp yield and intrinsic viscosity (Dyunyasheva, 2017). Table 2-1 outlines the composition of prehydrolysis sulphate pulp after refining and bleaching, with the quality of the pulp being influenced by the quality and composition of wood chips utilized in the cooking process.

Table 2-1: Prehydrolysed sulphate pulp composition (Dyunyasheva, 2017).

Measurement	**Composition (%)**
α-cellulose	94.5-96.9
Pentosanes	2-2.5
Resin	0.01-0.06
Ash	0.02-0.06

2.4.1.2 Acid-Sulphite process

The acid sulphite process is ammonia-based. During the process, hemicelluloses, lignin, and other minor components are removed from wood chips and then dissolved in a spent sulphur liquor (SSL) which can then be converted into value-added products such as lignosulfonates, vanillin, xylitol, and ethanol (Chen et al., 2016). The brown stock fraction, after several purifying steps such as hot alkali extraction or bleaching steps, is converted into dissolving pulp. Figure 2-8 shows the sulphite pulping process followed at the Sappi Saiccor Mill.

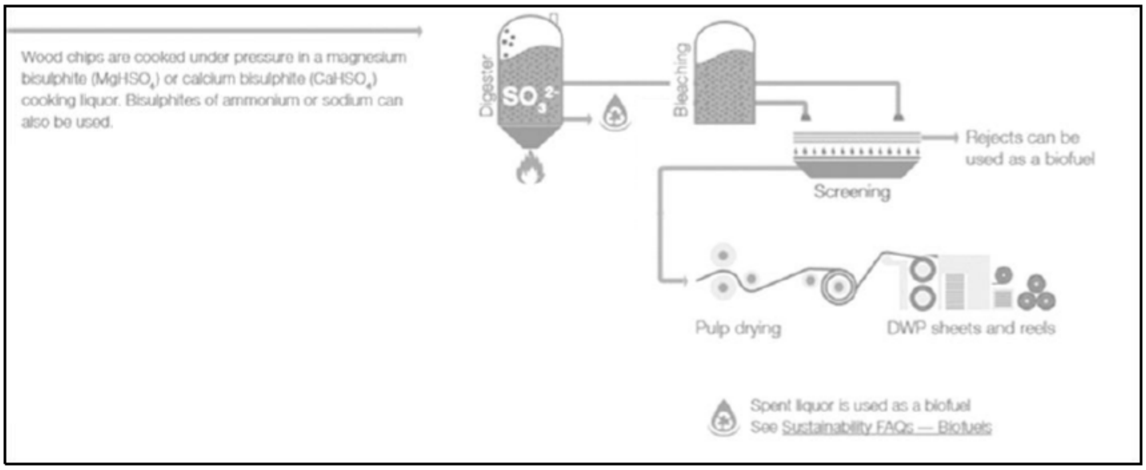


Figure 2-8: Sulphite pulping process (used at Saiccor Mill) to produce DWP (Sappi, 2019b).

According to Saska and Matsumara (2004), the acid sulphite cooking process involves the combustion of sulphur to generate SO_2 gas within a cationic base solution. Subsequently, wood chips are cooked in this liquor, comprising sulphurous acid ("free SO_2") and alkaline base sulphite ("combined SO_2"). To prevent pulp discolouration, cationic base chemicals such as calcium, magnesium, sodium, and ammonium are utilized, with the selection based on cooking conditions, resulting pulp yield, and quality considerations.

The composition of the cooking liquor ranges from 5-10% in total SO_2, 3-6% in combined SO_2, and 0-15% in free SO_2 (Saska and Matsumara, 2004). The recommended liquor-to-wood ratio falls between 3.5 and 6.1. Wood chips are cooked under pressure at 130-150°C, at 75-125 psi for 4-8 hours. This prevents undesirable lignin polycondensation and ensures the desired pulp yield, intrinsic viscosity, and 10% NaOH solubility of the resultant pulp (Saska and Matsumara, 2004). Elevated temperatures, increased acidity, and extended cooking durations enhance hemicellulose removal, resulting in higher cellulose purity (Saska and Matsumara, 2004).

Dyunyasheva (2017) suggests pressure cooking at 135-150°C for 4-12 hours with cooking solutions maintaining a pH of 1.5-2.5. When employing this method, pulp refining is recommended to eliminate lignin, hemicellulose, and ash while altering the chemical and physical properties of the cellulose. The refined pulp's composition is detailed in Table 2-2.

Table 2-2: Pulp composition after the sulphite cooking (Dyunyasheva, 2017).

Measurement	Composition (%)
α- cellulose	95-98%
lignin	0.15-0.25
pentosanes	1.8-4.0
resin	0.07-0.14
ash	0.06-0.13

The sulphite pulping process exhibits sensitivity to wood species (Shahzad, 2012). In acid sulphite pulping, wood species with low extractive contents are preferred, as acid sulphite cooking has limited efficacy in dissolving extractives (Shahzad, 2012). Phenolic compounds in lignin pose challenges during sulphite cooking, as their condensation can easily occur at low pH or low concentrations of SO_2. Shahzad (2012) suggests acid conditions in the sulphite process promote the cleavage of glycosidic bonds in cellulose and hemicelluloses due to lower DP and amorphous state. Weaker glycosidic bonds and hemicelluloses are depolymerized more readily than cellulose, dissolving as mono sugars in the cooking liquor.

Cellulose chains are affected by acid hydrolysis during the cooking process, with significant depolymerization occurring towards the end of delignification. Temperature is a crucial parameter, in determining the rate of delignification in the sulphite process. Elevated temperatures increase pH, reduce SO_2 solubility, enhance lignin dissolution, and aid in carbohydrate decomposition (Shahzad, 2012).

In acid sulphite cooking, hydrolytic carbohydrate reactions take place, involving both cellulose and hemicelluloses. However, cellulose's participation in these reactions is minimal due to its low accessibility. Conversely, hemicellulose dissolution through hydrolysis is considerably low (Shahzad, 2012).

When acid sulphite pulping is employed for dissolving pulp production, the cooking temperature is typically set at 140-150 ºC, promoting significant hemicellulose dissolution, which is advantageous as dissolving pulp should ideally have low hemicellulose content (Shahzad, 2012).

As the kappa number decreases in the sulphite pulping process, the yield also decreases, resulting in a higher cellulose content due to the removal of more hemicellulose (Shahzad, 2012). When acid sulphite pulping is employed for dissolving pulp production, the cooking temperature is typically set at 140-150 ºC, promoting significant hemicellulose dissolution, which is advantageous as dissolving pulp should ideally have low hemicellulose content (Shahzad, 2012).

Both traditional sulphite and Kraft processes are intricate, involving high temperatures over extended durations to achieve the desired product. Additionally, each process is reliant on specific wood types for efficient operation. In parallel with these conventional methods, various initiatives have been explored for alternative approaches to DWP production, as extensively discussed by Balkissoon et al. (2022).

2.4.2. *DWP and its properties*

Sappi (2019) defines DWP as a refined cellulose pulp suitable for subsequent chemical conversion into a variety of products. DWP, often referred to as high-grade cellulose pulp, earns its name due to its low content of hemicelluloses, lignin, and extractives. It is a chemically refined bleached pulp recognized for possessing distinct characteristics, including a high α-cellulose content (> 90%), elevated brightness, low hemicellulose content (3-6%), trace lignin and impurity levels (<0.05%), and a narrow distribution of degree of polymerization (Chen et al., 2016). According to Sappi (2019b), adjusting pulp purity is a common practice, and the removal of lignin and hemicellulose is crucial for achieving high-purity DWP (91–98% cellulose).

According to Shahzad (2012) and Kumar and Christopher (2017), the quality of DWP is influenced by both the properties of the raw wood material and the pulping process. Consequently, different DWPs exhibit varying chemical and physical properties, such as distinct types and quantities of hemicelluloses, based on the wood type or process used, leading to variations in quality for final use (PharmaExcipients, 2023). Shahzad (2012) highlights the importance of cellulose and hemicellulose chemistry in optimizing high-purity dissolving pulp production, given their differing reactivity with chemicals.

Both softwoods and hardwoods can be used for DWP production. Both Saiccor and Ngodwana Mills use Eucalyptus (hardwood) woodfibre sourced from responsibly managed plantations in close proximity to the mills. Cloquet Mill uses mixed northern hardwoods: aspen (approximately 65%) and maple (35%)

(Sappi, 2019b). The morphological differences between these wood types, discussed in section 2.3, are crucial, impacting the appearance of fibres in their natural state and their alteration during the pulping process. Fibre properties and morphology, such as length, length distribution, roughness, and shape, significantly influence the physical properties of cellulose derivative products (Shahzad, 2012).

According to Jesus et al. (2013), high-quality dissolving pulps should meet criteria such as a high α-cellulose content (≥ 91%), Kappa number less than 1, intrinsic viscosity (450-550 ml/g), low hemicelluloses and extractives content, and high reactivity (> 60%). Different properties take precedence for different end-user products. For viscose-grade pulps, typical specifications include a hemicellulose content of 5 wt%, lignin content of 0.3 (expressed as kappa number), and extractives content of 0.2 wt% (Métais and Germer, 2019). Rayon grade dissolving pulp typically has an α-cellulose content between 92-94% for the AS process and 94-96% for the PHK process (Chen et al., 2016), attributed to the different chemistry in the pulping processes (Chen et al., 2016). Traditionally, very high-purity dissolving pulp (with a low hemicellulose content (<2.0%) and a high R-10 (up to 98%)) is used as the starting material for MCC (Mattheson et al., 2002).

In the manufacturing of dissolving pulp, the controlled variable is the Degree of Polymerization (DP), determined by measuring intrinsic viscosity. Specifications for higher-grade dissolving pulps specific to end-user applications include ethers (viscosity 470–600 ml/g), nitrates (viscosity 550–650 ml/g), acetates (viscosity 600–700 ml/g), and viscose (viscosity 300–500 ml/g) (Wennerstroom and Bylund, 2017). Very low viscosity can lead to gel-like swelling of the viscose solution, causing filtration difficulties and negatively affecting cellulose fibre strength. Conversely, very high viscosity can result in inhomogeneity for mercerization and xanthation reactions. However, a very high viscosity can cause inhomogeneity for mercerization and xanthation reactions. In contrast to the DWP viscosity requirements for producing viscose, manufacturers of MCC under the brands Avicel, Microcel, Librawcel, Vivapur, and RanQ recommend a DP<400 which is equivalent to a low viscosity of approximately 148 ml/g, hence it should be possible to reduce the DWP DP to the desired MCC DP.

According to Chen et al. (2016), the PHK process is noted for its effectiveness in reducing the molecular weight of cellulose, whereas the AS process is considered less effective in achieving this outcome. In AS pulps, some of the low molecular weight cellulose tends to dissolve during the determination of α-cellulose content, contributing to the observed lower α-cellulose content in AS pulps. To ensure accurate measurement of dissolving pulp purity, it is recommended to employ sugar analysis methods, such as Ion Chromatographic (IC) methods, to precisely determine the cellulose and hemicellulose compositions.

The attainment of a uniform molecular weight distribution (MWD) in DWP is also deemed advantageous for facilitating homogeneous reactions, such as mercerization and xanthation reactions, during the viscose process (Chen et al., 2016). Typically, AS pulp exhibits a broader MWD compared to PHK pulp, attributed to the distinct chemistries involved in their pulping processes (Chen et al., 2016). The broader MWD of AS pulp aligns well with the presence of short-chain cellulose and higher alkali solubility, even at comparable viscosity levels (Chen et al., 2016). The variation in MWD between AS and PHK pulps is linked to the cooking conditions. However, a broader MWD, as seen in AS pulp, is considered undesirable for rayon processing due to its impact on processability and property variations, given that both high and low molecular weight fractions are deemed unfavourable (Chen et al., 2016).

Another important property of DWP is the brightness. According to Sixta (2017), brightness should be greater than 85% for most end-user applications such as viscose, cellulose acetates, and cellulose ethers. For MCC, the brightness levels are not explicitly specified but the product is expected to resemble an almost white or white powder which requires a high brightness, especially for pharmaceutical applications (Valchev et al., 2020).

An overview of the typical characteristics of dissolving pulp and the particular properties essential for the most prevalent applications of DWP is summarized in Table 2-3 (Sixta, 2017). Different and specific pulping characteristics are targeted for the different applications and the characteristics can be used as a basis for the targeted end-user application.

Table 2-3 Dissolving pulp standard specifications for end-user applications (Sixta, 2017).

	Viscose grade pulp	**Cellulose acetate**	**High viscosity ethers**
Intrinsic viscosity (ml/g)	450-500	650-900	>1500
DP<100 (wt%)	3-6	<2	0
Alkali resistance R18 (wt%)	94-97	98-99	~95
Alkali resistance R10 (wt%)	89-92	94-98	~94
Hemicellulose (xylan+ man) (wt%)	3-5	1-2	4-6
Acetone extractives (wt%)	0.2	0.05	0.1
Lignin (Kappa number)	<0.3	<0.2	<0.5
Total ash (wt%)	0.1	<0.08	<0.2
Mn (ppm)	<0.5	<0.5	0.5
Fe (ppm)	<5	<3	<5
Ca (ppm)	<20	<15	<50
Si (ppm)	<20	<10	<15
Brightness (%ISO)	89-93	<92	>85
Density (g/cm^3)	~0.9	<0.6	~0.8

2.4.3. *Cellulose protectors*

Cellulose protectors (CPs) are generally introduced to suppress cellulose degradation during ozone bleaching (Jablonský et al., 2006). Several cellulose protectors can be used and are selected based on suitability to the process as well as based on the effect it has on pulp characteristics. Table 2-4 outlines some of the CPs commonly used.

Table 2-4: Summary of cellulose protectors and their effects on pulp characteristics.

Cellulose protector	Advantages	Recommended dosages	References
Methanol before bleaching	Positive effect on viscosity, kappa number & brightness	80-90% on pulp	Jablonský et al. (2004)
Ethanol before bleaching	Not stated	Not stated	Jablonský et al. (2004)
Isopropanol	Not stated	Not stated	Jablonský et al. (2004)
n-butyric acid	Not stated	Not stated	Jablonský et al. (2004)
i-butyric acid	Not stated	Not stated	Jablonský et al. (2004)
i-valeric acid	Positive effect on viscosity, kappa number & brightness	Not stated	Jablonský et al. (2004)
oxalic acid	Positive effect on viscosity, positive and negative effect on kappa number & positive effect on brightness. enhances both the DP and the viscosity of pulp, while preserving favourable mechanical and optical characteristics. The use of oxalic acid in the pre-treatment process yields valuable pulp properties at higher rates. Additionally, the oxalic acid pre-treatment leads to a reduction in screen loss.	1.5% v/v, 10 mins @ 130 ℃ as a prehydrolysis treatment	Jablonský et al. (2004), Üner et al. (2016)
Sulfamic acid	Positive effect on viscosity, kappa number & brightness	Not stated	Jablonský et al. (2004)
Citric acid	Not stated	Not stated	Jablonský et al. (2004)
$MgSO_4$	Has a significant impact on slowing down the cleavage rate of the cellulose chain, and this effect is notably more pronounced than that of phenol.	10 wt%	Chen and Lucia (2003)
Phenol	Sole usage does not bring about a substantial enhancement in the selectivity of the process. In contrast, $MgSO_4$ alone effectively reduces the cleavage rate of the cellulose chain and enhances selectivity. The combination of $MgSO_4$ and phenol further amplifies selectivity, reaching even	10 wt%	Chen and Lucia (2003)

Cellulose protector	Advantages	Recommended dosages	References
	higher levels.		
D-mannitol	Used in ozone bleaching. Decreases the number of chain scissions by 53%. Increased brightness. Slight improvement in the kappa number.	1% on o.d pulp	Jablonský et al. (2006)

2.5 Bleaching chemistry

The primary objective of the bleaching process is to enhance the brightness of pulp and regulate pulps' intrinsic viscosity across various stages (Bajpai, 2010, Magina, 2005, Potgieter, 2018). Bleaching is a multi-step process that refines and brightens pulp by targeting lignin and impurity removal (Dladla, 2018). The bleaching sequence and number of stages are mostly dependent on the requirement of brightness levels. The fundamental purpose of this process involves the dissolution of residual, brown-coloured lignin, which persists after the pulping (cooking) phase, while simultaneously preserving the structural integrity of the pulp fibres. This is achieved through the utilization of oxidative chemicals such as chlorine dioxide (designated D stage), oxygen (O), ozone (Z), sodium hypochlorite (H), and hydrogen peroxide (P) (Potgieter, 2018).

The effectiveness of the bleaching process is influenced by various factors, including pH, temperature, retention time, consistency, nature of the pulp, and the method of chemical application. The choice of an appropriate bleaching sequence is contingent upon investment costs, operating costs, pulp quality, environmental waste discharge, and health and safety considerations (Potgieter, 2018). For the production of high-purity pulp, Potgieter (2018) suggests the need for multiple stages to eliminate extractives and hemicellulose while preserving the intrinsic viscosity of the pulp. Tailoring the order, concentration, and reaction time of bleaching agents allow for the production of customized pulp.

Chlorine dioxide bleaching, a well-established technology, is widely adopted in the pulp industry today (Magina, 2005, Potgieter, 2018). Common bleaching stages encompass the oxygen stage (O2), chlorination stage (D1), extraction stage (E or EP), second chlorination stage (D2), hydrogen peroxide stage (P), and the hypochlorite stage (H) (Dladla, 2018). Each stage is characterized by its specific bleaching agent, pH, temperature, and duration. Following each stage, the pulp undergoes a washing process to remove residual bleaching chemicals and dissolved lignin before progressing to the next stage (Potgieter, 2018).

After the final stage, the pulp is concentrated, conveyed to the storage tower, diluted, and then subjected to screens and cleaners to eliminate contaminants. Subsequently, it is directed to pulp machines for sheet formation (Potgieter, 2018). Chemical analysis, including lignin content determination and brightness assessment, serves as indicators of whiteness and facilitates the evaluation of bleaching process outcomes (Bajpai, 2010, Magina, 2005). The kappa number analysis is employed in mills to control delignification during pulping and calculate the chemical requirements for bleaching (Magina, 2005).

During the bleaching process, certain chemicals are lost in side reactions and chemical consumption is influenced by constituents associated with extractives, such as resins in pulp fines. The resins and other extractives can react with bleaching chemicals such as chlorine, chlorine dioxide, or hydrogen peroxide. These reactions can lead to the formation of undesirable byproducts or consume bleaching chemicals, reducing their effectiveness. For example, resin acids can react with chlorine to form chlorinated organic compounds, which may increase chemical usage and result in reduced bleaching efficiency. Consequently, the bleaching process incurs substantial costs (Potgieter, 2018). The chemicals and their respective stages used during bleaching and their purpose are summarized in Table 2-5.

Table 2-5: Typical chemicals used in different pulp bleaching stages and their functions (Chunilall, 2009, NCASI, 2013, Potgieter, 2018)

Bleaching chemical used	**Bleaching stage abbreviation**	**Role of chemicals in the bleaching stage**
Chlorine Dioxide (ClO_2)	D	Specialized bleaching agent that selectively removes lignin, resulting in the brightening of pulp.
Sodium Hydroxide (NaOH)	E	Eliminates chlorinated and oxidized lignin by-products from the pulp following the D stage. Can be EP stage where it is reinforced with Hydrogen peroxide.
Sodium Hypochlorite (NaOCl)	H	Reacts with both lignin and cellulose. Its effectiveness is significantly influenced by the pH value. Under a pH < 8, it reacts with cellulose, leading to fibre degradation. The chemical consumption rate is also influenced by temperature.
Hydrogen Peroxide (H_2O_2)	P	Enhances the brightness of pulps during the final stages of the bleaching process. Also applied in the E stage and frequently employed at the end of a bleaching sequence to forestall the reversion of pulp brightness.
Ozone (O_3)	Z	Efficient delignifying agent that enhances the brightness of pulp. It functions as an exceptionally potent oxidizing agent.
Oxygen (O_2)	O	Eliminates lignin and alters other colouring components. Can also be applied during the alkaline extraction stage, in conjunction with hydrogen peroxide, specifically in the EOP stage.

Bleaching chemical used	Bleaching stage abbreviation	Role of chemicals in the bleaching stage
EDTA or DPTA (Chelating Agents)	Q	Removal of heavy metals in the pulp.
Sodium hydrosulphite ($Na_2S_2O_4$)	Y	Bleaching through reduction is particularly effective for recycled fibres.

The selection of chemicals and associated stages is significantly influenced by the characteristics of the unbleached pulp and the desired properties of the final product for its intended use. A typical bleaching sequence comprises multiple stages, each utilizing different chemicals, working in concert to accomplish the ultimate bleaching objectives. In the context of DWP, a common example involves a five-stage bleaching process. Nebamoh (2012) outlines the sequence as the oxygen stage (O2), followed by the chlorination stage (D0), extraction stage (E or EP), the second chlorination stage (D1), and finally, the hypochlorite stage (H). The shorthand notation of this bleaching sequence is commonly referred to as the OD0ED1H bleaching sequence. Other examples of typical bleaching sequences used in the production of DWP include (D0ED1H) or (D0ED1P) depending on the desired end product i.e., 91α, 92α or 96α dissolving pulp (Christoffersson, 2005).

2.6 Microcrystalline cellulose (MCC)

MCC is a high-purity form of cellulose produced from an α-cellulose precursor that has undergone partial depolymerization (Rasheed et al, 2020). It is chemically inert, odourless, tasteless, and is typically a white crystalline compound offering multiple applications in the food, pharmaceutical, cosmetics, personal care, paints, and coatings sectors (Pulidindi and Pandey, 2019, Globenewswire, 2020, Rasheed et al, 2020, Sundarraj and Ranganathan, 2018, Vila et al, 2014). The product was initially discovered in 1955 by Battista and Smith, commercialized under the branded name Avicel, and processed using acid hydrolysis of purified wood celluloses (Sundarraj and Ranganathan, 2018, Kopesky et al, 2003). MCC is produced from high-purity dissolving pulp. As discussed earlier, growing demands for DWP and the challenges and limitations encountered around producing low-cost MCC remain.

MCC is a versatile product that possesses desirable traits such as non-toxicity, biodegradability, biocompatibility, high mechanical strength, and a large surface area. (Rasheed et al, 2020). The wood-based MCC market is the largest share of the market and is commonly used in the manufacture of food products and vitamin tablets and supplements in the pharmaceutical industry. Nevertheless, its growth may be hindered in the future due to concerns about deforestation and the need to discover alternative sources of raw materials. (Pulidindi and Pandey, 2019, Kharismi and Suryadi, 2018). MCC exhibits distinctive properties such as high surface area, high durability, low density, and low thermal expansion.

According to Chaerunisaa et al. (2019), MCC is a purified, partially depolymerized cellulose with the chemical formula $(C_6H_{10}O_5)$ n. Its preparation involves treating α-cellulose with mineral acids (type Ib). This polysaccharide polymer, MCC, comprises of several hundred β(1→ 4) linked D-glucose units, forming linear chains of β-1,4-danhydroglucopyranosyl units.

For pharmaceutical-grade MCC, a high-quality pulp is essential, and wood serves as the most common source. Both softwoods and hardwoods can be employed. These woods exhibit differences not only in chemical composition but also in structural organization, specifically in regions that are relatively more crystalline or amorphous. Amorphous regions are more susceptible to acid hydrolysis, resulting in shorter and more crystalline fragments (Chaerunisaa et al., 2019).

MCC derived from various sources varies significantly in chemical composition, structural organization, and physicochemical properties, including crystallinity, moisture content, surface area and porous structure, and molecular weight, among others (Chaerunisaa et al., 2019). The heightened demand for pharmaceutical-grade MCC has prompted the exploration of locally available and naturally occurring materials for MCC production.

2.6.1 *MCC global markets and trends*

In 2023, the MCC global market had a value of approximately US$1.2 Billion (ResearchandMarkets, 2024). It is anticipated that the market will increase US$2.1 Billion by 2030, growing at a compound annual growth rate (CAGR) of 7% between 2023 and 2030 (Globenewswire, 2020b, ResearchandMarkets, 2024, Sundarraj and Ranganathan, 2018).

The expansion of pharmaceutical applications has also facilitated a rise in MCC demands due to its widespread use in the form of an inactive ingredient, used as a filler in medications. The MCC market share is predicted to augment due to the growing demand for paints and coatings in the Middle East and Asia Pacific (Pulidindi and Pandey, 2019). The expansion of the pharmaceutical industry in France and Germany, accompanied by potential drivers for the increasing interest in bio-based products among consumers has sparked European MCC demands (Sundarraj and Ranganathan, 2018). The market is highly competitive and fragmented due to the presence of several strong players, and also several smaller players (Globenewswire, 2020b). It is evident that China and the US lead in global markets for MCC but with reduced costs and increased availability of raw materials, regulations, and lack of skilled labour, a shift of production bases to Asia Pacific, Japan, India, and Vietnam is being observed (Sundarraj and Ranganathan, 2018).

The MCC market growth distribution is steered by the pharmaceutical, food manufacturing, cosmetics, and personal care, as well as the paint and coating industries respectively (Figure 2-9). The pharmaceutical applications are experiencing a high growth rate. Figure 2-10 demonstrates that MCC serves multiple purposes in pharmaceutical manufacturing, functioning as a filler, binder, disintegrant, suspending agent, lubricant, and glidant (Globenewswire, 2020b). MCC is a crucial component in various oral dosage forms, such as pellets, capsules, tablets, sachets, suspensions, and emulsions in the pharmaceutical industry (Globenewswire, 2020b).

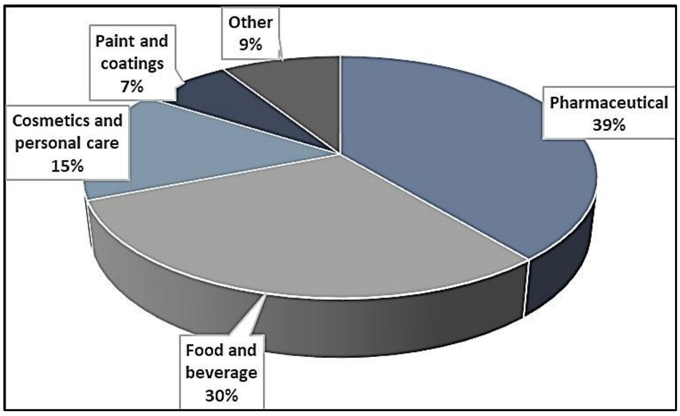


Figure 2-9: Distribution of MCC usage by key industries (Futuremarketinsights, 2022).

Several uses exist for MCC in the food sector (Figure 2-10), where it is used as a texturizer to enhance the texture of food items or even as a fat substitute. The product's adoption is expected to increase due to growing populations, rising obesity rates, and changing consumer attitudes toward healthier food options.

Microcrystalline cellulose is widely used in products designed for maintaining healthy skin, hair, and teeth. to improve their efficacy and quality (Figure 2-10).The increasing demand for cosmetic products in the Middle East and Africa, driven by factors such as affordability and expanding medical industries, is projected to fuel MCC demands in these regions (Sundarraj and Ranganathan, 2018).

The MCC market is expected to witness substantial expansion in the personal care sector, driven by improving consumer lifestyles worldwide. Microcrystalline cellulose is employed in several areas, including rough materials used for cleaning, compounds that stabilize emulsions, and substances that enhance lubrication to improve their chemical properties. The rise in personal income in countries such as India, China, Malaysia, and Indonesia, driven by improved economic circumstances, is expected to boost the demand for MCC in this sector (Pulidindi and Pandey, 2019).

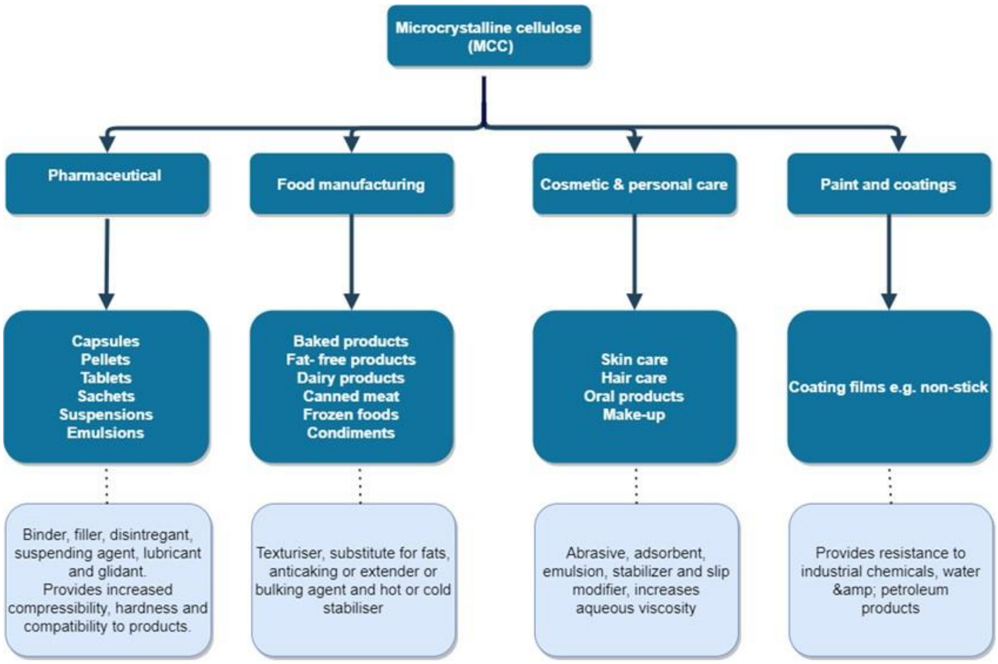


Figure 2-10: Overview of end-user applications of MCC and their functionalities (Rasheed et al., 2020, Pulidindi and Pandey, 2019, Globenewswire, 2020b, Sundarraj and Ranganathan, 2018).

2.6.2 *MCC synthesis and characterization*

Microcrystalline cellulose can be synthesized using various methods including reactive extrusion, enzyme-mediated hydrolysis, steam explosion, mechanical disintegration, and acid hydrolysis (Hindi, 2017, Valchev et al., 2020). The prevalent industrial method is the breakdown of cellulose by dilute mineral acids through hydrolysis (El-Sakhawy and Hassan, 2007). Enzymatic hydrolysis is not preferred due to its lengthy retention period (Vanhatalo and Dahl, 2014). The quality of MCC depends on the raw material used and the method of production, with variations in crystallinity, moisture content, surface area, porous structure, and molecular weight (El-Sakhawy and Hassan, 2007). Different grades of MCC can result from different raw material sources and processing conditions, with variations in size, moisture content, and additives.

In the acid hydrolysis process, the amorphous domains of cellulose are more susceptible to hydrolysis than the crystalline regions, which exhibit higher resistance to acid attack (Kopesky et al., 2003, Valchev et al., 2020). According to PharmaExcipients (2023), the DP, representing the number of glucose units in the cellulose chain or the length of the polymer chain in MCC, depends on the source of wood pulp and various parameters of the hydrolysis reaction, including reaction temperature, pressure, acid concentration, and reaction time. Acid treatment of cellulose material breaks glucosidic linkages, causing a decrease in DP (Palme et al., 2015). Initial degradation is rapid, slowing down as the reaction progresses until reaching a certain DP termed the "levelling-off" degree of polymerization (LODP) (Palme et al., 2015), with characteristic levels like 180-210 for hardwoods and 210-250 for softwoods (Crowley and Crean, 2016). Commonly used acids, such as sulfuric acid, hydrochloric acid, and nitric acid, facilitate liquid hydrolysis followed by dehydration, drying, and grinding of the resulting product. To enhance efficiency and reduce costs, alternative processes like steam, one-step hydrolysis and bleaching, and partial hydrolysis of semi-crystalline cellulose have been proposed, utilizing reactors pressurized with oxygen and/or carbon dioxide gas at temperatures ranging from 100 to 200 °C (Kopesky et al., 2003).

Microcrystalline cellulose can be obtained through acid hydrolysis of high-purity dissolving pulps, where amorphous domains preferentially hydrolyse, while crystalline regions resist acid attack (Eartrakulpaiboon and Tonanon, 2015). The use of sulfuric acid as the hydrolysing agent results in charged surface sulfate groups, contributing to more stable suspensions.

According to Chaerunisaa et al. (2019), the acid hydrolysis process is advantageous due to its shorter duration, potential for continuous application, and limited acid consumption. Although it yields finer MCC particles as the final product, the process's lower unit cost, stemming from fewer chemicals used, is a noteworthy advantage. Fibrous plant pulp undergoes hydrolysis with mineral acid under heat and pressure, breaking cellulose polymers into smaller chain polymers or microcrystals. The separation of soluble components like beta and gamma celluloses, hemicelluloses, and lignin occurs during washing, followed by filtration. The resulting pure α-cellulose is neutralized to produce the final slurry product, which is then dried to obtain the white, odourless, tasteless powder known as MCC.

Another synthesis procedure of the MCC reported on by Chaerunisaa et al. (2019) involves hydrolysing α-cellulose with hydrochloric acid at a boiling temperature of 105 ℃ for 15 minutes. The neutralized slurry is washed, and the fraction passing through a 710 μm sieve is stored at room temperature. Microcrystalline cellulose is commonly dried from the slurry using the spray-drying method, allowing manipulation of the degree of agglomeration and moisture content. Smaller particle sizes can be achieved through further milling, and various drying techniques may be employed, requiring additional screening steps to control particle size distribution. Adjusting spray-drying conditions allows manipulation of agglomeration and moisture content, while additional milling can produce smaller particle sizes. Higher bulk density grades are attainable by using specific cellulose pulps as raw materials, and further milling can achieve median particle sizes below 50 mm.

Alternative drying methods may be employed, necessitating additional screening steps after drying to regulate particle size distribution. Utilizing specific cellulose pulps as raw materials can yield higher bulk density grades, while further milling of Microcrystalline Cellulose (MCC) allows for obtaining median particle sizes below 50 mm (Chaerunisaa et al., 2019). A widely shared agreement emphasizes the impact of MCC moisture content on compaction properties, tensile strength, and viscoelastic properties. Table 2-6 shows the different types of MCC commercially produced and their properties.

Table 2-6: Types of the commercial MCC based on particle size (Chaerunisaa et al., 2019).

MCC Type	Particle size (micron)	Utilization
PH 101	50	Commonly employed in direct compression tableting, wet granulation, spheronization, and capsule-filling processes
PH 102	100	Utilized in the same manner as PH-101, but its increased particle size enhances the flow of fine powders.
PH 103	50	Identical particle size as PH-101 but possessing a lower moisture content of 3%. Applications for moisture-sensitive pharmaceutical active ingredients.
PH 105	< 50	Highly compressible among the PH products. Features the smallest particle size. Recognized as a notable excipient for direct compression involving granular or crystalline materials. When combined with PH-101 or PH-102, it imparts specific flow and compression characteristics. Additionally, it finds applications in roller compaction.
PH 112	100	Equivalent particle size to PH-102 but a reduced moisture content of 1.5%. Employed for pharmaceutical active ingredients highly sensitive to moisture.
PH 113	50	Equivalent particle size to PH-101 but lower moisture content (1.5%). Employed for high moisture-sensitive pharmaceutical active ingredients
PH 200	180	Characterized by a substantial particle size that enhances flowability, it is utilized to minimize weight variation and enhance content uniformity in both direct compression and wet granulation formulations.
PH 301	50	Equivalent particle size as PH-101 but denser, providing more flow ability and tablet weight uniformity. Useful for making smaller tablets and in capsule filling excipients.

As mentioned earlier, MCCs produced by various manufacturers possess different characteristics due to the raw materials that they inherited and their respective manufacturing conditions (Chaerunisaa et al., 2019). However, the existing processes offer several challenges before achieving a product of desired quality such as purification of the cellulose materials, multiple steps following acid hydrolysis to purify the MCC, and low solid reaction mixtures which in turn require longer reaction times and lower yields. Table 2-7 provides a summary of the typical characteristics derived from previous experimental work and the typical chemical composition of some grades of commercial MCC.

Table 2-7 Summary of typical properties of different grades of commercial MCC according to product specification sheets (Avicel, Microcel, Librawcel, Vivapur RanQ) and properties of some grades produced from experimental work.

Properties	
Particle size (µm)	22*, 15-250
Degree of polymerisation (DP)	230*, <350, <400
Crystallinity index (CrI%)	82*,71-84
Bulk density (g/ml)	0.14-0.50
Loss on drying (%)	NMT 1.5, 3-5, NMT 6
pH	5-7
Extractives (%)	0.6*, 0.1
Total lignin (%)	10.3*, 0.4-0.5
AIL (%)	10*, 0.1
ASL (%)	0.3-0.4
Total carbohydrates (%)	89.1*, 99.4-99.5
Monosaccharides	
Arabinose (%)	nd
Galactose (%)	nd
Rhamnose (%)	nd
Xylose (%)	0.6*,1.9-6.4
Glucose (%)	87.7*, 87.3-97.2
Mannose (%)	0.8*, 0.4-5.7

* Refers to values quoted for brown MCC
NMT (Not more than)
nd= not detected

Another important factor considered when producing MCC is the crystallinity index. The Segal empirical method is typically used to determine the degree of crystallinity (Segal' et al., 1959). This method has been widely used for the study of the crystallinity of native cellulose (Hassan and El-Sakhawy, 2005, Terinte et al., 2011, Viera-Herrera et al., 2020).

The DP expresses the number of glucose units in the cellulose chain (Hellström, 2012). It decreases exponentially as a function of hydrolysis conditions, including temperature, acid concentration, and time of reaction (Hellström, 2012).

The levelling-off degree of polymerization (LODP) value is specific to a particular raw material and typically falls within the range of 200 to 300. Further hydrolysis to lower the DP is challenging for cellulose with a LODP in the range of 200-300 (Hellström, 2012). Cellulose materials that have DP values above the plateau of the LODP are more challenging to manage because they are more sensitive to hydrolysis (Hellström, 2012). Microcrystalline cellulose with a LODP higher than 200-300 tends to have a fibrous nature, resulting in lower bulk density. This can improve tablet ability but may hinder powder flow (Hellström, 2012). Microcrystalline cellulose with a LODP value below 200-300 is typically less fibrous and denser but may also have reduced tabletability. There is no clear relationship between tabletability and a specific DP value (Hellström, 2012).

The physical characteristics of MCC are believed to be more decisively influenced by the origin of the raw materials and the production method, rather than the DP (Hellström, 2012). The DP value serves as a guideline for the manufacturer regarding the hydrolysis of MCC, while for the user, it is a distinguishing characteristic between the properties of MCC and powdered cellulose (Hellström, 2012).

2.7 Corrosion rates on material of construction

The delignification process mandates the utilization of a pressurized reaction vessel, wherein operational temperatures of 60-70 °C are achieved. This pilot reactor must also facilitate continuous agitation and be compatible with the manipulation of both sawdust material and APS chemical, the latter of which serves as a potent oxidizing agent. Owing to the high oxidative potential inherent to APS, its interaction with biomass triggers an exothermic reaction, resulting in the liberation of heat.

Given the exothermic nature of the APS-biomass interaction, compounded by the utilization of a pressurized vessel, the imperative of procuring a vessel equipped with an efficient cooling mechanism to regulate temperature and pressure becomes necessary. Notably, conventional pulp digesters were precluded from consideration due to this inherent limitation. Considering these stringent prerequisites governing the reaction vessel, the most viable alternative capable of satisfying the stipulated criteria emerges in the form of a Bioreactor vessel.

The assessment of corrosion rates assumes a paramount role in the meticulous evaluation of a given process, with the overarching objective of forestalling the emergence of severe structural impairments or potential hazards throughout experimental proceedings. Such vulnerabilities, if unaddressed, could potentially engender substantial financial ramifications or, in more critical scenarios, undermine safety considerations.

Notably, the construction material of choice for most reaction vessels used in pulp cooking operations consists of stainless steel varying in grades. Of prominence is 316 stainless steels, renowned for its robust resistance to corrosive agents and elevated temperatures. For the impending pilot experimental trials, a Bioreactor fashioned from 316 stainless steel has been selected as the designated vessel. Schweitzer (2007) provides some correlations for estimating corrosion rates according to the chemicals used and the material of construction. The correlations corresponding to the proposed process and the designated symbols were adapted from the text to estimate the corrosion rates (Figure 2-11 and Table 2-8).

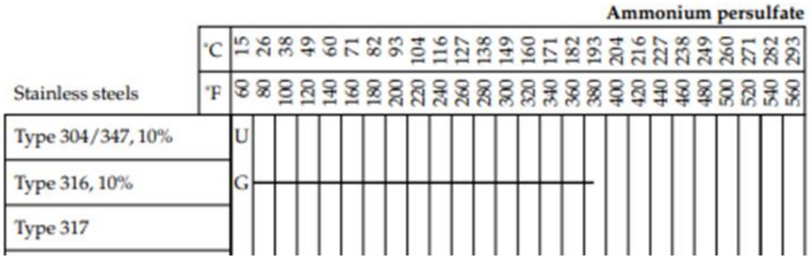


Figure 2-11: The corrosion effects of ammonium persulfate on different types of metals (Schweitzer, 2007).

Table 2-8: Symbols used to designate specific corrosion rates for stainless steel and high-nickel alloys (Schweitzer, 2007).

Symbol	Corrosion rate
E	< 2 mpy
G	2 - 20 mpy
S	2-50 mpy
U	>50 mpy, therefore not recommended for this service

*mpy- mils per year

2.8 Hazard and operability study (HAZOP)

According to DEKRA (2023), the Hazard and Operability (HAZOP) methodology is a systematic team-based technique that can be used to effectively identify and analyse the risks of potentially hazardous process operations. The principal mandate of the HAZOP methodology resides in forestalling the release of hazardous substances and associated energy, coupled with the subsequent improvement of consequences should such releases transpire, all while proactively averting the emergence of non-compliant end products (DEKRA, 2023, PQRI, n.d, Safetyculture, 2023). Of quintessential importance within the HAZOP framework is the unambiguous imperative for the interdisciplinary team to diligently scrutinize and discern the complete spectrum of hazards intrinsic to the process under examination, extending beyond overtly evident risks (DEKRA, 2023). Performing a HAZOP study offers advantages such as mitigating the risk associated with the release of hazardous substances and energy, minimizing the consequences of such releases, and identifying less apparent hazards. Additionally, it helps to prevent substantial harm to workers, minimizing property damage, and safeguarding the reputation of the company (DEKRA, 2023, Safetyculture, 2023).

Following the imperatives of engineering safety best practices, a comprehensive Hazard and Operability study (HAZOP) was diligently undertaken as a preliminary endeavour preceding the initiation of pilot trials. The HAZOP analysis comprehensively elucidated all facets of safety concerns, pre-emptive precautionary measures, and appropriate contingency actions requisite for addressing prospective safety risks. A comprehensive exposition of the intricate HAZOP study findings has been archived in the Appendices section of this study for reference.

The management of chemical substances and their derivatives, encompassing recovery and recycling protocols, assumes paramount significance within any industrial operation, thus mitigating the generation of chemical waste. Inaccurate disposition of these materials carries the potential to engender deleterious ramifications upon the ecosystem, including jeopardizing aquatic, botanical, and human components. According to Lessons (2019), companies face greater pressure to find more sustainable outlets for their by-product and waste streams. Among the emerging strategies, the concept of regeneration has garnered heightened traction.

The bleaching filtrates from the washings used for the chemicals such as Chlorine dioxide, Hydrogen peroxide, and sodium hydroxide were collected and neutralised to a pH of 7 before disposing of the chemicals. No recovery considerations were made concerning these chemicals as there are no known processes for recovering these chemicals and the dosages used are rather low.

2.9 Chemical recycling and by-product recovery

2.9.1 *Delignification by-product recovery*

The proposed process utilises large quantities of ammonium persulphate (APS) during delignification. Ammonium persulphate is a strong oxidising agent. In addition, large costs would be incurred by industries to correctly dispose of the chemical waste. From a pilot scale, approximately 8.5 kg of waste filtrate is generated from processing 1 kg of sawdust. For the above-mentioned reasons and to improve the techno-economic viability of the process, consideration was given to quantify and recognise possible methods of recovery of the excess APS waste.

Following the method used by Lam et al. (2013) in which a one-pot green procedure for the treatment of cellulosic biomass with ammonium persulfate (APS) was developed for the synthesis of highly crystalline carboxylated nanocrystalline cellulose (NCC−COOH), two by-products namely ammonium sulphate (AS) and sulphuric acid were identified and quantified. The method used ammonium hydroxide to neutralise the solution to pH 8 (this is believed to affect the formation of additional AS from H_2SO_4 in solution) and three equivalents of ethanol (EtOH) were used thereafter to precipitate ammonium sulphate (AS) out of solution. The precipitate was then dried and subjected to Raman and Thermogravimetric analysis (TGA) analyses. The powder exhibited the Raman signature of AS with 94% of the AS recovery, based on the amount of APS used in the experiment. Nearly 60% of the sulphate ions in the solution were found to exist as sulphuric acid.

2.9.2 *Acid recovery (HCl)*

Beta utilizes vacuum evaporation to filter impurities and concentrate spent hydrochloric acid for recycling (BetaControl systems, 2023). Their continuous recovery system is designed to maintain the acid at its optimal concentration and purity. The simplified process is illustrated in Figure 2-12.

Waste acid is propelled through a pre-filter by a pump and directed into the evaporator loop, consisting of the evaporator exchanger and the separator tank. In this loop, the spent acid undergoes pressurized circulation through a corrosion-resistant heat exchanger.

The solution is heated beyond the boiling point of both acid and water. Upon entering a controlled vacuum environment, a unique "co-flash" reactor causes the hydrochloric acid and water to vaporize. The resulting HCl and water vapours ascend through the liquid/vapor separator into the rectifier. The residual metal salt solution (metals + H_2O) continues circulating through the pressurized boiling loop until it reaches a specific concentration, and then it is discharged into a storage tank.

In the rectifier, the acid concentration is meticulously regulated to produce high-quality, re-concentrated acid for the process tank. The remaining water vapour, stripped of acid, proceeds to the condenser where it undergoes sub-cooling and condensation, yielding good-quality water that can be reused in the process.

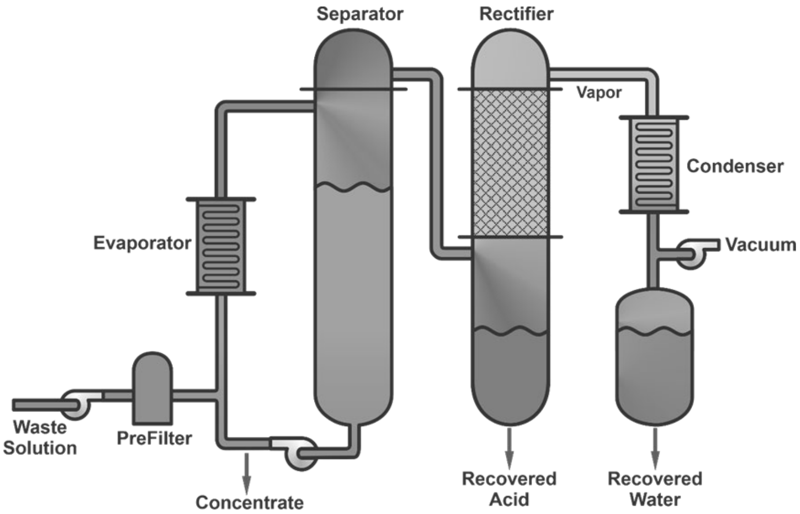


Figure 2-12 Recommended process for regeneration of HCl (Betacontrol Systems, 2023)

Some advantages of their system include.

- Decreases acid consumption and pickling times, resulting in a rapid return on investment
- Utilizes an environmentally safe vacuum process, ensuring a clean and safe work environment
- Features a distinctive heat exchange mechanism that minimizes energy requirements

- Boasts a compact design that seamlessly integrates into current facilities
- Allows for remote monitoring of system operation through a smartphone app

2.10 Techno-economic evaluation

In today's rapidly evolving technological landscape, businesses face the ongoing challenge of optimizing their operations to achieve greater efficiency, profitability, and sustainability. To address these objectives, organizations often turn to techno-economic evaluations as a critical tool for assessing the economic feasibility and viability of implementing new processes or technologies.

A techno-economic evaluation involves a comprehensive analysis that combines technical and economic factors to assess the potential benefits, costs, risks, and overall economic impact of a proposed process. By integrating these two crucial aspects, decision-makers can make informed choices about whether to invest in the development, deployment, or optimization of a specific process.

The primary objective of a techno-economic evaluation is to provide a thorough understanding of the financial implications associated with the implementation of a process. It considers various elements, such as capital and operational costs, revenue potential, market demand, resource requirements, and potential risks. Additionally, it examines the potential social and environmental impacts, ensuring that the evaluated process aligns with sustainability goals and regulatory requirements.

Technoeconomic evaluations often involve conducting feasibility studies, cost-benefit analyses, and sensitivity analyses to explore different scenarios and assess the robustness of the proposed process under varying conditions. Such evaluations enable decision-makers to identify potential bottlenecks, optimize the process design, determine the breakeven point, forecast returns on investment, and evaluate the overall economic viability of the project.

The outcomes of a techno-economic evaluation provide valuable insights for stakeholders, including investors, engineers, policymakers, and other key decision-makers. These insights inform strategic decision-making, enabling organizations to allocate resources effectively, select the most promising projects, and pursue opportunities that offer the highest potential for economic and technological advancement. Conducting a techno-economic study requires the identification of various capital, fixed, and running costs which are sometimes not available in the exact equipment sizes or types. However, several chemical engineering design textbooks can be referenced to obtain calculations that use data from today and existing data to estimate the costs by applying simple calculations.

2.10.1 *MCC markets and demands in South Africa*

Understanding the market size and demands for a particular product forms the basis of a techno-economic study. According to the latest statistics retrieved from SARS (South African Revenue Services), large markets exist for MCC in SA. Data was retrieved over the last 3 years and trended to identify key role players and gauge an estimated quantity of MCC imported into the country (Table 2-9 and Table 2-10). Currently, no South African producers of MCC exist, resulting in large imports from abroad. This provides any potential producers with a competitive edge to locally supply MCC.

Table 2-9: Imports of MCC in SA over 4 years (SARS,2023).

Year	Imports (tons/year)
2020	222.49
2021	169.48
2022	201.81
2023 (until March)	80.06

Statistics from SARS that were further processed show that the leading imports in SA of MCC in the last three years have been India, Taiwan, China, and the US. India steadily leads the pack in the last three years with the other countries experiencing some shifts over the last three years.

Table 2-10: Significant role players in SA imports of MCC over three years.

Country	2021 (tons/year)	2022 (tons/year)	2023 (tons/year)
India	113.8	170.0	61.9
Taiwan	27.0	1.00	10.0
China	3.75	11.8	2.03
Germany	24.4	12.8	5.20
US	0.007	0.005	0.10

On average, simple calculations showed that on average 0.55 tons per day of MCC is required to meet annual demands in SA. This provides a basis for understanding the typical plant production quantity required per day.

2.10.2 *The cost considerations*

2.10.2.1 Capital costs

For those design engineers who lack access to reliable cost data or estimating software, the correlations given in a table in the design textbook Towler and Sinnott (2008) can be used for preliminary estimates (shown in Appendix A).

The correlations in the table provided must be used in the equation below

$$Ce = a + bS^n$$

Where

Ce - purchased equipment cost on a U.S. Gulf Coast basis, January 2006 (CE index=478.6, NF refinery inflation index = 1961.6)

a, b - cost constants in the Table mentioned above

S - size parameter, units given in Table above

n -exponent for that type of equipment.

Correlations are provided for various types of equipment commonly used in chemical processes. However, it is important to note that the correlations are valid only between the lower and upper values of S indicated. The prices calculated are all for carbon steel equipment except where noted in Table 2-11. However, a factor can be applied to calculate the price for a different material of construction (Towler and Sinnott, 2008).

Table 2-11: Materials cost factors (f_m), relative to Plain Carbon Steel (Towler and Sinnott, 2008).

Material	**f_m**
Carbon steel	1
Aluminium and bronze	1.07
Cast steel	1.1
304 stainless steel	1.3
316 stainless steel	1.3
321 stainless steel	1.5
Hastelloy C	1.55
Monel	1.65
Nickel and Inconel	1.7

Another method that can be used to estimate equipment costs is the cost escalation method where equipment that was priced historically can be used to estimate the price of a new piece of equipment by using the cost indices published each year. This method can be used in the case that the previous method cannot be used. The equation is given by;

$$\text{Cost in year A} = \text{Cost in year B} \times \frac{\text{Cost index in year A}}{\text{Cost index in year B}}$$

According to Peters and Timmerhaus (1991), estimating the cost of equipment becomes feasible in the absence of specific cost data for a particular operational capacity. The six-tenths-factor rule, a logarithmic relationship, proves effective in such cases, especially when dealing with equipment of a size similar to one for which cost data are available. As per this rule, if the cost of a unit at one capacity is known, the cost of a similar unit with X times the capacity is approximately (X) 0.6 times the cost of the initial unit. Different equipment types may have distinct exponents, and consulting literature is advised to identify these.

$$\text{Cost of equipment. a = Cost of equip x } (\frac{Capacity\ equip\ a}{capacity\ equip\ b})^{0.6}$$

Peters and Timmerhaus (1991) also discuss estimations for installation costs, which encompass labour, foundations, supports, platforms, construction expenses, and other factors directly tied to equipment erection. The literature offers installation cost ranges as a percentage of the purchased equipment cost for various equipment types. Installation labour cost, relative to equipment size, exhibits considerable variations based on previous estimates. The text includes a table featuring exponents ranging from 0.0 to 1.56 for selected equipment types.

The plant's location significantly impacts project profitability and future expansion possibilities (Towler and Sinnott, 2008). Several factors must be taken into account when selecting a suitable site, including location, raw material supply, transport facilities, availability of labour, utilities (water, fuel, power), suitable land availability, environmental impact (including effluent disposal), local community considerations, climate, and political and strategic considerations.

The rent of land (and/or buildings) is typically estimated at 1 to 2% of inside battery limits investments (ISBL) plus offsite (OSBL) investment. Most projects assume land rental instead of purchase, but in certain cases, land acquisition costs are added to the fixed capital investment and recovered at the plant's end-of-life.

2.10.2.2 Running costs (Utility, raw material, and waste disposal) costs

Several running costs are incurred during plant operation. The main costs are covered briefly in the study and literature can be consulted for more details. Utility and raw material costs must be incorporated in a techno-economic study. To accurately estimate the utility consumption of a process and raw materials cost material and energy balances must be conducted (Peters and Timmerhaus, 1991, Towler and Sinnott, 2008). Utilities can be hot or cold utilities and include resources such as process water and air for various applications like washing, stripping, and instrument air supply (Towler and Sinnott, 2008). The electricity demand can include the power needed for instruments, lighting, and other smaller consumers.

The expenses related to utilities, such as steam, electricity, process, and cooling water, exhibit considerable variation contingent upon consumption levels, plant location, and source (Peters and Timmerhaus, 1991). Some facilities can generate their electricity through a gas-turbine cogeneration plant, employing a heat recovery steam generator (waste heat boiler) to generate steam (Towler and Sinnott, 2008). According to Peters and Timmerhaus (1991), steam requirements encompass not only the amount consumed in the manufacturing process but also the quantity essential for auxiliary purposes. Additionally, allowances for radiation and line losses must be factored into the calculations.

With raw materials, certain materials serve as production agents and can be partially recovered. When estimating raw material costs for preliminary cost analyses, direct price quotations from potential suppliers are preferred over published market prices (Peters and Timmerhaus, 1991). It is suggested that freight and transportation costs also be considered. The proportion of raw-material costs to the total plant cost can vary significantly depending on the type of plant. In chemical plants, for example, raw-material costs generally range from 10 to 50% of the total product cost (Peters and Timmerhaus, 1991).

The expenses associated with waste disposal are of notable significance. Materials generated by the process that cannot be repurposed or sold as by-products necessitate proper disposal as waste. Waste primarily originates as by-products or unused reactants from the process or as off-specification products resulting from misoperation (Towler and Sinnott, 2008). Additional treatment may be required to concentrate the waste stream before its ultimate disposal. Dilute aqueous streams are generally directed to wastewater treatment facilities unless the contaminants present are toxic to the bacteria employed in the wastewater plant (Towler and Sinnott, 2008). Dilute aqueous streams are typically directed to waste-water treatment facilities unless the contaminants present are toxic to the bacteria employed in the waste-water plant.

Acidic or basic wastes undergo neutralization before treatment, often achieved using a base or acid forming a solid salt, facilitating precipitation from the water. This prevents an excessive total dissolved solids (TDS) load on the wastewater plant. Inert solid wastes can be sent to landfills. Wastes resulting from the neutralization of spent sulfuric acid often produce calcium sulphate (gypsum), suitable for use as road fill, or ammonium sulphate, marketable as fertilizer.

Concentrated liquid streams that cannot be locally incinerated (such as compounds containing halogens) and non-inert solids must be categorized as hazardous waste and subjected to appropriate disposal. This entails shipping the material to a hazardous waste company for incineration in specialized plants or long-term storage in suitable facilities. The cost of hazardous waste disposal fluctuates based on factors like the plant's location, proximity to waste disposal facilities, and the nature of the hazardous waste. These costs need individual assessment, taking into account the specific circumstances of each situation.

Towler and Sinnott (2008) advocate for adopting the hierarchy of waste management when handling waste, prioritizing:

- Source reduction: Avoid creating waste in the first place, considered the best practice.
- Recycle: Identify a purpose for the waste stream.
- Treatment: Mitigate the severity of the environmental impact.
- Disposal: Adhere to legal requirements.

The wages paid to plant operators and supervisors are a fixed cost of production (Towler and Sinnott, 2008). Many plants, including batch plants, operate on a shift-work basis. Such an arrangement allows for a shift rotation that considers weekends, vacations, holidays, and some potential overtime. Generally, a minimum of three shift positions is required in most plants (Towler and Sinnott, 2008). These positions typically include one operator in the control room, one outside, and one stationed in the tank farm or another area responsible for shipping and receiving feed and products. Plants that utilize a greater amount of mechanical equipment, particularly those involved in solids handling, usually require more shift positions. Additionally, handling highly toxic compounds often necessitates a higher number of shift positions for safety purposes.

The salaries of operators vary based on factors such as regional differences and experience levels. According to Peters and Timmerhaus (1991), in chemical processes, the portion attributed to operating labour typically constitutes around 15% of the total product cost. In initial cost assessments, the volume of operating labour can frequently be approximated based on a company's experience with comparable processes or from available information on analogous processes. Due to the non-linear correlation between labour needs and production rates, a capacity ratio raised to the power of 0.2 to 0.25 is commonly employed when plant capacities are scaled up or down.

An alternative method for approximating labour requirements based on plant capacity involves aggregating the key processing steps detailed in the flowsheets, following the approach outlined by Peters and Timmerhaus (1991). In this technique, a process step is defined as any repetitive or continuous unit operation, unit process, or a combination thereof, occurring within one or more integrated equipment units. Examples of such steps include reactions, distillation, evaporation, drying, filtration, and so forth.

When determining labour costs, various factors need to be considered, including the type of workers required, the geographical location of the plant, prevailing wage rates, and worker productivity (Peters and Timmerhaus, 1991). Direct supervisory and clerical labour must also be given consideration. Direct supervisory and clerical labour costs typically average around 15% of the total cost for operating labour (Peters and Timmerhaus, 1991).

2.10.3 *Revenue considerations*

2.10.3.1 By-product revenue

Significant process design effort is assigned to analysing by-product recovery (Towler and Sinnott, 2008).

Possible valuable by-products encompass:

- Substances generated in stoichiometric proportions by the reactions constituting the primary product. If not recuperated as by-products, the expenses related to waste disposal could become exorbitant.

- Constituents are generated in substantial quantities through secondary reactions.
- Constituents are created in significant amounts from impurities present in the feed.
- Constituents are generated in minimal quantities yet possess considerable value.

Information regarding by-product prices can be obtained from the same sources utilized for main product pricing. However, determining the feasibility of recovering a by-product poses a challenge. For a by-product to be deemed valuable, it must align with specific material specifications, which might necessitate additional processing expenses. The design engineer must thoroughly assess whether the supplementary cost of recovering and refining the by-product is justified by its intrinsic value and the expenses saved on waste disposal. This evaluation plays a pivotal role in deciding whether the material should be categorized as a valuable by-product or treated as part of the waste stream.

It is imperative to factor in not only the purification cost of the by-product but also its potential for transformation into something more valuable. This involves exploring possibilities like reintegrating the by-product into the process, potentially enhancing main product yields, or generating a more valuable by-product. When scrutinizing the viability of by-product recovery, the value generated through recovery encompasses both the revenue from by-product sales and the saved costs of by-product disposal. A general guideline suggests that the net benefit from by-product recovery should surpass $200,000 per year (Towler and Sinnott, 2008). The net benefit is calculated by adding the by-product revenue to the avoided waste disposal cost.

Evaluating the economic viability of by-product recovery requires careful consideration of various factors, and the net benefit criterion helps provide an initial assessment of the potential value of such efforts.

CHAPTER 3 EXPERIMENTAL METHODOLOGY

3.1 Raw material preparation

Raw material preparation was applied to alter the physical attributes, specifically particle size, to enhance the efficiency of the subsequent processes. The preparation process aimed to produce a sample size of uniformity and homogeneity. In addition, chemical characterisation of the raw material was conducted to generate a profile of the starting material to compare the efficacy of the subsequent processes.

Three wood samples were evaluated for microcrystalline cellulose (MCC) production – The first sample was pin chips (undersized wood chips from the wood chip screening process preceding pulp production as shown in Figure 3-1) obtained from a local pulp mill. The wood processed by the pulp mill was a mixture of 53% *Eucalyptus dunnii*, 37% *Eucalyptus grandis*, and 10% clonal timber. To produce sawdust, the pin chips were subjected to a commination process, involving sequential treatment with a hammer mill and Wiley mill. This sample was henceforth labelled/ referred to as the mixed hardwood (MHW) sawdust sample.

Figure 3-1: Photo of pin chips before milling into sawdust.

The second and third samples included *Pinus Patula* softwood (SW) and *Eucalyptus grandis* hardwood (HW) sawdust samples procured from local sawmills. Particle size distribution (PSD) analysis was conducted employing a shaker apparatus equipped with a series of screens ranging in size from 0 to 1180 µm (0, 53, 150, 250, 425, 530, 710, 1180 µm). The PSD analysis (UNE-EN, 2016) involved the screening of 100 g aliquots of the sawdust samples, executed in duplicate for 30 minutes. An overview of the process is depicted in Figure 3-2. The residual sawdust accumulated on each screen was quantified in terms of mass.

The sawdust obtained from the sawmills was subjected to a screening process to achieve particle sizes below 1180 µm. The initial wood feedstock was subjected to chemical characterization following the standard methods prescribed by the Technical Association of the Pulp and Paper Industry (TAPPI). This characterization encompassed the determination of lignin content (both acid soluble by test method

TAPPI 1985b (TAPPI, 2006) and acid-insoluble by test method no. T222 om-88 (TAPPI, 1997)), monosaccharide composition (Test method no. T249 cm-85, TAPPI (1997)) using high-performance liquid chromatography (HPLC) and the use of a Dionex ICS-5000 high-pressure ion chromatograph (Thermo Scientific, United Kingdom), ash content by Tappi T211 om-02 (TAPPI, 2007), cellulose content by the Siefert method (Fengel and Wegener, 1983), and water-soluble and solvent (acetone, ethanol, benzene and dichloromethane) extractives content (Test method no. T204 om-88, (TAPPI, 1997)).

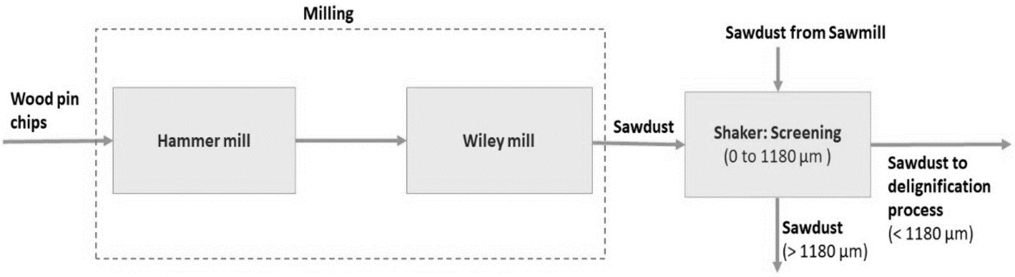


Figure 3-2: Process flow diagram of the sawdust preparation process.

3.2 Delignification stage

Following raw material preparation, the sawdust was then subjected to the first stage of chemical treatment termed delignification on a benchtop scale. This process aimed at targeting the removal of lignin and hemicelluloses and the final product targeted was an unbleached raw pulp. The process also focussed on the optimisation of operating parameters by carefully applying a design of experiments.

3.2.1 *Prehydrolysis of sawdust*

The HW (800 g) screened sawdust sample was subjected to prehydrolysis treatment in a stirred tank digester (East Coast Instruments, South Africa) using water with a L:W ratio of 10:1 and 1 kg of o.d sawdust (Figure 3-3). The treatment was applied as a preliminary trial at 150 and 170 °C for 45 minutes and 150 °C for 90 minutes. The treated sawdust was left to air-dry for a few days and stored for usage.

This characterization encompassed the determination of lignin content (both acid soluble by test method no. TAPPI 1985b (TAPPI, 2006) and acid-insoluble by test method no. T222 om-88 (TAPPI, 1997), monosaccharide composition (Test method no. T249 cm-85, TAPPI (1997)), and the use of a Dionex ICS-5000 high-pressure ion chromatograph (Thermo Scientific, United Kingdom), ash content by TAPPI T211 om-02 (TAPPI, 2007), cellulose content by the Siefert method (Fengel and Wegener, 1983), and water-soluble and solvent extractives content (Test method no. T204 om-88, (TAPPI, 1997)).

3.2.2 *Delignification experiments*

The subsequent phase of experimentation encompassed the delignification process targeting the pre-treated sawdust, having been air-dried, and conducted under conditions outlined in

Table 3-1. Employing ammonium persulphate (APS) as a chemical agent, concentrations ranging from 1 to 3 M were introduced into a 500 ml round bottom flask containing 20 g of oven-dry (o.d) sawdust. The initial series of tests adhered to a screening experimental design in randomised order to avoid confounding effects using 3 factors (APS concentration), temperature, l:w ratio) with 3 levels each, one response and 2 repeats giving a total of 26 tests per species (Appendix A). Temperature ranged from 60 to 80 ℃, the liquid-to-wood (L: W) ratio of 5:1, 7.5:1, and 10:1, as well as APS concentration (1 M, 2 M, and 3 M). During this phase, the time interval was held constant at 6 h. The response factors were categorized qualitatively, denoted by a scale of -1, 0, and 1, corresponding respectively to unpulped, semi-pulped, and fully pulped states. The second set of experimental tests focussed on an optimisation DOE (Appendix A), by using optimal conditions (temperature and chemical concentration and L:W ratio) from the screening experiments and evaluating the time taken to achieve a fully pulped state. A full factorial experimental design was used in randomised order to avoid confounding effects. Amounting to 18 tests per species. The DOE design is shown in Appendix A.

The agitation of the mixture was executed using an overhead stirrer operating at 200 rpm. Each experiment was carried out in triplicate. The resultant pulps from each experiment were filtered under vacuum and then subjected to air drying. The waste filtrate following each experiment was collected, neutralized to a pH of 7, and disposed of in an environmentally safe manner. The process is outlined in Figure 3-3. The determination of pulp yield was calculated by determining the moisture content using the TAPPI standard method (TAPPI test method T550-D). Pulp characterisation entailed intrinsic viscosity using the Scandinavian method SCAN-CM 15:88 (Sappi, 2018) and DP through intrinsic viscosity, ISO brightness (ISO-2470, 2016), Micro kappa number by French method FDT No. 12-019 to determine lignin content and hemicelluloses content determination via HPLC using the TAPPI test method no. T249 cm-85 (TAPPI, 1997) and the use of a Dionex ICS-5000 high-pressure ion chromatograph (Thermo Scientific, United Kingdom). The DP was subsequently calculated using the equation below that was proposed by Evans and Wallis (1987).

$$DP^{0,85} = 1.1\,[\eta] \quad \text{………(Evans and Wallis, 1987)}$$

Where η= intrinsic viscosity

Figure 3-3: Two-stage pathway for pulp production from sawdust.

Table 3-1 Summary of processing conditions used for the delignification process optimisation (Balkissoon et al., 2021).

Process step	Parameter	Conditions
Delignification process	Temperature	60-80 ℃; ∆10 ℃
	Time	3-6 h
	APS concentration	1, 2 and 3 M
	Liquid-to-wood ratio (L: W)	5:1, 7.5:1, 10:1

3.2.3 *Cellulose protector addition during delignification*

Benchtop delignification trials were conducted using 1%, 3%, and 5% dosages of D-mannitol on 20 g o.d sawdust and following the same procedure as the delignification trials described above. The intrinsic viscosity of the pulp using the Scandinavian method SCAN-CM 15:88 (Sappi, 2018) was measured, and the resultant DP was calculated.

3.3 Bleaching of pulp

Generally, hemicelluloses are not desired to produce dissolving wood pulp (DWP). To improve purity and brightness, the unbleached sawdust pulps from the pilot trials were subjected to a post-delignification bleaching process on a benchtop scale. Four bleaching sequences DED, D(EP)D, D(EP)P, and DEDP were evaluated using chlorine dioxide (referred to as the "D stage"), sodium hydroxide (known as the "E stage") or a combination of sodium hydroxide extraction with hydrogen peroxide reinforcement (referred to as the "EP" treatment), hydrogen peroxide (the "P stage"). These sequences were applied to the different unbleached pulps as illustrated in Figure 3-4 and summarised in Table 3-2.

The bleaching experiments were conducted in a temperature-controlled water bath, with temperature settings adjusted as required. The unbleached pulps were weighed (equivalent to 50 g o.d) taking into consideration the moisture content. Subsequently, the pulps were carefully transferred to double-layered polyethylene bags. Within these bags, the respective chemicals corresponding to the chosen bleaching sequence were added and mixed with the pulp.

The determination of micro kappa numbers was instrumental in calculating the appropriate dosages of chlorine dioxide. It is noteworthy that the established method outlines the Kappa number determination for values below 10. Standard TAPPI Method T236 is deemed less accurate for Kappa numbers at such low levels. In the case of the Do stage, the micro kappa number was determined using the French method (FDT no. 12-019). This value was utilized for the calculation of the appropriate dosage of chlorine dioxide. The calculation method employed for determining the dosage is outlined below:

$$\boldsymbol{\%ClO_2(as\ active\ chlorine)} = kappa\ factor\,(e.g\ 0.2) \times kappa\ number$$ …………..(Potgieter, 2018)

Following the addition of the respective chemicals, the polyethylene bag was sealed and placed into a water bath for the prescribed reaction time. During the reaction time, the pulps were intermittently mixed to ensure uniform exposure to the chemicals.

Upon concluding each bleaching stage's designated reaction time, the pulps were carefully extracted from the water bath, underwent a cooling process, and approximately 50-100 ml samples of the resultant bleaching filtrates were collected. These samples were then subject to pH measurement and, where applicable, assessment of chemical consumption. The pulps underwent thorough washing until the filtrate exhibited clarity, and the pH of the filtrate was adjusted to neutrality.

After washing, the pulp was advanced to the next bleaching stage within the bleaching sequence. The cumulative yield of the bleached pulp was calculated at the end of the bleaching sequence. All waste filtrates generated during the bleaching process were neutralized before disposal.

The network flow diagram depicted in Figure 3-4 provides an overview of the bleaching sequences applied to each pulp, with the bleaching conditions summarized in At the end of each bleaching stage, the pulps were removed from the water bath and allowed to cool to room temp. Approximately 50-100 ml aliquots of the bleaching filtrates were collected. The pH of the filtrates was recorded and in the case of the D and P stages, the residual chemicals were measured. The pulps were thoroughly washed until the filtrate ran clear. Finally, the filtrates were neutralised and discarded. Pulp characterisation entailed intrinsic viscosity using the Scandinavian method SCAN-CM 15:88 (Sappi, 2018) and DP using intrinsic viscosity as shown in section 3.2.2 and ISO brightness (ISO-2470, 2016).

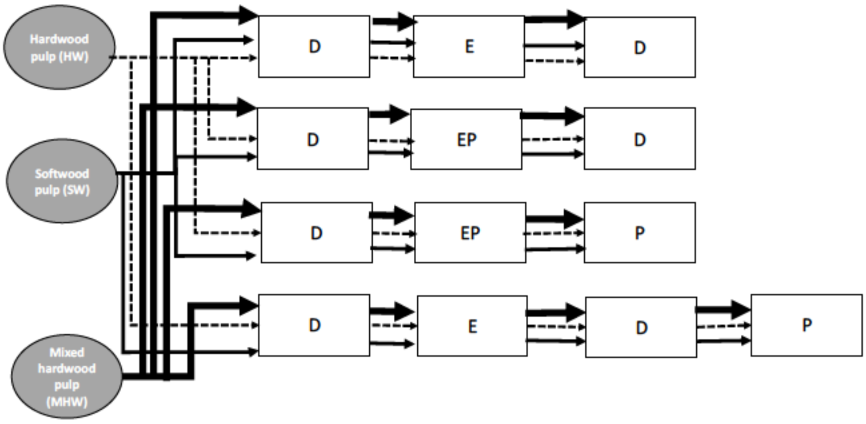


Figure 3-4:Network diagram showing the different bleaching sequences applied to each of the pulps.

Table 3-2: Processing conditions used for each bleaching stage.

Bleaching stages	Parameter	Conditions
D_0-stage	Time (mins)	120
	Temperature (℃)	70
	Kappa factor	0.25
	ClO_2 dosage as TAC (%)	HW- 0.75, SW-1.25, MHW- 1.15
	ClO_2 dosage pure (%)	HW- 0.29, SW-0.48, MHW- 0.44
	End pH	2-3
E-stage	Time (mins)	60
	Temperature (℃)	70
	NaOH dosage (%)	1.5
	End pH	10.5-11
D_1-stage	Time (mins)	120
	Temperature (℃)	70
	Chlorine dioxide dosage (%)	1.3
	End pH	4-5
E_p-stage	Time (mins)	60
	Temperature (℃)	70
	NaOH dosage (%)	1.5
	Hydrogen peroxide dosage (%)	0.3
	End pH	10.5-11
P-stage	Time (min)	180
	Temperature (℃)	80
	NaOH dosage (%)	1.0
	Hydrogen peroxide dosage (%)	0.6
	End pH	11-11.5

3.4 MCC from sawdust pulp

The unbleached pulp following the respective bleaching processes for all prepared pulp variants contained a high DP which had to be further reduced to meet MCC quality standards of a DP<400. The acid hydrolysis tests were applied to target the reduction of DP of the pulp. Since acid hydrolysis is a well-known process, conditions were inherited from a similar study and only hydrolysis time was optimised.

3.4.1 *LODP experiments*

Preliminary LODP experiments investigations were executed according to the methodology by Palme et al. (2015). The hydrolysis was conducted using 4 M HCl at 80 ℃. The reaction times were varied up to 1 h (15, 20, 30 and 60 minutes). 10 g (o.d. equivalent) of the bleached pulps were mixed with HCl (L:S ratio 50:1), contained in a 500 ml beaker. The beaker containing the pulp mixture was then placed in the water bath for the prescribed reaction period. The pulp mixture was stirred during the reaction using an overhead stirrer. Upon completion of hydrolysis, the pulp was removed and washed under vacuum filtration until a pH of 7 was achieved.

Following this, the pulp was weighed, and the moisture content was ascertained. These determinations facilitated the subsequent calculation of the pulp yield. Pulp yields were calculated by determining the moisture content according to the TAPPI test method T550-D (TAPPI, 2013).In a sequential progression, the washed pulps were subjected to an air-drying regimen. The air-dried pulps were then blended and characterised for intrinsic viscosity using the Scandinavian method SCAN-CM 15:88 (Sappi, 2018). The 91α DWP obtained from a local pulp mill was also subjected to the same acid hydrolysis treatment.

3.4.2 *Acid hydrolysis experiments*

Approximately 20 g of the bleached pulp was acid hydrolysed using 4 M hydrochloric acid (HCl), at L:S ratio of 50:1, contained in a 500 ml round bottom flask that was placed in a temperature-controlled water bath set at 80 ℃, as depicted in Figure 3-5 and Table 3-3. The reaction times for the acid hydrolysis for each pulp were established from the preliminary LODP profiles as discussed in section 3.4.1 above. After acid hydrolysis, the resultant pulps were washed and neutralized as described previously in section 3.4.1. The pulp yields after acid hydrolysis were calculated as previously described in section 3.4.1. The acid hydrolysed pulps were subsequently air-dried to facilitate chemical characterization. Reduction of particle size for the purposes of chemical characterization was accomplished using a domestic blender.

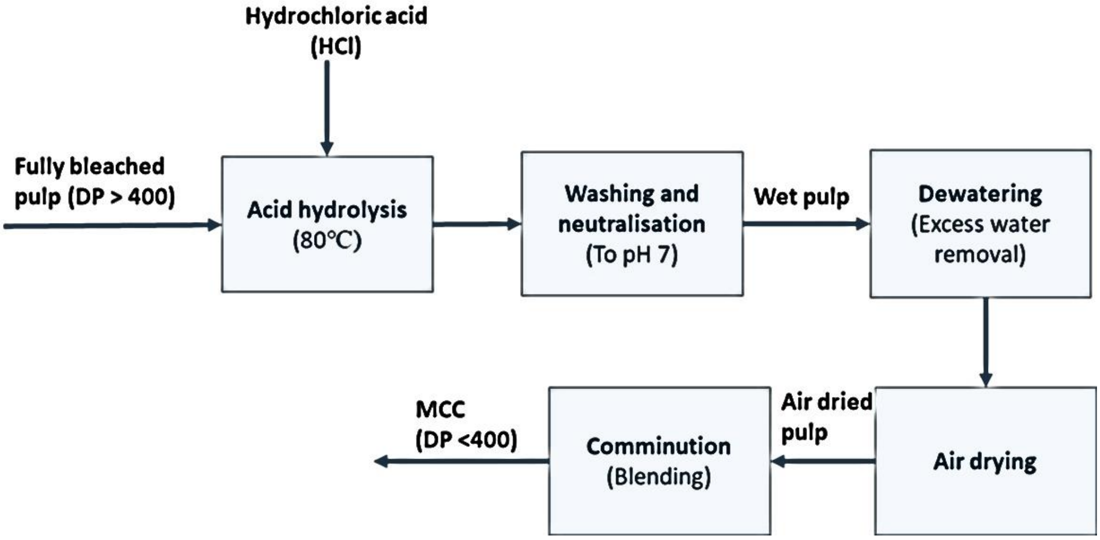


Figure 3-5:Overview of the benchtop acid hydrolysis process.

Table 3-3: Processing conditions used for the acid hydrolysis benchtop tests.

	HW	**SW**	**MHW**
Parameter		**Conditions**	
Mass of bleached pulp (g)	20	20	20
Temperature (℃)	80	80	80
Chemical concentration (M)	4	4	4
Liquid to solid ratio (L: S)	50:1	50:1	50:1

3.4.3 *Characterisation of sawdust, sawdust pulps, and MCC*

The characterization of pulps and final MCC products encompassed a range of analytical techniques. Characterisation tests entailed intrinsic viscosity using the Scandinavian method SCAN-CM 15:88 (Sappi, 2018) and DP through intrinsic viscosity using the equation in section 3.2.2, ISO brightness (ISO-2470, 2016), and hemicelluloses content determination via HPLC using TAPPI test method no. T249 cm-85 (TAPPI, 1997) and the use of a Dionex ICS-5000 high-pressure ion chromatograph (Thermo Scientific, United Kingdom).

Pulp yields were determined according to the TAPPI test method T550-D (TAPPI, 2013). Additional analyses encompassed Fourier Transform Infrared Spectroscopy (FTIR) utilizing a Frontier FTIR Spectrophotometer with a universal Attenuated Total Reflectance (ATR) accessory (Perkin Elmer, USA), X-ray Diffraction (XRD) was carried out utilizing a Rigaku MiniFlex600 instrument (Akishimashi, Tokyo, Japan). The diffraction patterns were recorded utilizing Cu radiation within a scan angle range of $2\theta = 10 - 90°$, employing a step size of 0.02 2θ and a scan rate of 10 2θ.

The Crystallinity index (CrI) value was computed employing the following equation:

$$\mathrm{CrI}\ (\%) = \frac{\mathrm{I200} - \mathrm{I(Non-cr)}}{\mathrm{I200}} \times 100\% \text{....................(Terinte et al., 2011)}$$

Where I (200) represents the diffraction intensity at 2θ equal or close to 22° corresponding to the crystalline material and I (Non-Cr) represents the diffraction intensity at 2θ equal to 18° representing the amorphous material (Hassan and El-Sakhawy, 2005, Terinte et al, 2011, Viera-Herrera et al, 2020).

Thermogravimetric analysis (TGA) was also conducted (Perkin Elmer STA 6000 instrument, USA) under an inert atmosphere of dry nitrogen and at a heating rate of 10 °C/min. The sample preparation for TGA was done by weighing 10-30 mg of the samples. The samples were decomposed at a temperature range of 30 to 600 °C.

3.5 Pilot scale trials

Pilot-scale experiments play a pivotal role in scientific and industrial research by bridging the gap between laboratory-scale studies and full-scale implementations. The aim of conducting such experiments involved testing and refining the proposed process on a larger but still controlled scale before moving to commercial production. The pilot scale experiments were conducted to develop insight into scalability, and feasibility, and identify potential challenges. The pilot scale tests also established the basis for a proof of concept and assessment of the economic viability. The pilot-scale experiments aimed to minimize risks and uncertainties associated with scaling up, leading to more efficient and successful transitions from lab bench to practical application.

3.5.1 *Delignification*

For each of the three sawdust samples, the delignification process was upscaled in a 30 L bioreactor (Sartorius Biostat® Cplus, Germany) as shown in Figure 3-6 and Figure 3-7. This scale-up employed 1 kg of sawdust along with the optimal operational parameters that had been determined through previous laboratory trials, as outlined in Table 3-4. Subsequent to this process, the resultant pulps underwent a series of washing steps involving vacuum filtration, followed by additional washing rounds, and subsequently passed through a Somerville screen (AB Lorentzen and Wettre, Sweden) to eliminate unpulped rejects. The yields corresponding to each of these steps were quantified.

The determination of pulp yield was calculated by determining the moisture content following the TAPPI test method T550-D (TAPPI, 2013). Following this, the pulp samples were subjected to chemical characterization, specifically with respect to micro kappa numbers, as per the French method FDT NO. 12-019. The characterized pulp samples were subsequently stored at a temperature of 4 °C, assigned for subsequent downstream processing stages encompassing bleaching and acid hydrolysis.

Effluent washings obtained from the filtration process were collected and managed by a specialized hazardous waste management entity. A measured quantity of approximately 1L from these filtrate washings was reserved for future analysis, specifically for exploring potential avenues for waste recovery.

Table 3-4: Processing conditions for pilot scale reactor.

	HW	**SW**	**MHW**
Parameter		**Conditions**	
Mass sawdust o.d (kg)	1	1	1
Temperature (℃)	60	60	70
Time (h)	4	6	3
Chemical concentration (M)	3	3	3
Liquid-to-wood ratio (L: W)	10:1	10:1	10:1

Figure 3-6: Pilot scale 30L Sartorius Bioreactor.

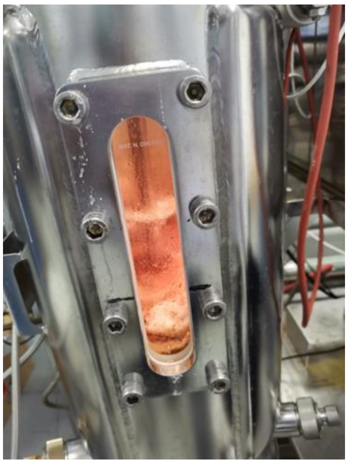


Figure 3-7: Inside the Bioreactor during an experiment.

3.5.2 *Bleaching*

An approximate quantity of 350-450 g of pulp was subjected to optimized bleaching protocols, which had been refined through prior benchtop trials. Subtle adjustments were made solely to the initial Do stage, prompted by the observation of a marginally elevated micro kappa value in the delignified pulps when compared to the corresponding measurement from the benchtop trials. The bleaching regimen was executed following the established procedure from the benchtop trials, with all pulp consistencies maintained at 10% on an oven-dried basis (o.d).

Following the bleaching process, the resultant pulps underwent characterization procedures to determine ISO brightness and intrinsic viscosity. The specific conditions applied during these procedures are encapsulated below in Table 3-5.

Table 3-5: Processing conditions for bleaching tests.

	HW	**SW**	**MHW**
	DEpD	DEDP	DEDP
Parameter		**Conditions**	
Mass of bleached pulp (g)	450	500	350
D_0-stage			
Kappa factor		0.28	
Clo_2 as TAC (%):	1.50	1.10	1.40
Clo_2 pure (%)	0.58	0.38	0.45
Temperature (℃):	70	70	70
Time (h):	2	2	2
Ep stage			
NaOH (%):	1.5	-	-

	HW DEpD	**SW** DEDP	**MHW** DEDP
Hydrogen peroxide (%)	0.3		
Temperature (℃):	70	-	-
Time (h):	1	-	-
E-stage	-		
NaOH (%):	-	1.5	1.5
Temperature (℃):	-	70	70
Time (h):	-	1	1
D_1-stage			
Clo$_2$ (%):	1.3	1.3	1.3
Temperature (℃):	70	70	70
Time (h):	2	2	2
P-stage			
Hydrogen peroxide (%):	-	0.6	0.6
NaOH (%):	-	1.0	1.0
Temperature (℃):	-	80	80
Time (h):	-	3	3

3.5.3 *Acid hydrolysis*

Approximately 80 grams of oven-dried (o.d) bleached pulp underwent an acid hydrolysis procedure, employing a 4-6 M hydrochloric acid (HCl) solution within a 5-litre round-bottomed flask. This treatment was conducted in a controlled environment using a water bath set at 80 ℃, adhering to the well-established conditions that had been fine-tuned through earlier benchtop trials. The execution of these trials adhered to a procedure analogous to that of the benchtop trials.

A reassessment of the time parameter became necessary considering the elevated initial DP observed in the starting bleached pulp. The conditions that were used are tabulated in Table 3-6. Pulp yields were calculated by determining the moisture content according to TAPPI test method T550-D (TAPPI, 2013). The pulp characterization encompassed intrinsic viscosity evaluation (Scandinavian method SCAN-CM 15:88), DP as calculated from intrinsic viscosity shown in section 3.2.2, and quantification of hemicellulose content via HPLC using TAPPI test method no. T249 cm-85 (TAPPI, 1997) and the use of a Dionex ICS-5000 high-pressure ion chromatograph (Thermo Scientific, United Kingdom).

Additional analyses encompassed FTIR utilizing a Frontier FTIR Spectrophotometer with a universal Attenuated Total Reflectance (ATR) accessory (Perkin Elmer, USA), and XRD was carried out utilizing a Rigaku MiniFlex600 instrument (Akishimashi, Tokyo, Japan). The diffraction patterns were recorded utilizing Cu radiation within a scan angle range of 2θ = 10 - 90°, employing a step size of 0.02 2θ and a scan rate of 10 2θ. Scanning Electron Microscopy (SEM) imaging facilitated by the Quorum Q150R S plus sputter coater with gold and the Phenom Pharos desktop SEM using 10kV at 100 µm scale. Thermogravimetric analysis (TGA) was also conducted (Perkin Elmer STA 6000 instrument, USA) under an inert atmosphere of dry nitrogen and at a heating rate of 10 °C/min. Molecular weight was determined by Liquid chromatography- Mass spectrometry (LC-MS) method (Shimadzu LCMS-2020 Single Quadrupole instrument, USA) using a full scan mode from 100 to 1200 m/z was performed with a source temperature at 140 ℃. The solvent used was Acetonitrile 50%. A Malvern particle size analyser (Malvern Mastersizer 3000, UK) was used to determine particle size distribution. These techniques were harnessed to ascertain various physical attributes and enable comprehensive comparative analysis.

Table 3-6: Processing conditions for the acid hydrolysis experiments.

	HW	**SW**	**MHW**
Parameter		**Conditions**	
Mass of bleached pulp (g)	220	215	130
Temperature (℃)	80	80	80
Chemical concentration (M)	4	6	4
Liquid to solid ratio (L: S)	50:1	50:1	50:1

3.6 Recovery and by-product consideration

3.6.1 *Delignification by-product recovery*

Persulfates or their solutions could be effectively assessed using a back titration method employing a standardized solution of potassium permanganate or ceric ammonium sulphate along with a standardized ferrous ammonium sulphate solution. This analytical approach was utilized to quantify APS in the waste liquid post-delignification.

In a 250 ml Erlenmeyer flask, 2-20 ml of the persulfate solution (depending on the approximate concentration) was pipetted. Approximately 50 ml of 1 N H_2SO_4 solution was added. Exactly 40 ml of 0.5 N ferrous ammonium sulphate solution was added. Constant swirling was maintained while incorporating the ferrous ammonium sulphate solution. The mixture was allowed to stand for one minute and was titrated with 0.5 N $KMnO_4$ until a permanent pink colour was achieved. The calculations required a blank titration using precisely 40 ml of ferrous ammonium sulphate (FAS) solution, as employed earlier, in 50 ml of the 1 N H_2SO_4.

The APS concentration was calculated as below.

$$\text{Ammonium persulfate (g/L)} = \frac{(A-B)C}{D} \times 114$$

A = ml $KMnO_4$ solution used for titrating the blank.

B = ml $KMnO_4$ solution used for titrating the sample.

C = Normality of the $KMnO_4$ solution used.

D = Weight of sample in grams.

To establish the method's precision and validity before subjecting the actual waste liquid to analysis, preparatory measures were undertaken to create solutions of 1 M, 2 M, and 3 M APS concentrations. The subsequent APS precipitation trial involved the utilization of 500 ml of APS filtrate. The precipitation process adhered closely to the procedural explanation in section 2.9.1 (Lam et al., 2013). Ammonium hydroxide solution was introduced, bringing about neutralization of the APS filtrate to a pH level of 8. The process necessitated the addition of approximately 320 ml of ammonium hydroxide for the pH to reach 8. Further intervention involved the incorporation of 3 equivalents of ethanol, amounting to 263 ml, to effectuate the precipitation of solids from the solution. Following the successful separation of the solid phase via filtration, the resultant solids were subjected to an air-drying regimen.

Insights into the composition and nature of both the solid and liquid samples were determined through the application of Raman spectroscopy and FTIR. Employing a Renishaw inVia Raman microscope characterized by a wavelength of 514 nm, X20 objective, and a laser power set at 10%, the solid and liquid specimens underwent meticulous analysis. A standardized exposure duration of 10 seconds was maintained during the analytical process.

3.6.2 *Acid recovery (HCl)*

The filtrate from the washings was also collected and neutralised to a pH of 7 before disposal. However, for the industrial scale process, the known recovery process is described in section 2.9.2. is recommended (BetaControl systems, 2023).

3.7 Techno-economic evaluation

In this techno-economic evaluation, the process of producing MCC from sawdust waste material is undertaken to determine its feasibility and economic viability. By conducting a comprehensive analysis of both the technical and economic aspects a clear understanding of the benefits, costs, and risks associated with the process can be identified. Ultimately, this evaluation will serve as a vital tool for decision-making, ensuring that informed choices to drive sustainable growth, enhance competitiveness, and maximize economic returns can be made.

3.7.1 *Plant process flow diagram (PFD) and process description*

The process description described below (Figure 3-8, Figure 3-9, and Table 3-7) is specific for a DEDP bleaching sequence and will be slightly different for a DEpD sequence. APS and water are channelled into a designated mixing vessel MT-1 to produce a 3 M APS slurry. The resultant slurry is pumped to a chemical reactor consisting of a cooling jacket configuration. Cooling water will be supplied from a cooling tower to regulate temperature. Sawdust will be introduced to reactor R-1 via a conveyor and mixed with the slurry before starting the reaction. The Reactor-1 will be configured to the desired temperature (60 or 70 ℃) and time (3,4 or 6 hours) and the delignification process will proceed. At the end of the delignification reaction, the filtrate from the delignification stage exiting R-1 will be MT-2 where it will be mixed with ammonium hydroxide (NH_4OH) until a pH of 8 is achieved. Three equivalents of ethanol (EtOH) will be added to the tank to precipitate the solid ammonium sulphate (AS) out of the solution. The resultant slurry will be sent to a centrifuge C-1 to separate the solid and liquid. The AS solid precipitate will then be conveyed to a dryer D-1 followed by a storage tank ST-1 where it will be readily available for packaging and sale. The remaining liquid will be subjected to solvent extraction or multi-stage distillation for ethanol recovery and recycled back into the AS recovery process.

The resultant pulp exiting R-1 is pumped to a rotary drum vacuum filter RDV-1 where the pulp is washed and screened to remove chemicals and rejects and is discharged at an 8-12% consistency. Chlorine dioxide (ClO_2) and water are pumped to a high-shear mixer HS-1 and transferred to a bleaching tower BT-1. The pulp enters the first bleaching tower BT-1 where it is subjected to the first Do bleaching stage at 70 ℃ for two hours. The bleached pulp is pumped to RVD-2 and is discharged at an 8-12% consistency and then pumped to BT-2. Sodium hydroxide (NaOH) and water (H_2O) pass through HS-2 before entering BT-2. The pulp exiting RDV-2 is discharged at an 8-12% consistency and pumped into BT-2 where it will undergo the E-stage bleaching process at 70 ℃ for 1 hour. The bleached pulp is pumped to RDV-3 and discharged at an 8-12% consistency before being pumped to BT-3. Chlorine dioxide (Clo_2) and water will pass through HS-3 before entering BT-3. The pulp exiting RDV-3 is pumped into BT-3 where it undergoes the D1 stage bleaching process at 70 ℃ for 2 hours. The bleached pulp is pumped to RDV-4 before being pumped to BT-4. The hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), and water (H_2O) will pass through HS-4 before entering BT-4. The pulp exiting RDV-4 is discharged at an 8-12% consistency and is pumped into BT-4 where it will undergo the P-stage bleaching process at 80 ℃ for 3 hours. The bleached pulp is pumped to RDV-5 before being pumped to the glass-lined reactor R-2. Water (H_2O) and Hydrochloric acid (HCl) will enter R-2 and be subjected to acid hydrolysis for the respective time at 80 ℃. After the reaction is completed, the acid water is pumped to a recovery and recycle process and the water will go to a water treatment process whilst the recovered HCl will be pumped back into the process. The resultant MCC exiting R-2 is pumped to RDV- 6 where it will be washed and discharged at an 8-12% consistency. It is then sent to a spray dryer SD-1 and the MCC storage tank ST-2, ready for packaging and sale.

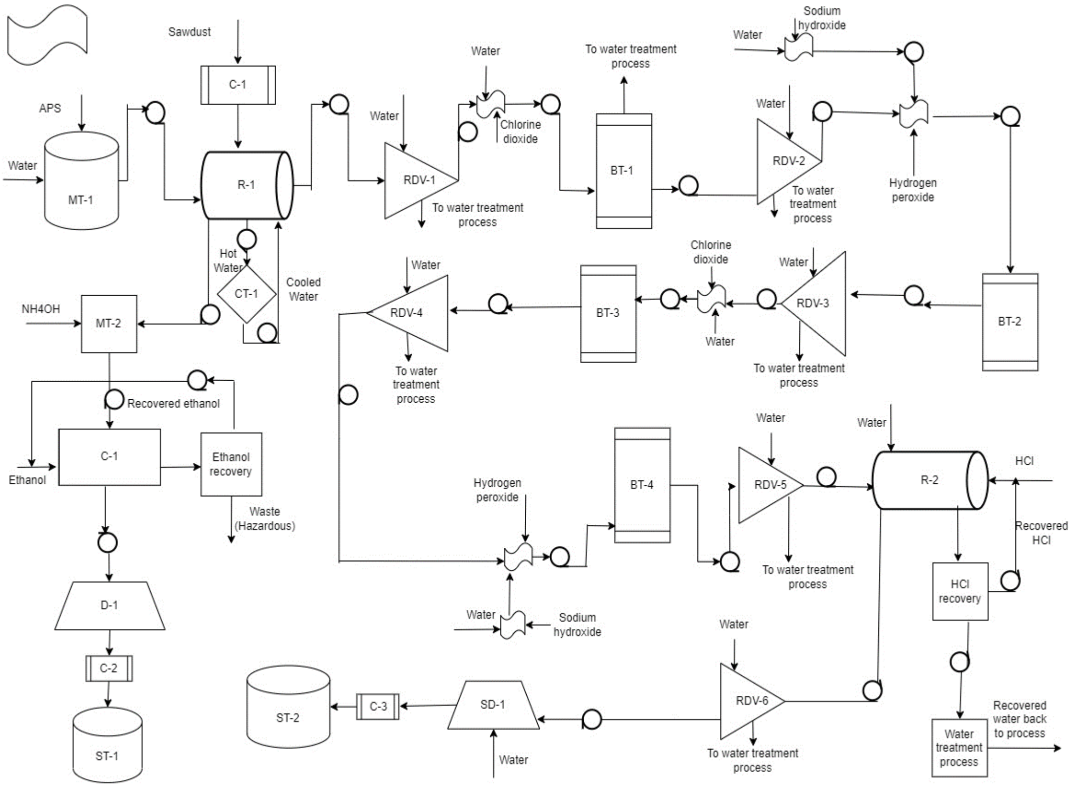
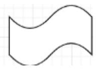


Figure 3-8: Proposed process flow diagram for MCC production.

Table 3-7: Symbols on PFD not defined in the PFD.

Symbol/Abbreviation	Meaning
	Pump
 HS	High shear mixer
RDV	Rotary drum vacuum filter/washer
MT	Mixing tank
C	Conveyor

Symbol/Abbreviation	Meaning
BT	Bleaching tower
SD	Spray dryer
D	Dryer
R	Reactor
CF	Centrifuge
ST	Storage tank
CT	Cooling tower

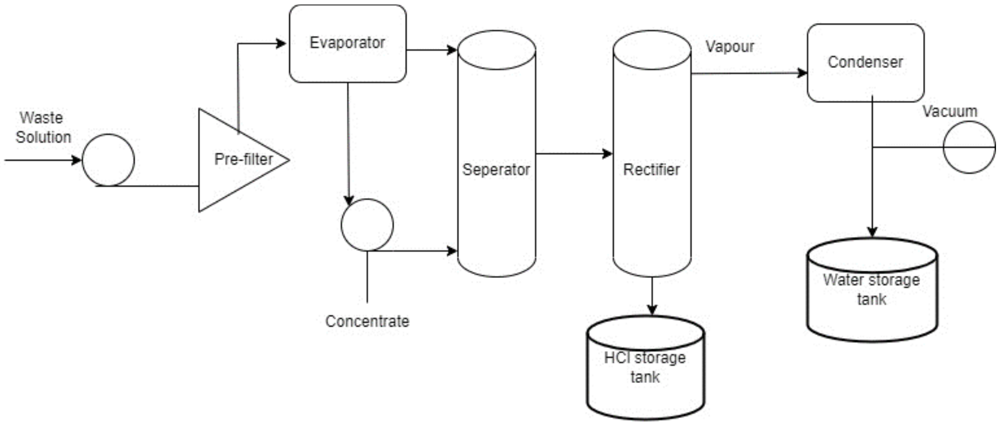


Figure 3-9: Proposed HCl recovery process.

3.7.2 *Mass and energy balances*

Material balances were conducted by calculating the flow of inputs and outputs per unit based on approximately 1 kg basis of MCC produced with an average yield of 46% for HW-derived MCC as a starting point. The same was applied for SW and MHW species using their respective yields.

Energy balances were conducted based on the material inputs and outputs. The estimated energy requirements were calculated using the equation.

$$Q= \frac{\mathrm{mcp}\Delta\mathrm{T}}{t}$$

Where m-mass flow rate in kg

Cp- specific heat capacity (KJ/kg. °C)

ΔT-change in temperature (T_{Out}-T_{in})

t- time in h

Q- energy in KJ

3.7.3 *Costs*

Only the very high-level costs were considered for the scope of the study as other minor costs are not expected to significantly impact the total estimated costs.

Equipment costs were estimated using the method outlined in Towler and Sinnott (2008) and described in section 2.10.2.1. Each unit was sized based on the material balances and the correlations were then applied to calculate an estimated cost per unit. The total equipment cost was then determined by summing the various unit costs. The installation costs were also determined by the method of using the installation factor for each unit of equipment (Towler and Sinnott, 2008). Maintenance costs (including both materials and labour) were calculated as 3 to 5% of ISBL (inside battery limits) investment, depending on the expected plant reliability. Plants with more moving equipment or more solids handling usually require higher maintenance (Towler and Sinnott, 2008).

Utility (water and electricity) rates were adapted from the local eThekwini municipality tariff guide 2022/23. The tariffs for standard commercial businesses were used. A monthly service charge of approximately R350 must be added to the electricity usage charged at approximately R2.54 per KWh.

Raw material and consumable costs were retrieved online from industrial chemical suppliers. Hazardous waste costs were based on the hazardous costs charged for the pilot process and then scaled up as an estimate. However, the delignification filtrate and the acid filtrate are being considered for potential chemical and water recovery processes.

Labour costs were estimated by using the rules outlined in section 2.10.2.2. The average salaries per skilled worker were estimated based on the rates paid typically in SA for the respective skills. A minimum of two operators/technicians/process engineers per unit were allocated to permit shifts and account for leave etc.

Land costs were estimated based on the requirement for the estimated plant layout. The yard for sawdust storage also had to be taken into account and the facility had to be located within proximity to a timber mill and pulp mill.

3.7.4 *Revenue*

To calculate the expected revenue per month, the average expected production rate had to be determined. Production rates were based on using the market size in SA over three years obtained from SARS import data. However, as with all data, discrepancies do exist and hence only one grade of MCC might be compensated for. Hence a slightly higher production rate is estimated to also compensate for potential exports and international markets.

In addition, the average selling price for MCC per kg was determined to identify a competitive selling rate and estimate potential revenue. In addition, revenue for AS was also determined by identifying the selling rate per kg.

All other revenue considerations such as payback period (PBP), return on investment (ROI) and internal rate of return (IRR) were calculated using equations recommended by Towler and Sinnott (2008)

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Raw material preparation

The particle size distribution for all sawdust samples is depicted in Figure 4-1. Notably, the HW SW sawdust samples exhibited a high concentration of particles exceeding 1180 µm. Hence, these particles above 1180 µm were eliminated from consideration. This exclusion was necessitated by their incompatibility with delignification preliminary trials, resulting in an incomplete reaction of the sawdust particles which was further supported by literature indicating that large chips and sawdust particles hamper the PHK cooking process (Dyunyasheva, 2017). This was attributed to the limited surface area which is characteristic of the larger-sized particles.

Additionally, in the case of the pin chips sourced from the pulp mill, the comminution process aimed to transform them into sawdust (MHW). While the MHW sawdust displayed a relatively minimal presence of particles surpassing 1180 µm (<1%) compared to the HW (~15%) and SW (~34%) species, they were also selectively removed. The selective removal was executed to ensure consistency and homogeneity in particle size across the experimental setup. While the MHW sawdust derived from the milled pin chips displayed a relatively minimal presence of particles larger than 1180 µm (<1%) as compared to the HW (~15%) and SW (~34%) species, they were also selectively removed. The selective removal was executed to ensure consistency and homogeneity in particle size across the experimental setup. The SW sawdust also exhibited a wider distribution, with particle sizes larger than 710 µm, almost twice as much as HW, and about 5% more than the MHW. The HW and MHW sawdust showed a much higher distribution (4-10%) of smaller particle sizes, less than 425 µm, as compared to SW. However, for the particle size range 425-710 µm, similar distributions were observed for SW and HW sawdust (22-24%), and higher amounts were observed for MHW (44%). Overall, the MHW particle size could be attributed to the milling processes used to reduce the pin chips to sawdust. The overall differences in particle size were expected to affect the processing conditions and pulp quality in the downstream processes.

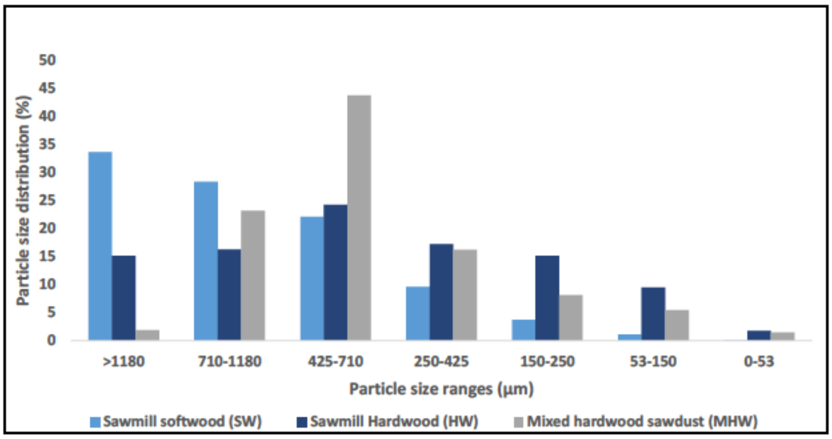


Figure 4-1: Average particle size distribution for sawdust samples (100 g sample size) (Balkissoon et al., 2021).

Subsequently, each sawdust sample was chemically characterized, and the results are shown in Table 4-1. Notably, the cellulose and lignin content of all wood species fell within the ranges expected with a cellulose content ranging from 40-50% and lignin content ranging from 15-35%) as reported by SWST (2017). Moreover, a notable difference was observed with the SW sawdust showing a significantly lower lignin content (33%) in comparison to HW and MHW (36-37%). This was an unexpected result since it is known that softwoods possess a higher lignin content than HW (Subrahmanyam et al., 2004, Tarasov et al., 2018). It was suspected later that there were challenges experienced with AIL measurements which became more prominent when analysing the pulp.

Table 4-1 Chemical composition of different sawdust species used (Dry wood basis).

Analysis	HW	SW	MHW
Solvent extractives (%)	0.39	0.29	0.40
Hot water extractives (%)	2.09	1.96	3.27
AIL (Acid insoluble lignin) (%)	34.2	30.8	31.7
ASL (Acid soluble lignin) (%)	2.25	2.67	4.49
Siefert Cellulose (%)	42.7	41.6	44.1
Ash content (%)	0.23	0.17	0.70
Monosaccharides			
Arabinose (%)	0.12	0.95	0.66
Galactose (%)	0.86	1.94	0.86
Xylose (%)	11.6	6.1	13.1
Glucose (%)	47.9	42.9	39.9
Mannose (%)	nd	3.09	0.95

nd– not detected/less than detection limits
Standard errors in measurements reported in Appendix A

Elevated concentrations of xylose were found in the HW MHW sawdust, which was significantly higher than that found in the SW sawdust. Conversely, a high concentration of mannose and galactose was found in the SW sawdust, in line with findings by other studies (Gladyshko, 2011). It is notable that hardwoods typically show an elevated proportion of xylose, while softwoods are characterized by high amounts of mannose and galactose as outlined by Gladyshko (2011). This distinction is reflected in the chemical compositions of the respective species.

Furthermore, the HW sample displayed a marginal increase in glucose composition when compared to both the SW and MHW sawdust. Additionally, HW and MHW samples exhibited a higher amount of cellulose relative to the SW sample. In terms of ash composition, the MHW sawdust showed a relatively higher concentration in comparison to the HW and SW samples. This observation implied that the MHW sample possesses a slightly greater degree of inorganic compounds compared to the HW and SW samples.

4.2 Delignification

4.2.1 *Prehydrolysis*

Milder prehydrolysis conditions were selected due to the smaller particle size of sawdust compared to conventional conditions used for wood chips. Furthermore, previous studies highlighted the efficacy of pre-treatment in the context of wood chips, successfully achieving hemicellulose removal. The parameters governing the prehydrolysis treatment were informed by previous research endeavours (Andrew et al., 2018, Dyunyasheva, 2017, Gladyshko, 2011, Johakimu and Andrew, 2013, Saska and Matsumara, 2004). Chemical characterisation results are compared in Table 4-2.

Table 4-2: Summary of prehydrolysed HW sawdust characterisation (Dry sawdust basis).

Analysis	**HW (150 ℃, 45 mins)**	**HW (150 ℃, 90 mins)**	**HW (170 ℃, 45 mins)**
Solvent extractives (%)	0.72	0.40	0.56
Hot water extractives (%)	1.83	3.69	1.22
AIL (%)	30.4	30.4	29.0
ASL (%)	2.55	2.23	2.77
Siefert Cellulose (%)	45.6	44.8	45.9
Ash content (%)	1.07	1.13	1.20
Arabinose (%)	0.02	0.16	0.04
Galactose (%)	0.85	0.76	0.81
Xylose (%)	10.3	11.3	9.0
Glucose (%)	49.3	49.6	49.1
Mannose (%)	0.00	0.00	0.00
Standard errors in measurements reported in Appendix A			

In comparison to the untreated sawdust samples, slight reductions in cellulose compositions and minor reductions were observed in hemicellulose content, indicating that the introduction of a pre-treatment process did not exhibit significant advantages in terms of hemicellulose removal and resulted in slight cellulose degradation. Minor differences were also observed between an increase in time for the 150 ℃

experiment and the increase in temperature from 150-170 ℃. This finding was not consistent with other studies where prehydrolysis showed significant benefits (Asim, 2012, Martino et al., 2017, Rusanen et al., 2018). However, this may be due to the differences in the raw material such as wood chips as opposed to sawdust or the prehydrolysis conditions. Other reaction times or sawdust species were not evaluated at this stage since the main objective was to understand if the pre-hydrolysis treatment would be beneficial in the subsequent delignification process.

4.2.2 *Delignification screening experiments*

As discussed by FMC (2001), upon heating solutions of persulfates, free radicals are generated. In the presence of appropriate monomers, these radical anions serve as initiators for polymerization, leading to the formation of polymer molecules. The principle of delignification is to therefore effect such a polymerisation. As a result, lignin in the sawdust is depolymerised into smaller fragments that render it soluble. By solubilising the lignin and removing it, the cellulosic fibres are liberated. Both the prehydrolysed sawdust and the untreated sawdust underwent delignification processes to ascertain their response.

It was observed that the prehydrolysed sawdust samples subjected to temperatures of 150 ℃ and 170 ℃ remained unpulped even after an extended reaction period of 6 h. Notably, the sawdust samples treated at 120 ℃ achieved pulping only after 6 h, with a notable prevalence of rejected material. This outcome substantiates that prehydrolysis was not suitable for the subsequent pulping process. A plausible explanation is that the prehydrolysis procedure resulted in the degradation of pulp fibres to a degree that hindered effective pulping or exerted an impediment on the subsequent delignification process using APS. One observation that supports the assumption, is the slightly lower cellulose content measured in the treated sawdust. Further investigations would have to be conducted in this regard.

In the context of the screening experiments involving untreated sawdust (without prehydrolysis), delignification at temperatures higher than 60 ℃, coupled with APS concentration of 3 M, led to the effervescence of the reaction solution (particularly in the case of hardwood and softwood species). Conversely, at lower chemical concentrations (1M and 2 M) and elevated temperatures beyond 60 ℃, the conditions proved insufficient to achieve adequate delignification for all sawdust, resulting in a significant proportion of unpulped sawdust particles (rejects) even after 6 h reaction period. Furthermore, instances of inadequate pulping emerged at lower liquid-to-wood (L:W) ratios due to insufficient wetting of the sawdust particles. This result is elucidated by other studies which suggest that higher L: W ratios permit efficient wetting of the wood material, a more uniform cook, and enable lignin fragments to dissolve completely in the cooking liquor, thereby achieving lower kappa numbers (Andrew et al., 2018, Hasibuan et al., 2018). Lower ratios are said to result in the redeposition of lignin, which increases the kappa number consequently decreasing the pulp quality (Hasibuan et al., 2018).

Optimal conditions that resulted in sawdust pulps were: 3 M APS, L:W ratio of 10:1, and 6 h, for all sawdust species (Figure 4-2 and Table 4-3). The optimum reaction temperatures were 60 °C for HW and SW, and 70 °C for MHW sawdust.

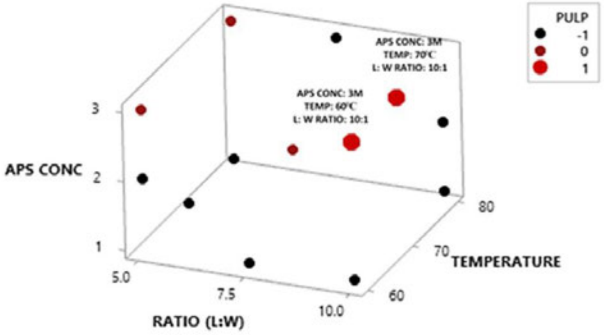


Figure 4-2: Plot showing optimal conditions that resulted from the DOE for the delignification process optimisation.

Table 4-3: Response factor key for screening design of experiments.

Pulp response factor levels	Meaning
-1	Unpulped
0	Semi-pulped
1	Fully pulped

The subsequent phase of the optimization studies was centred on the optimisation of reaction time, utilizing the parameters derived from the preliminary screening experiments to minimise extensive use of resources and time. Consequently, uniform concentrations of 3 M were employed across all species, while maintaining a consistent liquid-to-wood (L: W) ratio of 10:1. Specifically, for the hardwood sample, pulping was effectively achieved within a 4 h reaction time at 60 °C, whilst the mixed hardwood (MHW) sample required a higher temp of 70 °C and a reaction time of 3 h. In contrast, the softwood sawdust required a longer reaction time, with the optimal conditions identified at 60 °C for 6 h. The effect of sawdust particle size is a possible explanation for the differences in pulping temperatures and times, together with the different delignification rates for the different wood species.

Using the aforementioned conditions for the respective sawdust samples, uniform pulping was achieved, with minimal rejects. The unbleached pulp yields ranged between 44% to 53% for the three wood sawdust samples. These yields were comparable with unbleached AS dissolving wood pulp (DWP) (45-46%), and marginally higher than unbleached PHK DWP (35-40%), as shown by Dyunyasheva (2017). The relatively lower yields associated with PHK DWP may be attributed to the prehydrolysis step (Dyunyasheva, 2017). The transition of the sawdust into a pulp over the elapsed time during the delignification process is shown in Figure 4-3 with the final image depicting the washed air-dried unbleached pulp.

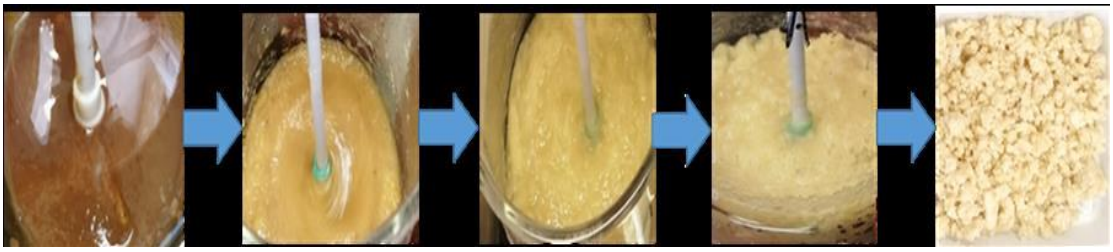


Figure 4-3: Transition of sawdust to pulp during benchtop delignification process using low temperatures between 60-70˚C (Balkissoon et al., 2021).

The unbleached pulp was characterised, and results are reported in Table 4-4. Brightness ranged between 65-72%. This was significantly higher than the brightness of unbleached PHK DWP (34-43%) reported by Sixta (2006). The high brightness achieved after delignification suggested that minimal improvements in brightness would be required in stage 2 to reach comparable brightness levels of commercial DWP. Micro kappa numbers were also measured as indication of lignin and showed relatively low levels in comparison to reported values of about 30-35 for softwoods and 14-20 for hardwoods in bleached kraft mills that employ conventional cooking methods (EOFDROF-Chlorinated, 2013). As a result of the challenges experienced with AIL measurements not equating to accurate overall mass balances, lignin content was estimated using the relationship between kappa number and lignin as specified by TAPPI method T236.This highlighted the advantage of the proposed delignification process benefitting downstream bleaching processes in removing residual lignin. Hemicellulose content overall following delignification was also significantly reduced. This was observed by the reduction in monosaccharide content with a 100% removal of arabinose and galactose and approximately a 50-60% removal of xylose and mannose for all wood species. A low hemicellulose content is a key requirement for DWP grades (Chen et al., 2016). However, considering the initial raw material hemicellulose composition, separate studies will need to be undertaken to evaluate the pre-extraction of the hemicelluloses before delignification for possible beneficiation of the hemicelluloses.

Table 4-4: Chemical characterisation of unbleached pulps at a benchtop scale (Air dried pulp basis).

Analysis	MHW	HW	SW
Micro kappa number	4.60	3.00	5.00
% Lignin (based on Micro kappa number x 0.13)	0.60	0.40	0.65
Intrinsic viscosity (ml/g)	313	195	380
DP	966	553	1213
ISO Brightness (%)	66.9	72.0	66.0

Analysis	MHW	HW	SW
		Monosaccharides	
Arabinose (%)	0.00	0.00	0.00
Galactose (%)	0.00	0.00	0.00
Xylose (%)	4.72	3.68	4.82
Glucose (%)	77.8	80.5	74.0
Mannose (%)	2.14	0.00	5.34

Standard errors in measurements reported in Appendix A

Earlier, it was discussed that prehydrolysis was not successful in achieving such results. However, previous studies have shown that the removal of hemicellulose before the pulping process may aid in delignification, thus requiring milder delignification conditions (Miao et al., 2014, Hemanathan Kumar and Christopher, 2017, Liu et al., 2013, Koradiyaa et al., 2016). For this reason, other types of hydrolysis methods may be investigated. Such investigations would require a separate detailed evaluation of different combinations of prehydrolysis treatments ranging from alkaline to enzymatic prehydrolysis methods before delignification which is beyond the scope of this study.

It was evident that after the delignification step, the intrinsic viscosity and corresponding degree of polymerisation (DP) were reduced significantly. This highlighted that the process resulted in some cellulose degradation and severe depolymerisation. It was at this stage that it was realised that the viscosity and DP of the pulp for viscose production would be too low, more specifically because the pulp would still have to undergo a subsequent bleaching process, causing further reductions.

4.2.3 *Cellulose protector addition during delignification*

In an attempt to improve the viscosity of the unbleached pulps, the use of cellulose protectors was evaluated during APS delignification reactions. D-mannitol was selected as a cellulose protector for investigation as the result of the effectiveness and availability of information such as dosages (Jablonský et al., 2006). A 1% dosage showed a 20% improvement in intrinsic viscosity; however, this was not sufficient to improve the intrinsic viscosity and DP to a point that was desirable for DWP. Attempts were made at higher dosages using 3 and 5% on o.d sawdust but the experiment failed since effervescence was experienced. This observation pointed to the fact that the D-mannitol was not compatible with the APS used in the delignification process as APS is a strong oxidiser. Further studies into the compatibility of the CPs identified from the literature revealed that none of them would be compatible with a strong oxidiser. For this reason, no further work was done in this area. At this stage, it was established that the production of viscose from the grade of DWP was not possible and the production of microcrystalline cellulose (MCC) looked more promising since it required a DP of less than 400.

4.3 Bleaching of pulp

In the context of DWP production, the presence of hemicelluloses and lignin is generally undesirable due to their potential impact on both purity and brightness. To enhance these critical attributes, the unbleached sawdust pulps, derived from the pilot trials, underwent a subsequent delignification bleaching process at a benchtop scale.

The micro kappa numbers measured were 3.0, 5.0, and 4.6 for the HW, SW, and MHW unbleached pulps (UB), respectively. Subsequently, the chlorine dioxide dosage was computed utilizing the kappa number, incorporating a chosen kappa factor of 0.25 following the prescribed experimental procedure. It can be noted from the results that the D-stages, employing chlorine dioxide (ClO_2), contributed significantly to both further delignification and augmentation of brightness. Since it was established from the delignification trials that the viscosity of the unbleached pulps was not suitable and could not be altered to target viscose production, the focus was then diverted to microcrystalline cellulose (MCC) production.

The results of bleaching are shown in Table 4-5. Observations reveal slight reductions in yields, potentially suggestive of pulp degradation or losses incurred during the washing phases. DP values showed a drop in comparison to the unbleached pulps for all species. It can also be noted that the bleaching stages applied resulted in depolymerisation since the intrinsic viscosity and DP were reduced further following each stage. In addition, the DP values remained well below the benchmark value for commercial DWP, further highlighting the non-suitability for viscose production. Since the DP remained >400, this conveyed the need for further modification for MCC which highlighted the need for acid hydrolysis treatment. The SW pulp displayed the highest DP followed by the MHW and HW pulps, indicating the SW pulp would require more severe acid hydrolysis conditions in the subsequent stages. Brightness increased by approximately 20% after bleaching but was slightly lower than that measured for commercial DWP.

Table 4-5 Bleached pulps derived from three different wood sawdust species (Air dried pulp basis).

Measurements	**Commercial DWP (91α Measured in lab)**	**HW pulp**					**SW pulp**					**MHW pulp**				
		UB	DED	DEpD	DEpP	DEDP	UB	DED	DEpD	DEpP	DEDP	UB	DED	DEpD	DEpP	DEDP
Micro kappa no.	Not available	3.0					5.0					4.6				
Bleaching yield (%)	Not available	-	87	90.4	88.4	93.7	-	91.6	84.7	84.3	89.1	-	92.5	91.2	93.1	86.8
Overall yield (%)	Not available	51.0	44.4	46.1	45.1	43.5	52.0	47.8	45.3	43.8	46.3	44.0	40.9	40.1	40.1	38.1
Intrinsic viscosity (ml/g)	421	195	189	180	200	183	380	331	370	342	310	313	243	242	222	205
DP	1316	553	533	503	569	512	1213	1031	1176	1073	954	966	717	714	646	587
ISO brightness (%)	93	67.0	87.4	88.5	81.0	87.0	66.0	86.9	84.7	77.4	88.4	72.0	86.0	86.1	75.4	86.3

Standard errors in measurements reported in Appendix A

Chemical characterisation to determine monosaccharide composition was only conducted on the optimised bleached samples to understand if any residual hemicellulose removal occurred during bleaching and benchmark the final bleached pulps against commercial DWP. The results are summarised in Table 4-6. Slightly higher concentrations were observed for xylose and mannose for the sawdust pulps in comparison to commercial DWP. In comparison to the unbleached pulps following delignification, the result suggests that little to no hemicelluloses were removed during bleaching. This could be attributed to the fact that the bleaching sequence applied may have approached its maximal efficacy in the removal of hemicellulose components. A picture of the air-dried bleached pulp is shown in Figure 4-4.

Table 4-6: Summary of monosaccharide analysis for the optimal bleached samples compared to commercial DWP (Air dried pulp basis).

Measurements	**Commercial DWP- HW derived (91α Measured in lab)**	**HW pulp**	**SW pulp**	**MHW pulp**
Bleaching conditions	-	DEpD	DEPD	DEDP
Glucose	91.8	85.5	89.1	89.5
Xylose	3.22	4.34	5.47	7.17
Mannose	0.72	0.00	6.89	1.64

Arabinose	0.00	0.00	0.00	0.00
Galactose	0.00	0.00	0.00	0.00

Standard errors in measurements reported in Appendix A

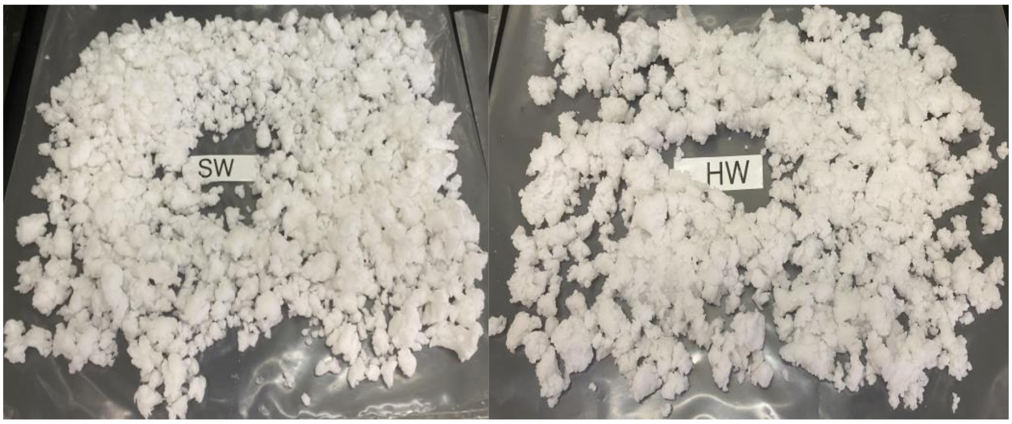


Figure 4-4: Air dried pulps after the bleaching and washing process (SW and HW).

Lignin content was not measured since the TAPPI AIL method is not suitable for bleached pulps. The brightness observed in comparison to the unbleached pulps suggests that any residual lignin remaining was effectively removed during bleaching since lignin imparts a yellowish-brown colour to the pulp which was no longer visible as shown in Figure 4-4 (Bodhlyera et al., 2015).

In this discerning context, the selection criteria culminated in the adoption of the DEpD sequence for HW pulps, while the DEDP sequence was deemed optimal for SW and MHW variants. These chosen sequences demonstrated the highest levels of brightness. Since the focus was diverted to MCC production, the optimum bleaching sequences were also selected based on the viscosity and brightness characteristics, conducive to the envisioned MCC production objectives.

4.4 MCC from sawdust pulp

The bleached sawdust pulps demonstrated promise as a viable feedstock for MCC production. However, to attain an analogous caliber of MCC as found in commercially accessible variants, additional refining of the bleached pulps was imperative. The process adopted to achieve this refinement was acid hydrolysis. The initial trials involving the LODP on the bleached pulps were instrumental in determining the requisite conditions for the acid hydrolysis process tailored to each distinct sawdust species.

4.4.1 *LODP experiments*

The LODP curves for the different bleached sawdust pulps are shown in Figure 4-5. The HW sawdust pulp reached a LODP of approximately 255 within 15 minutes using 4 M HCl and a hydrolysis temperature of 80 °C. These conditions were considerably milder compared to other studies, where, for example, MCC production from steam-exploded pulps necessitated temperatures as high as 170 °C to achieve LODP values in the range of 100-400 (Ewan et al., 1998). Toikka (2016) reported a LODP of 252 for Eucalyptus wood-derived MCC using the sulphite process which is within proximity of the value attained in this experiment. Similarly, the MHW sawdust pulp yielded comparable outcomes to the HW pulps, attaining an LODP of approximately 255, but over a longer duration of 30 minutes.

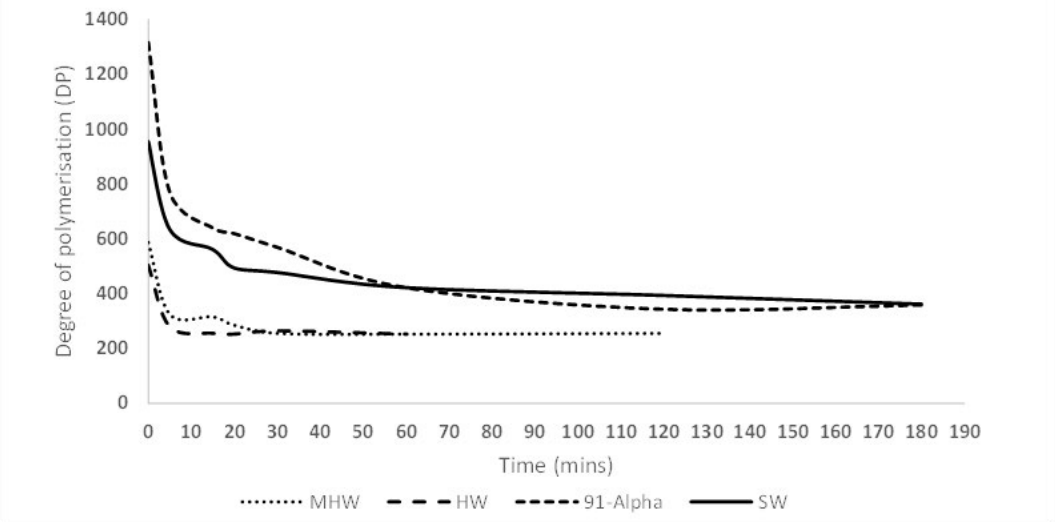


Figure 4-5: LODP curves for the different bleached sawdust pulps and 91α DWP.

In contrast, the softwood (SW) pulp required significantly longer hydrolysis times greater than 60 minutes to reach the LODP of 422. Similarly, the 91α commercial DWP also required a longer hydrolysis time of greater than 60 minutes before reaching LODP of 422. These findings highlight the extended processing period required for softwood material and 91α DWP to achieve the DP requisite for MCC production. In addition, studies have shown that the LODP of softwoods lies between 210-250, suggesting that an even longer time may have been required before seeing a level-off (Crowley and Crean, 2016). Toikka (2016) reported a LODP of 297 for pine wood-derived MCC using the sulphite process. An alternative consideration may involve the application of higher temperatures to expedite this process. Although some differences in LODP reported by other studies are noted, this could be attributed to the reaction conditions and type of pulp or raw material source. The results showed that the HW and MHW pulps showed a greater advantage in reaching LODP in comparison to the SW pulp and 91α DWP which is in agreement with results reported in other studies (Crowley and Crean, 2016, Toikka, 2016).

Interestingly, the outcomes also allude to the potential suitability of softwood for lyocell production, owing to its comparatively elevated DP. Overall, it was found that the HW sawdust pulp required milder acid hydrolysis conditions to reach a DP <400, which was one of the prerequisites for MCC. This was closely followed by the MHW pulp. The findings highlighted significant differences between the different sawdust pulps that may lead to diverse MCC grades.

4.4.2 *Characterisation of sawdust-derived MCC and comparison to commercial MCC*

The predetermined acid hydrolysis conditions (that which reached a DP < 400) were applied across to the respective bleached pulps. Subsequently, the resultant MCC was air-dried and chemically characterized. A comparative analysis was then performed between the MCC produced in this study to commercial MCC grades, as shown in Table 4-7. A decision was undertaken to focus on the chemical characteristics of the MCC since physical attributes such as particle size could be manipulated through subsequent processing steps such as milling or spray drying to achieve the desired granularity or a more homogenous powder morphology, as dictated by the exigencies of specific industrial applications. A preliminary trial involving rapid spray drying was evaluated to ascertain the feasibility of producing a powdered MCC sample. It was found that a finely powdered MCC material could be produced. This MCC material exhibited a color spectrum ranging from off-white to white which may be due to the wood source from which it was derived.

As shown in Table 4-7, the acid hydrolysis yields achieved were above 90% for all sawdust-derived MCC. Correspondingly, the DP values were all <400. These values compared well to the conventional range stipulated for commercial MCC grades, where DP typically lies below 350-400.To establish comparative benchmarks regarding the acid hydrolysis conditions for achieving the desired DP for MCC production, commercial DWP was subjected to analogous processing conditions. Notably, the 91α DWP and SW-derived MCC required an extended hydrolysis time ranging between 60-120 minutes to attain the desired DP in contrast to the HW and MHW pulps which required much shorter hydrolysis times. The milder acid hydrolysis conditions required for the HW and MHW pulps implied that more economical MCC production processes may be expected.

Whilst specific yield values for commercial MCC are not readily accessible, meaningful parallels can be drawn with MCC obtained from diverse agricultural by-products, such as corn cobs (19.7%), bagasse (7.4%), rice husk (10.9%), and cotton (60.4%) (Rojas et al., 2011). On a sawdust basis, the MCC yields for the three wood species ranged between 34-45% and were significantly higher compared to the aforementioned yields, except for cotton.

Table 4-7 Summary of typical properties of different grades of MCC produced.

	Commercial MCC	**91α MCC***	**HW MCC**	**SW MCC**	**MHW MCC**
Acid hydrolysis		80 ℃, 4 M HCl,120 min	80 ℃, 4 M HCl, 5 min	80 ℃, 4 M HCl, 120 min	80 ℃, 4 M HCl, 5 min
Overall yield (% based on sawdust)	nd	nd	45	44	34
Acid hydrolysis yield (%)	-	95	98	96	90
Viscosity (ml/g)	127	129	109	146	124
DP	334	343	279	393	325
		Monosaccharides			

Arabinose (%)	nd	nd	nd	nd	nd
Galactose (%)	nd	nd	nd	nd	nd
Glucose (%)	91.4	97.4	98.9	93.7	94.4
Xylose (%)	1.34	0.00	0.61	0.00	2.74
Mannose (%)	0.12	0.00	nd	2.98	nd

*nd- not detected (less than detection limits)
91α MCC produced from 91α DWP as part of this study
Standard errors in measurements reported in Appendix A

Although it was difficult to find results for the chemical characterization of MCC in the literature, one study by Vanhatalo et al. (2016) showed that for Avicel PH101the xylose content was 1.9%, while mannose and glucose content was 0.4% and 97.2%, respectively. Notably, no arabinose and galactose were detected. These results compared well to the results shown in Table 4-7, and the differences may be attributed to differences in the starting wood species and subsequent processing conditions for pulping, bleaching, and acid hydrolysis. Moreover, Vanhatalo et al. (2016) delved into different MCC grades derived from softwood kraft pulp. MCC with a DP value of 300 exhibited glucose, xylose, and mannose contents of 95, 2, and 2.5%, respectively. Comparatively, MCC attaining a DP of 450 displayed a reduced glucose content of 87.3%, alongside higher xylose (6.4%) and mannose (5.7%) levels. Finally, brown cellulose showcased glucose, xylose, and mannose contents of 87.7, 0.6 and 0.8%, respectively (Vanhatalo et al., 2016). The synthesized HW MCC exhibited monosaccharide concentrations similar to the DP 300 and the MHW and SW-derived MCC, slightly lower than DP 450 reported in the study by Vanhatalo et al. (2016).

In the context of additional monosaccharides, specifically arabinose, and galactose, their presence registers at exceedingly minuscule levels, thereby eluding detection via the instrumentation, an observation reported across other investigations (Vanhatalo et al., 2016). Nonetheless, it remains noteworthy that a slightly elevated hemicellulose content relative to the commercial MCC grade was discernible within the MHW and SW MCC variants. To ameliorate this disparity, the consideration of more robust bleaching conditions targeted at residual hemicelluloses and lignin appears meritorious. Alternatively, the feasibility of incorporating prehydrolysis treatment of the sawdust could potentially address this.

Figure 4-6 shows the transition from unbleached sawdust pulp to bleached sawdust pulp, culminating in MCC after acid hydrolysis. Based on the results from chemical characterization, a pronounced reduction in lignin content, manifesting through a discernible shift in colouration from light brown to near-white underscored the substantial alteration from the original starting material. Furthermore, a reduction in hemicellulose content was achieved, affirming the efficacy of the process.

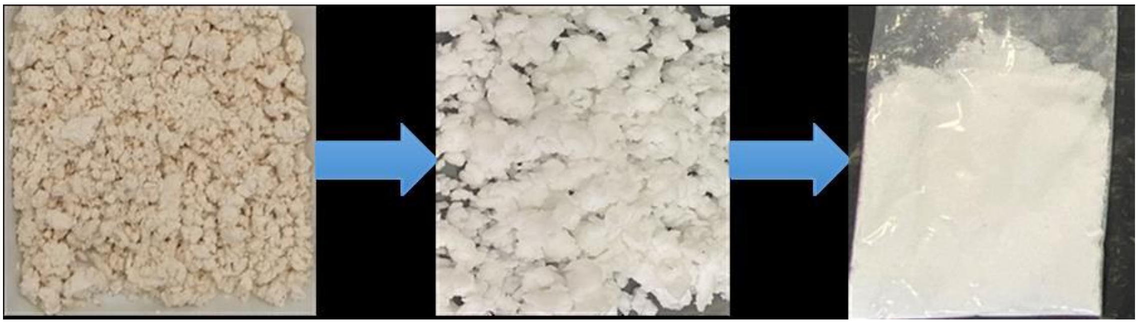


Figure 4-6: Transition of unbleached sawdust pulp, to bleached pulp and finally MCC following acid hydrolysis and spray drying.

4.4.2.1 Fourier transform infrared spectroscopy (FTIR)

FTIR was conducted on the sawdust-derived MCC samples and compared to commercial MCC (Figure 4-7) The library identification tool was used to identify the best fit and all 3 prepared samples and the commercial MCC was identified to best match Avicel PH101 commercial grade MCC. This confirmed that the FTIR analysis library identification showed high accuracy as the known grade of Avicel PH101 was used as the control sample for comparison. The best matching outcomes for all three formulated MCC samples consistently exceeded a 97% correspondence with Avicel PH101, confidently affirming the potential for characterizing the prepared MCC using FTIR spectroscopy. Notably, the FTIR spectra of the prepared MCC samples exhibited a noteworthy similarity, mirroring the spectra of the commercial MCC. This observation suggests a shared chemical structure among the samples, despite their distinct origins from varying source materials.

A close examination of the various characteristic peaks of cellulose was conducted to identify significant functional groups. Slight shifts in peaks were observed in comparison to those reported in the literature. A summary is provided in Table 4-8.

Table 4-8: Summary of possible functional groups associated with peak wave numbers.

Peak wavenumber (cm $^{-1}$)	**Possible functional group designation**	**Reference**
3338	O-H stretching, including hydrogen bonds, rupture of cellulose hydrogen bonds	(Chen et al., 2015, Rojas et al., 2011, Vora and Shah, 2017)
2901	CH and CH2 stretching rupture of cellulose methyl/methylene group	(Chen et al., 2015, Liu et al., 2017, Rojas et al., 2011, Vora and Shah, 2017)
1640	Close enough to 1650 cm ^{1} -OH absorbed from water or to carboxylic acids/ester groups	(Chen et al., 2015, Rojas et al., 2011)
1426	CH2 symmetric bending or intermolecular hydrogen at the C6 (aromatic ring)] group or aromatic skeletal vibrations, combined with -OCH3 in-plane deformations	(Chen et al., 2015, Rojas et al., 2011, Vora and Shah, 2017)

Peak wavenumber (cm $^{-1}$)	Possible functional group designation	Reference
1369	Aliphatic C-H stretch in CH3 was a possibility of CH bending.	(Kurian et al., 2015, Rojas et al., 2011)
1315	C-O of syringyl ring, which is an indication of lignin, also not far from 1330 cm^{-1} - O-H in-plane bending	(Rojas et al., 2011)
1158	Close to 1163 cm^{-1} C-O in lignin and xylan or 1161-1163 cm^{1-} C-O-C asymmetric stretching (β-glucosidic linkage)	(Chen et al., 2015, Liu et al., 2017, Rojas et al., 2011, Vora and Shah, 2017),
1102	The –COH stretching vibrations of secondary (C2 and C3) alcohols from glucose units which occurs at 1104 cm^{-1} or the crystalline to amorphous cellulose ratio that occurs at 1100 cm^{-1}	(Chen et al., 2015, Liu et al., 2017)
1053	C-O stretch in secondary alcohol which occurred at 1059cm^{-1} or a C–O–C pyranose ring skeletal vibration which occurs at 1054 cm^{-1}	(Chen et al., 2015, Liu et al., 2017)
1028	C-O stretch in primary alcohol occurring at 1030 cm^{-1}	(Chen et al., 2015)
900	Amorphous cellulose region or asymmetric (rocking) C-1 (β-glycosidic linkage) out-of-plane stretching vibrations that occur at 898 cm^{-1} or C-H rock vibration of cellulose occurring at 896 cm^{-1} or β-glucosidic linkages of amorphous cellulose which occurs at 895 cm^{-1}	(Chen et al., 2015, Liu et al., 2017, Rojas et al., 2011, Vora and Shah, 2017)

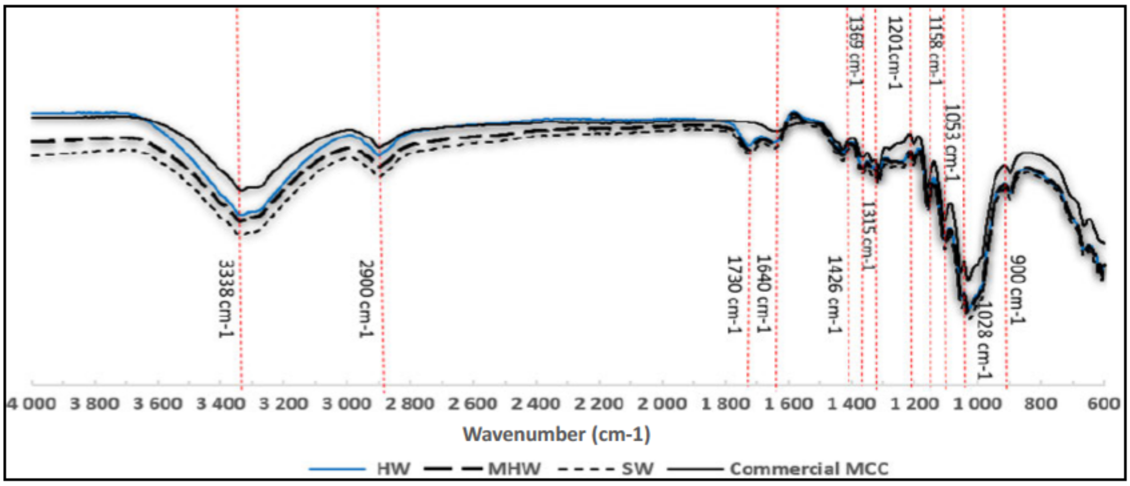


Figure 4-7: FTIR spectrum (Y-axis-Absorbance) for synthesized MCC versus commercial MCC.

The only slight variation for all synthesized MCC spectra in comparison to the commercial MCC, occurred at 1730 cm^{-1}. The narrow small peak may be attributed to C=O stretching of acetyl or carboxylic acid which may be associated with lignin and hemicelluloses which contain higher C=O linkage at 1765–1715 cm^{-1} (Azizan et al., 2016, Mora´n et al., 2008). However, the chemical characterisation showed that the measured monosaccharides for HW-synthesized MCC contained slightly lower amounts of hemicelluloses and all synthesized MCC exhibited lower levels of ASL than commercial MCC. However, AIL could not be measured and there is no direct measurement of hemicelluloses so there is a possibility that the presence of some hemicelluloses available in very small quantities is not accounted for. Alternatively, the peak could also be related to the peak at 1728 cm^{-1} described in a study which was attributed to oxidation (Mora´n et al., 2008). Since all synthesized MCC was derived from an initial oxidation process, this is highly possible especially because the peaks overlap for all synthesized MCC at this wavelength.

Further modification can be applied to eliminate lignin if necessary, however, lignin-rich MCC could be utilized in applications where the brown colour is acceptable, such as a plastic filler or a supplement in medication production (Vanhatalo et al., 2016). As reported, the phenolic group of lignin can form chemical bonds with plastic polymers, promote the combination of MCC and matrix, and give the composite better thermal stability properties. It was reported that the addition of a minute quantity of lignin to the feed could enhance the growth rate of broiler chickens and inhibit the proliferation of *Escherichia coli* (Yue et al., 2021). Lignin is among the key constituents of indigestible dietary fibre in humans. MCC, on the other hand, is a popular feed supplement used to improve cecum fermentation in animals or as a food additive to promote gastrointestinal well-being in humans. Therefore, lignin-enriched MCC has the potential to be utilized in various areas, such as polymer fillers, food additives, and pharmaceuticals (Yue et al., 2021).

4.4.2.2 Thermogravimetric analysis (TGA)

TGA was conducted on the three MCC samples and was compared to commercial MCC. The results are shown in Figure 4-8. The prepared MCC samples and the commercial MCC showed a loss of absorbed water at < 100 ℃ with approximately a 12-18% and 8% mass loss respectively, indicating that the synthesized MCC has a greater hydrophilic nature than the commercial MCC (Rasheed et al., 2020), whilst the e SW derived MCC showed a lower hydrophilic nature than the MHW and HW derived MCC.

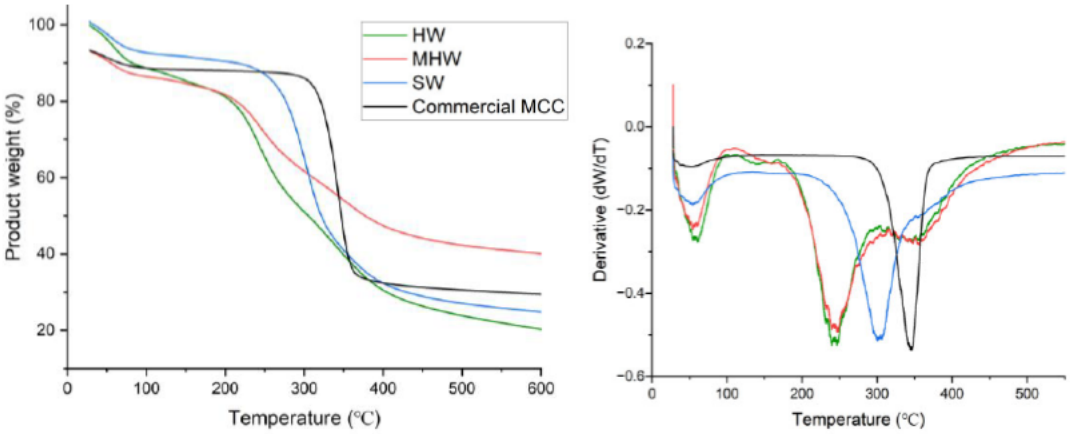


Figure 4-8: TGA and DTG curves for synthesized MCC versus commercial MCC.

Degradation peaks were also observed in the cellulose region for both prepared and commercial grades of MCC, representing decarboxylation, depolymerisation, and decomposition which occur in cellulose and hemicellulose fragments (Jahan et al., 2011, Rasheed et al., 2020). The decomposition began at around 174-197 °C for the prepared MCC samples and 293 °C for the commercial MCC suggesting a much greater degree of molecular arrangement of the commercial MCC (Rasheed et al., 2020). This also indicated that commercial MCC displayed the highest thermal stability followed by the SW, HW, and MHW MCC. This implied a high crystallinity of cellulose in the commercial MCC followed by the fact that the SW MCC would have a higher crystallinity than the MHW and HW, which would also share a similar crystallinity. The results confirmed the result seen in the CrI values later on in the XRD analysis. The reorientation of the crystals in cellulose is believed to promote increases in the initial temperature for degradation to occur (Hornung et al., 2021).

The decomposition peaks of the maximum mass loss were at approximately 240 °C for the HW and MHW-derived MCC, and 300 °C for SW synthesized MCC with a mass loss of approximately 52 and 63% respectively. The commercial MCC experienced the highest mass loss at 343 °C which equated to approximately 77%. Thermal characteristics play a crucial role in various applications, such as the utilization of MCC in the manufacturing of biocomposites, where the processing temperature may rise above 200°C. In this context, the SW MCC may be more suitable, given its sustained thermal stability. The suitability of the prepared MCC will therefore be highly dependent on the processing conditions applied for the end user products targeted and hence can vary widely.

For HW and MHW synthesized MCC, additional decomposition peaks were observed at temperatures 138 and 154 °C respectively, compared to the commercial MCC. This variance is correlated to the degradation of hemicellulose, a structural component characterized by a repertoire of saccharides contributing to amorphous structures, as well as less thermally resilient lignocellulosic constituents, which occurs at 135-250 °C (Zeleke et al., 2022). While another source indicates that the decomposition of lignin starts at around 160 °C continuing gradually throughout the process which may indicate that any degradation peaks before 250 ℃ may also be attributed to lignin (Hornung et al., 2021). For the three synthesized MCC samples, an additional peak was observed overlapping with the cellulose region. The degradation occurring in the temperature range of 375–520 °C is also attributed to lignin, which is known to be more thermally stable and resistant to degradation (Zeleke et al., 2022). The results align congruently with chemical characterization and FTIR analysis, signifying the presence of hemicelluloses, lignin, or both, relative to the commercial MCC.

At temperatures exceeding 380 ℃, the char residue was higher (~11-14%) for the prepared MCC compared to the commercial MCC (6%). This indicated a larger quantity of impurities in the prepared MCC samples as compared to commercial MCC. However, this observation was made following the acid hydrolysis. It is presumed that some acid remains on the pulp after washing which may be the cause of the high ash content. To mitigate this, suggestions were proffered, advocating an ultrafiltration purification phase for impurity removal before subsequent chemical characterization.

In summation, the prepared MCC demonstrates good thermal stability when contrasted with the commercial MCC, yet avenues for enhancement remain viable through further processing endeavours aimed at elevating thermal resilience to meet the requisites of specific MCC applications. In the purview of thermal stability, the softwood-derived MCC emerges as the most thermally robust, while HW and MHW derivatives exhibit comparable and slightly diminished stability.

4.4.2.3 X-ray diffraction (XRD) and Crystallinity index (CrI)

The diffractograms shown in Figure 4-9 (background correction applied) are typical for Cellulose I and exhibit 4 crystalline peaks at diffraction angles of approximately 2Ө = 14°, 16°, 22°, and 34°, thus confirming that the integrity of cellulose was not compromised during processing (Landry et al., 2011). The highest intensity peak observed at 2θ = ± 22.5° attributed to the crystalline structure of the cellulose whilst the minimum intensity was observed at 2θ = ± 18.4°, represented the amorphous region (Hassan and El-Sakhawy, 2005). The crystallinity indices for the various samples are provided in Table 4-9 and the range was evaluated between 5-60° according to the recommendation given by Yao et al. (2020).

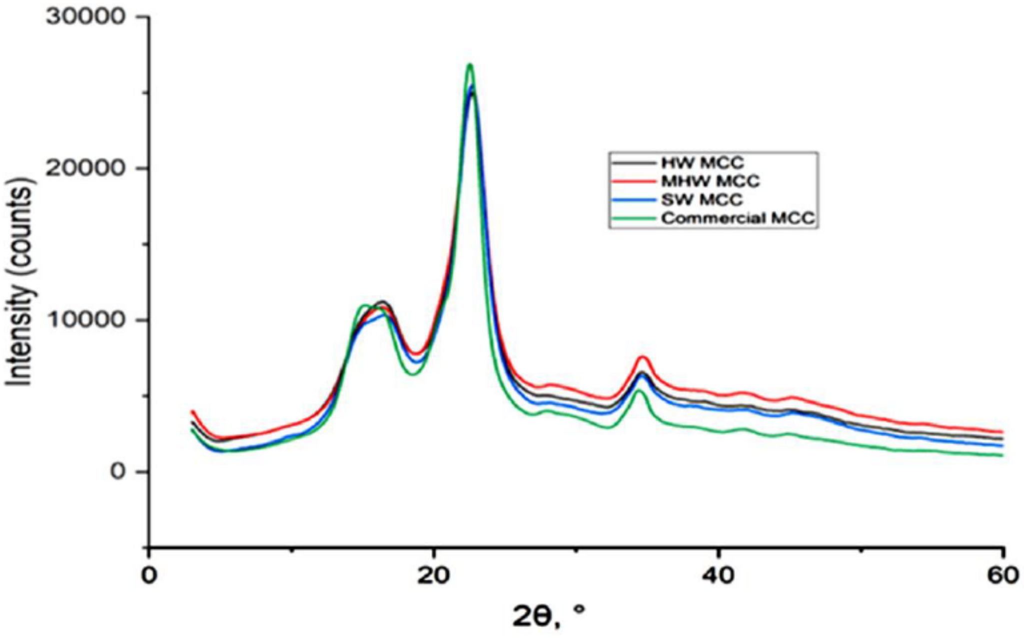


Figure 4-9: XRD plots illustrating the crystalline and amorphous regions for each of the synthesized MCC samples and commercial MCC using the Segal and peak convolution method.

An elevated CrI value indicates a rise in the amount of cellulose present (Jamasri and Yudhanto, 2021). This heightened content of crystalline cellulose contributes to enhanced chemical bonding, mechanical interlocking, and thermal stability (Jamasri and Yudhanto, 2021). It is suggested that the sharpening of the diffraction peak of MCC at 22.0° corresponds to an increase in crystallite size.

Two methods of evaluation were compared for accuracy and the results are shown in Table 4-9. In terms of the Segal method (Terinte et al., 2011) with a background subtraction applied, it was noted that the commercial MCC displayed a higher CrI (93%), whereas the HW and MHW, and SW-derived MCC showed similar values (approximately 86-90%). Similar values are reported in other studies using the peak height method (Getachew et al., Vanhatalo et al., 2016).

However, an imperative shift beyond the Segal method, accentuating the significance of peak deconvolution, is championed by French (2020). The peak deconvolution method (baseline subtraction applied) showed much lower CrI values. A deviation of approximately 18-23% materialized between the two analytical approaches. The values of commercial MCC with previously reported studies, employing the peak convolution method, ranged between 71 and 78% (Hassan and El-Sakhawy, 2005, Hussin et al., 2018, Kothari et al., 2019, Mittal et al., 2011). It is suggested that the Segal method is useful for comparing the relative differences between samples since the overestimation is relatively consistent across all samples as seen in this study (Park et al., 2010).

Table 4-9 Crystallinity indices for synthesized MCC compared to commercial MCC.

Sample	I (200)	I (am)	Total area of crystalline regions	Total area of amorphous and crystalline regions	CrI by Segal method (%)	CrI by peak deconvolution (%)
MCC commercial	28488	1967	47432	191903	93	74
Synthesized HW MCC	21532	2490	44039	197846	88	67
Synthesized MHW MCC	23245	3308	45743	204764	86	67
Synthesized SW MCC	25162	2404	51216	213393	90	72

In the realm of hydrolysis-based processing, encompassing variables such as temperature, duration, and acid concentration, it is observed that their influence on the degree of crystallinity remains relatively marginal. This pertains to the level of systematic order present in the arrangement of cellulose polymer chains (Hassan and El-Sakhawy, 2005). It appears that the origin of pulp has a greater impact on the crystallinity compared to processing conditions, which aligns with the manufacturing process of MCC, where acid treatment selectively targets the amorphous regions that vary with the type of pulp (Hassan and El-Sakhawy, 2005).

Results show that in terms of crystallinity, the different sawdust species, namely hardwood and softwood, did not affect the crystallinity significantly (<4%) since they are all from the same source (wood sawdust) but some differences were noted which can be attributed to the different wood species. In addition, the different delignification and bleaching conditions applied in the initial stages have not shown significant effects on the crystallinity of the synthesized MCC. The results correlate with the TGA results in which the SW sample having a lower decomposition onset temperature, was expected to have a greater degree of crystallinity as compared to the HW and MHW-derived MCC. As expected, the MHW and HW-derived MCC shared close similarities in decomposition onset temperatures and CrI values and the commercial MCC displayed the highest onset decomposition temperature and hence also exhibited the highest CrI.

It can however be deduced that the sawdust-derived MCC has a slightly lower (3-7%) crystallinity compared to the commercial MCC typically derived from DWP which uses wood chips. In terms of the TGA results, the commercial MCC shows a higher crystallinity (due to higher onset temperature) than the synthesized MCC which agrees with the CrI results. SW MCC also showed a slightly higher crystallinity than MHW and HW and was also in agreement with TGA findings since the SW onset temperature was observed to be slightly higher.

4.5 Pilot scale trials

4.5.1 *Delignification*

Initial assessments were conducted to evaluate the compatibility of Ammonium Persulfate (APS) with 316 stainless steels, a commonly utilized material for the construction of reaction vessels. A reference to work by Schweitzer (2007), revealed that the corrosion rate for 316 SS with APS at 60-70 °C corresponds to symbol G as shown in Table 2-8 and Figure 2-11 in section 2.7. This corresponds to a rate of 2-20 mpy. This symbol translates to a corrosion rate ranging from 2 to 20 mils per year (mpy), predicated upon a 10% APS solution. However, the envisioned process entails a considerably higher APS concentration, approximately 48.31%. This concentration surpasses that detailed in section 2.7 by a factor of approximately five. Consequently, we extrapolated a proportionally magnified impact, estimating a corrosion rate of around 100 mpy (2.54 mm/yr) under the assumption of a linear relationship and utilizing the upper boundary of the range. It's important to note that these calculations entail daily exposure, as the corrosion data pertains to stainless steel pipes. Based on this assessment, the corrosion risks were deemed minimal for the envisaged pilot trials' duration and scope.

The results are summarised in Table 4-10. Pulp yields obtained ranged from 35 to 51%, exhibiting a modest elevation over the corresponding outcomes achieved during the benchtop trials. The marginal differences in results in comparison to the benchtop trials are attributable to differences in the equipment design (stirring rates, materials of construction and mechanism, temperature maintenance etc.) and specific operational challenges which also resulted in unpulped rejects. The lower yield for the MHW sawdust-derived pulp is a result of an initial instance of effervescence, leading to the adherence of pulp to the inner walls of the reactor, resulting in incomplete pulping during the experiment. This phenomenon is attributed to the heightened operational temperature of 70 °C. Notably, the extent of rejected sawdust material remained at minimal levels, falling between 0.22-1.55 %.

The observed marginal reduction in yield is a foreseeable outcome, attributable to variations in operational procedures employed during the experimental trials. In terms of brightness measurements, the overall range spanned 66 to 72%, registering a slight decrement in comparison to the values attained in the benchtop trials. This diminution was expected, stemming from the utilization of dissimilar equipment as well as the incurrence of operational challenges.

The implications of the reduced brightness levels in the processed sawdust pulps necessitated a marginally augmented application of bleaching conditions downstream during Stage 2 processing. In light of the final targeted product MCC, a decision was made to restrict characterizations to those considered essential for progression to subsequent stages. This approach is intended to optimize the utilization of resources, with comprehensive characterization reserved exclusively for the fully prepared MCC product.

Table 4-10: Chemical characterization of sawdust derived unbleached pulp pilot scale.

	HW	**SW**	**MHW**
Delignification conditions	(3 M,60 ℃,4 h)	(3 M,60 ℃,6 h)	(3 M,70 ℃,3 h)
Yield (%)	46.0	51.2	35.0
Rejects (%)	1.35	0.22	1.50
Micro kappa no.	5.40	3.60	4.30

4.5.2 *Bleaching*

The characterisation of important parameters for the bleached pulps is summarised in Table 4-11. Efficacies in the realm of bleaching manifested in a range spanning from 92 to 98%. Subtle reductions in yield are reasonably attributed to the inherent processes of washing and the concomitant removal of residual hemicelluloses and lignin. When evaluated on a sawdust basis, the cumulative yields in this stage spanned from 32 to 50%.

A marginal adjustment necessitated the application of marginally elevated dosages of bleaching agents, stemming from the elevated kappa numbers observed in the unbleached pulps in comparison to the analogous observations made in the benchtop trials. Correspondingly, a kappa factor of 0.28 was introduced, informed by these empirical observations. It is worth noting that, analogous to the benchtop trials, the yields of the bleached pulps experienced a slight diminution. These losses, once again, trace their origins to the manipulations associated with handling and the sequential washing procedures.

Table 4-11: Chemical characterization of sawdust-derived bleached pulp pilot scale (Air dried pulp basis).

Measurements	**91α DWP**	**HW (DEpD bleached)**	**MHW (DEDP bleached)**	**SW (DEDP bleached)**
Bleaching yield (%)	Not available	97	92	98
ISO brightness (%)	92.6	83.8	78.8	85.7
Intrinsic viscosity (ml/g)	425	291	169	357
DP	1385	888	469	1127

Standard errors in measurements reported in Appendix A

As experienced with the benchtop trials, the intrinsic viscosity and corresponding degree of polymerisation (DP) were reduced significantly and the brightness and DP was significantly lower as compared to 91α DWP. This once again highlighted that the process resulted in some cellulose degradation and severe depolymerisation (due to the the oxidative nature of the APS) with even further reductions caused by bleaching as anticipated. Discernible differentiations were also evident in the pulp quality arising from the pilot trials as compared to the outcomes of the benchtop trials. A modest decrement in brightness, coupled with notably augmented intrinsic viscosity and DP, constituted the salient divergences. These disparities persisted despite minor adjustments introduced in the bleaching conditions. These outcomes collectively signify that the post-delignification pulp quality did not align with the standards achieved in the context of benchtop trials.

Despite the somewhat diminished brightness, the suitability for MCC production remained within acceptable bounds, given the product's inherent capacity to manifest as a white or near-white entity. However, the elevated DP values indicated the necessity for a more rigorous acid hydrolysis treatment regimen. Notably, the MHW pulp displayed the most visible variations in quality when compared with the benchtop trials. This discrepancy could be ascribed to the operational challenges that were encountered during the pilot trials. A picture of the bleached, air-dried, and blended variants before acid hydrolysis is shown in Figure 4-10.

Figure 4-10: Air-dried, bleached, and blended grade of pulp.

4.5.3 *Acid hydrolysis*

Yields for acid hydrolysis remained between 90-97%. Overall yields were found to be 30-42% which was slightly lower than that obtained in the benchtop trials. Given the elevated DP evident in the bleached pulps, a further refinement of the acid hydrolysis parameters was deemed necessary, mirroring the procedure established during the benchtop trials. Subsequent optimization led to the identification of optimal conditions: 4 M concentration and a 60-minute duration HW, 4 M concentration and a 5-minute duration for MHW, and 6 M concentration with a 120-minute duration for SW. The selection of these parameters was predicated upon maintaining a DP below 400 and achieving a CrI closely resembling that of commercial MCC. The chemical characterization of the final product is summarized in Table 4-12.

Noteworthy pH values for the prepared MCC products spanned the recommended range of 5-7. The MHW variant bordered on this range, potentially indicating the need for enhanced washing. Apparent from the analysis is a marginally heightened acidic character of the prepared MCC in comparison to its commercial counterpart. Subsequent to acid hydrolysis, the SW MCC exhibited discernible discolouration, which is believed to have arisen from the intensified acid concentration (6 M) utilized, potentially yielding a corrosive effect responsible for this outcome. A picture of the three different variants after blending is shown in Figure 4-11. Whilst reservations exist around using HCl due to environmental concerns, HCl was selected as the acid on the premise that some studies made mention of disadvantages of using it in the preparation of MCC such as the formation of sulfate groups onto cellulose chains; splitting of the sulfate groups during MCC thermal degradation may be the reason for the higher rate of degradation via weight loss and the possible attack of detached sulfate groups to the cellulose chains (Hanani et al., 2017). HCl is also believed to result in a higher crystallinity index of MCC as opposed to sulphuric acid (El-Sakhawy and Hassan, 2007). Considerations were however given to recovery of the HCl so as to minimize the negative environmental impacts.

Figure 4-11: Prepared MCC variants following acid hydrolysis, air drying, and blending.

Table 4-12 Chemical characterization of sawdust derived MCC from the pilot trials.

	Commercial MCC	**91α MCC**	**HW**	**SW**	**MHW**
Acid hydrolysis conditions	-	(4 M,80 ℃, 120 mins)	(4 M,80 ℃, 60 mins)	(6 M,80 ℃,120 mins)	(4 M,80 ℃, 5 mins)
Overall yield on sawdust basis (%)	-	-	42	41	30
pH	7.35	7.23	6.72	6.75	5.08
Molecular weight (g/mol)	339	339	339	339	339
Particle size (µm)	4-100	7-1100	4-1100	5-1100	9-1100
CrI (%)	89	87	84	84	76
LOD (%)	4.5	7.90	10	23	15
Intrinsic viscosity (ml/g)	142	129	131	147	102
DP	383	343	347	398	257
ASL (%)	0.30	0.67	0.29	0.51	0.32

	Commercial MCC	**91α MCC**	**HW**	**SW**	**MHW**
Acid hydrolysis conditions	-	(4 M,80 ℃, 120 mins)	(4 M,80 ℃, 60 mins)	(6 M,80 ℃,120 mins)	(4 M,80 ℃, 5 mins)
AIL (%)		Cannot be measured for bleached products			
Monosaccharides					
Arabinose (%)	0.00	0.00	nd	nd	nd
Galactose (%)	0.00	0.00	nd	nd	nd
Xylose (%)	2.10	0.00	nd	nd	nd
Mannose (%)	0.00	0.00	0.00	1.83	0.00
Glucose (%)	95.7	97.5	87.5	83.6	78.1

*nd- not detected (less than detection limits)
91α MCC produced in the laboratory using 91α DWP
Standard errors in measurements reported in Appendix A

Regarding loss on drying (LOD), notably elevated measurements were observed for the prepared MCC variants: 10% for hardwood (HW), 23% for softwood (SW), and 15% for mixed hardwood (MHW), in contrast to the 4.5 and 7.9% recorded for commercial MCC and 91α MCC respectively. The prescribed threshold for LOD does not exceed 6%. The elevated measurements are indicative of heightened moisture content, and it is envisaged that the application of a spray drying technique would prove efficacious in reducing the prevailing moisture levels.

Lignin analysis was constrained to the assessment of ASL, as an accurate representation of AIL measurements through the TAPPI method is restricted to semi-bleached products. Such methodology is unsuited for bleached products due to the anticipated AIL levels being below 1%. The ASL measurements for prepared HW and MHW samples closely mirrored those of the commercial MCC, while the ASL content in the SW and 91α MCC was slightly elevated. This variance, coupled with the significantly higher DP even after a 2-hour acid hydrolysis involving a higher acid concentration, substantiates the discernible divergence.

Monosaccharide analysis by high-performance liquid chromatography (HPLC) revealed indications of slight cellulose degradation in all prepared samples especially the MHW-derived MCC, as evidenced by the reduced glucose concentrations relative to the commercial MCC. However, the inability to detect monosaccharides characteristic of hemicelluloses, such as xylose, galactose, and mannose, in the prepared samples is indicative of substantial hemicellulose removal or reduction. Specifically, the absence of xylose in the prepared samples, whereas traces were detected in commercial MCC, underscores the profound reduction in hemicelluloses. Notably, traces of mannose were observed in the SW-prepared sample, a feature not observed in the other prepared samples or the commercial MCC. This observation aligns with expectations, as mannose is not typically associated with hardwoods.

4.5.3.1 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra are shown in Figure 4-12. Good similarities were observed between all prepared MCC products and the commercial MCC. All peaks corresponded and the only differences lay in the transmittance which is indicative of possibly different concentrations of the substances in the products. In addition, the library search once again identified all prepared MCC products to closely align with Avicel PH101 grade of commercial MCC. A best match of > 90% was found for all prepared MCCs. The FTIR results from the pilot scale samples showed an even greater overlap than that for all functional groups observed as compared to the benchtop trials since no distinctive peaks corresponding to lignin or hemicelluloses were observed between the synthesized and commercial MCC.

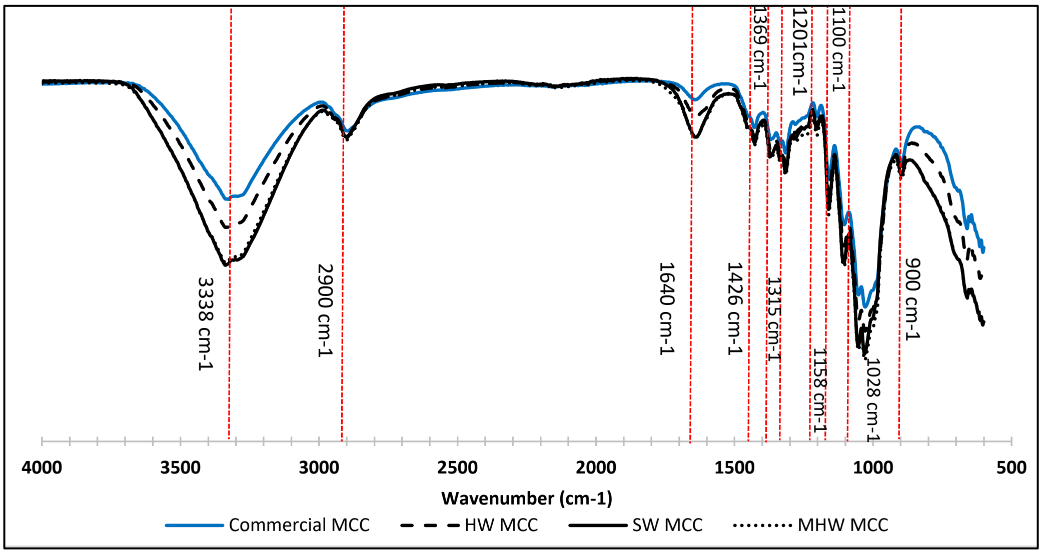


Figure 4-12: FTIR spectrum (Y-axis-Absorbance) for all final prepared MCC products against commercial MCC.

4.5.3.2 Thermogravimetric analysis (TGA)

The TGA plots are shown in Figure 4-13. The TGA results showed that all synthesized MCC and the commercial MCC had no peaks observed at 135-150 °C which is an indication of an absence or very low amounts of hemicellulose (Zeleke et al., 2022). No peaks were observed at 160-250 °C for all prepared MCC and the commercial MCC, also indicating an absence or very low amounts of lignin (Hornung et al., 2021). However, the commercial MCC exhibited a very small distinct peak at 463 °C, which may be attributed to the lignin at 375-520 °C or some other aromatization impurity (Zeleke et al., 2022). All synthesized MCC and the commercial MCC showed similar carbonization content beyond 380 °C (~7-8%).

Onset temperatures of the prepared MCC were found to be quite similar (250-289 °C) as compared to commercial MCC at 280 °C. This indicated good thermal stability of the prepared MCC. The temperatures corresponding to the greatest mass loss and corresponding to the cellulose region were between 329-352 °C for the prepared MCC and 332 °C for the commercial MCC. SW showed a mass loss of 69%, followed by commercial MCC (57%) while MHW and HW showed a loss of 36-38%. This result indicated that more cellulose was present in the SW sample which corresponds to the high onset temperature. The similarities between CrI should also be observed in this case.

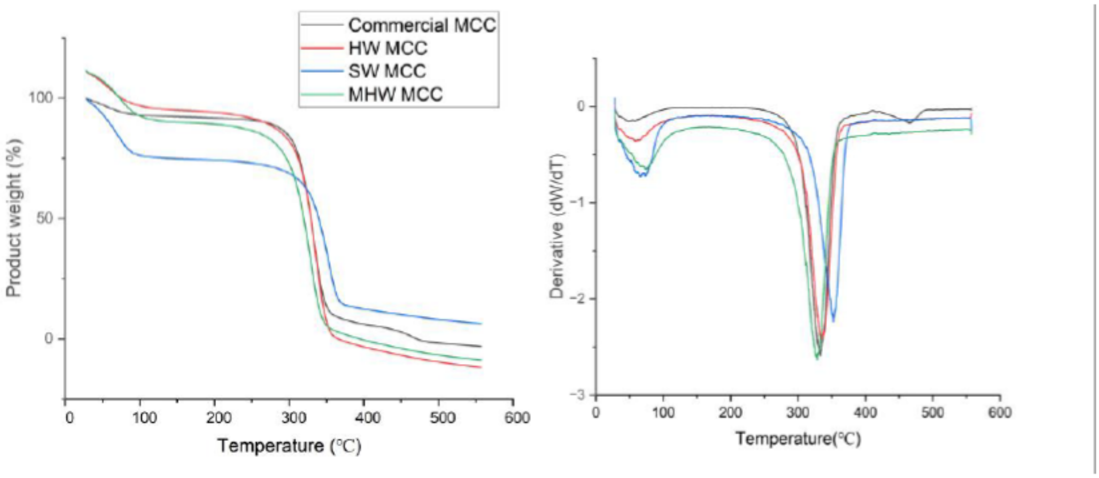


Figure 4-13: TGA and DTG plots for the synthesized MCC products against commercial MCC.

4.5.3.3 X-ray diffraction (XRD)

In terms of CrI, similar results to the optimized benchtop trials were achieved. XRD patterns are shown in Figure 4-14, where the 2θ value ranges from 0-60°. The four distinctive crystalline peaks associated with cellulose1β were observed for all three samples as expected. CrI values are calculated and presented using the peak height method since it was established that the Segal method is acceptable for relative comparison purposes in the benchtop trials (Table 4-13). The maximum intensity peak corresponding to I_{cr} was found located at approximately 22° whilst the minimum intensity corresponding to I_{am} was located at approximately 18° for all samples.

The HW and SW samples showed a closer CrI to the commercial MCC. A different batch of commercial MCC was used in the pilot trials comparison which explains the slight differences in CrI values as compared to that measured in the benchtop trials. The MHW MCC was slightly lower in comparison to the HW and SW-derived MCC. The 91α derived MCC displayed the closest CrI value to commercial MCC. This result was expected and can be confirmed with the corresponding monosaccharide measurements which showed MCC with a lower glucose content indicating some cellulose degradation and corresponds to the TGA findings of a lower onset of degradation temperature. In addition, it reflects on the theory discussed relating to the starting material playing a significant role in the acid hydrolysis process. The MHW delignification process operational issues encountered may have contributed to this finding.

Table 4-13 CrI results from pilot trials.

	Commercial MCC	**91α MCC**	**HW MCC**	**SW MCC**	**MHW MCC**
CrI (%)- Peak height method	89	87	84	84	76

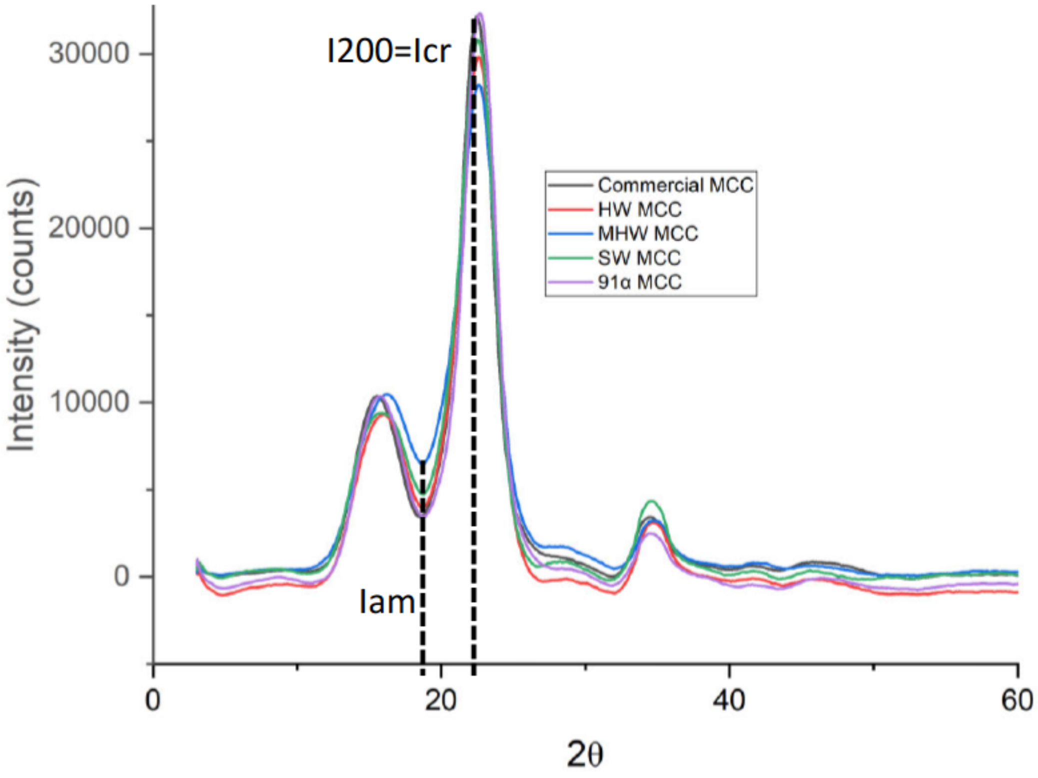


Figure 4-14: XRD patterns for the pilot scale prepared MCC and commercial MCC.

4.5.3.4 Scanning electron microscopy (SEM)

The SEM images (Figure 4-15) showed that the prepared MCC resembled non-uniform polydisperse particles as observed with commercial MCC, the MCC prepared from 91α DWP, and that of images found online. The prepared and commercial MCC also exhibits a rough texture which is also observed in literature images. However, it was observed that the prepared MCC appeared to be much larger, more aggregated, and agglomerated as compared to commercial MCC. This highlights the need for further particle size reduction and spray drying to assist in this area.

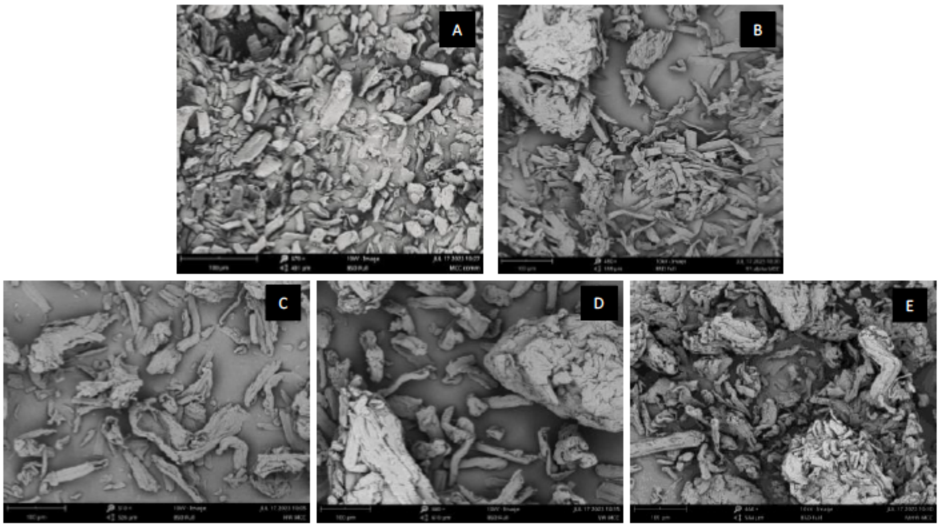


Figure 4-15: SEM images (100 µm) taken of the commercial MCC (A), 91α derived MCC (B) and HW (C), SW (D) and MHW prepared MCC (E).

Similarly, the SEM images from the literature (Figure 4-16) for different grades of MCC showed some aggregation and agglomeration. The non-uniform polydispersed particles are also evident.

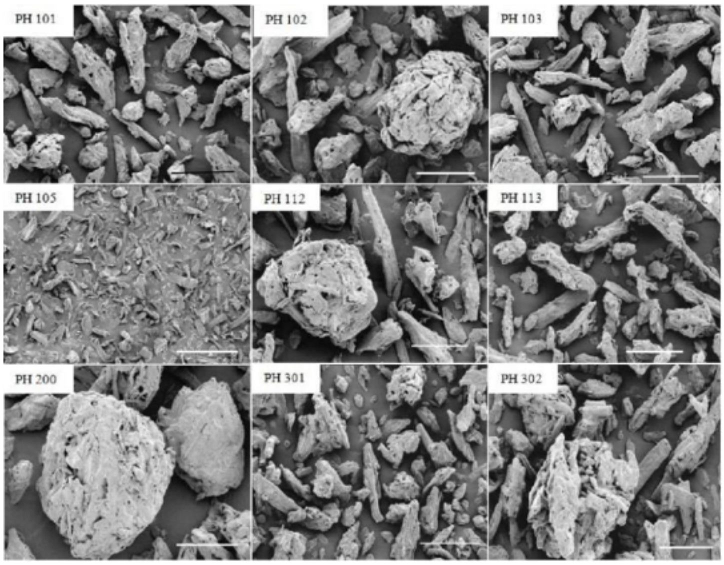


Figure 4-16: SEM images of different grades of MCC adapted from literature (Hindi, 2017).

4.5.3.5 Molecular weight determination by Liquid chromatography- Mass spectrometry (LC-MS)

Liquid chromatography- Mass spectrometry (LC-MS) spectra results (Figure 4-17) showed common peaks for all prepared samples and commercial MCC appearing at approximately 112, 311, 325, and 339 m/z with the largest peak representing the M^+ ion at approximately 339 m/z, therefore corresponding to a molecular weight of approximately 339 g/mol. This is in proximity with commercial grades which have a molecular weight of 325 and 342 g/mol (BOC-Sciences, 2023, ChemicalBook, 2023). The base peak was identified at 325 m/z for all samples, indicating some fragmentation occurred. The peak ion corresponding to 325 m/z may have resulted from the loss of a specific group or moiety from the parent ion, such as the loss of a small neutral molecule. The peak ion at 311 m/z may have resulted from a different cleavage or loss of specific atoms or groups from the parent ion. Slight differences in additional fragmentation peaks were noted for the MHW and SW MCC in comparison to the commercial MCC at approximately 137 m/z which could correspond to a type of monosaccharide ion called deoxyribose since the molecular weight is approximately 134 g/mol. MHW, SW, and commercial MCC also showed the presence of a compound at approximately 180 m/z which could correspond to mannose and or galactose ions, since the molecular weight is approximately 180 g/mol. The SW MCC peak showed additional peaks at 147 and 307 m/z. The 147 m/z peak may be associated with the xylose ion of which the molecular weight is approximately 150 g/mol. The 307 m/z peak may have resulted from a different cleavage or loss of specific atoms or groups from the parent ion.

The interpretation of mass spectrometry data often involves comparing observed ions with known mass spectra, fragmentation patterns, and chemical structures in the literature or databases, as well as considering the specific characteristics of your experiment and sample. Although the results may be correlated with findings from the HPLC results to deduce some conclusions, pinpointing the precise identity and origin of these ions would require more contextual information and would potentially require further analyses.

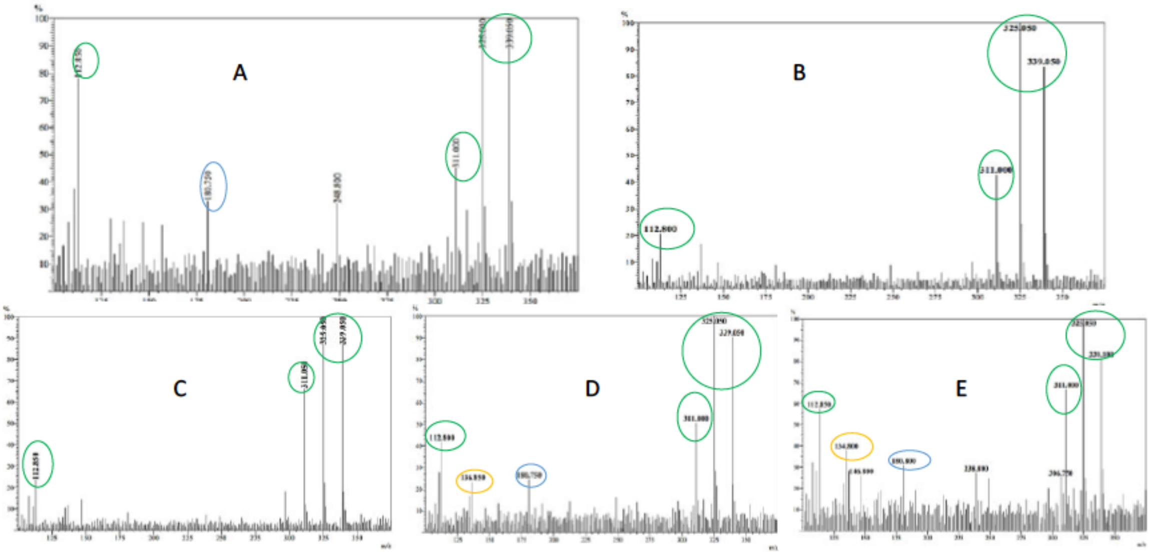


Figure 4-17: LC-MS spectra of prepared MCC and commercial MCC where A-Commercial MCC, B-91α MCC, C-HW MCC, D-MHW MCC and E-SW MCC.

4.5.3.6 Particle size distribution

Particle size analysis (Figure 4-18) showed that non-uniformity and a wide distribution were exhibited by the prepared MCC in comparison to the commercial MCC. In addition, the prepared MCC consisted of much larger particles (4-1850 µm) as compared to commercial MCC (4-100 µm). According to Chaerunisaa et al. (2019), this result reiterated the necessity for particle size modification by wet grinding or ball milling to attain a particle size suitable for the targeted grade.

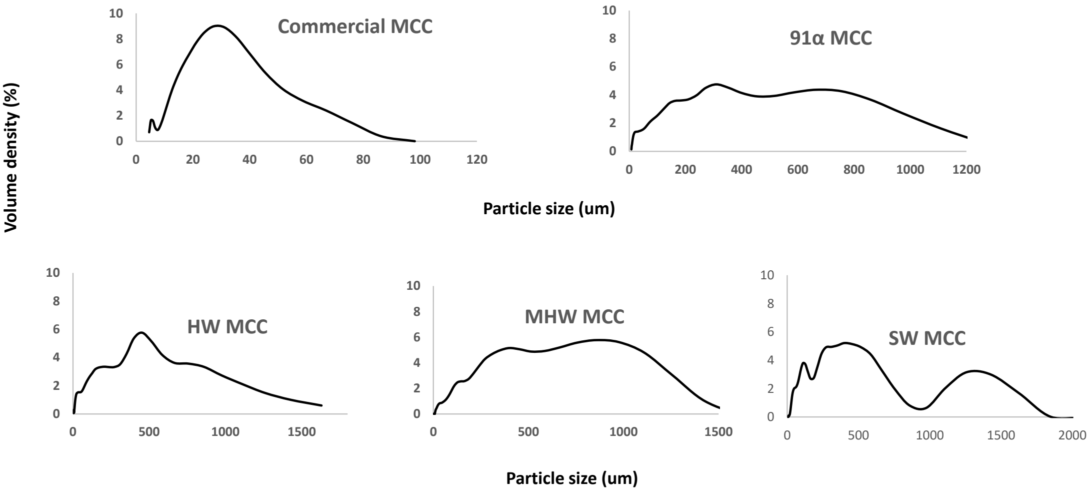


Figure 4-18: Particle size distribution for all prepared MCC samples versus commercial MCC.

4.6 Recovery and by-product consideration

4.6.1 *Delignification by-product recovery*

Table 4-14 below illustrates the results obtained from a test run to validate the titration method accuracy for quantification of APS in a solution. A few different sample volumes were attempted with 2 ml being the best candidate to obtain accurate results. Triplicate titrations per sample were conducted. As noted, the calculated concentrations obtained from the titrations agreed and highly comparable to the concentrations used to produce the solutions.

Research was conducted on APS recovery methods yielding techniques such as filtration, evaporation, and eutectic freeze crystallisation. Experimental endeavours elucidating filtration and evaporation at the benchtop scale, however, regrettably proved ineffectual in facilitating the retrieval of the target solid phase.

Table 4-14 Summary of titration results for APS.

Sample	Sample vol (ml)	APS concentration calculated (g/L)	APS mass used (g)/100 ml	APS concentration used (g/L)	Molar concentration (mol/L)	Molar concentration (average)
1 M	2.0	228	22.8	228.0	1.0	1.0
1 M	2.0	214	21.4	213.8	0.9	
1 M	2.0	228	22.8	228.0	1.0	
2 M	2.0	456	45.6	456.0	2.0	2.0
2 M	2.0	479	47.9	478.8	2.1	

The actual waste solution was then tested by titration using 2 ml of sample. However, a notable impediment surfaced during the titration process, characterized by difficulties in achieving the requisite endpoint colour change, signifying the establishment of a permanent pink colouration. This challenge potentially implied that the presence of APS within the filtrate might have been nominal, or possibly transformed into alternative chemical species.

Further research yielded the opportunity to extract ammonium sulphate (AS) and sulphuric acid by precipitation using ammonium hydroxide as a neutraliser and ethanol as a solvent followed by centrifugation (Lam et al., 2013). This method was attempted on a benchtop scale and the resultant precipitate was dried and together with the remaining liquid, both were analysed by raman spectroscopy to identify the peaks corresponding to AS and sulphuric acid. The first solid precipitate is a finely textured, powdery residue, whereas the second assumes the form of well-defined, elongated crystalline entities, resembling sharp rod-like structures. This visual distinction between the two solid forms is shown in Figure 4-19.

Figure 4-19: Solid residues emerging from precipitation.

The samples were then investigated using Raman spectroscopy (Figure 4-20 and Figure 4-21). According to Qiua et al. (2019), the most intense Raman peaks for AS are visible in the wavenumber range 975-992 cm^{-1}. The v2 mode occurs at about 449 cm^{-1}. The triplet v3 mode appears between 1092-1152 cm-^{1}. The v4 mode is found at 613-620 cm^{-1}. In Figure 4-20, the peaks corresponding to the v2 mode and the v4 mode at 452 and 612 cm^{-1} as well as the most intense peak lying around 973 cm^{1} agree with the findings that there is a presence of AS. In Figure 4-21, the intense peak at 973 cm^{-1} corresponds to an AS peak but the peaks at 1310 and 1449 cm^{-1} are not characteristic peaks of AS and may indicate the presence of some other compound or substance.

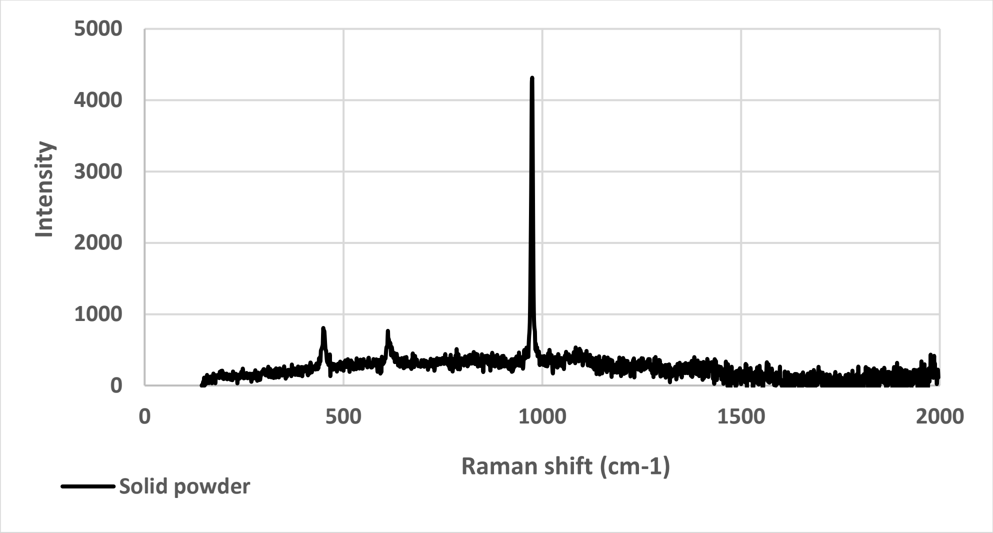


Figure 4-20: Raman spectrum for the solid powder residue emerging from precipitation.

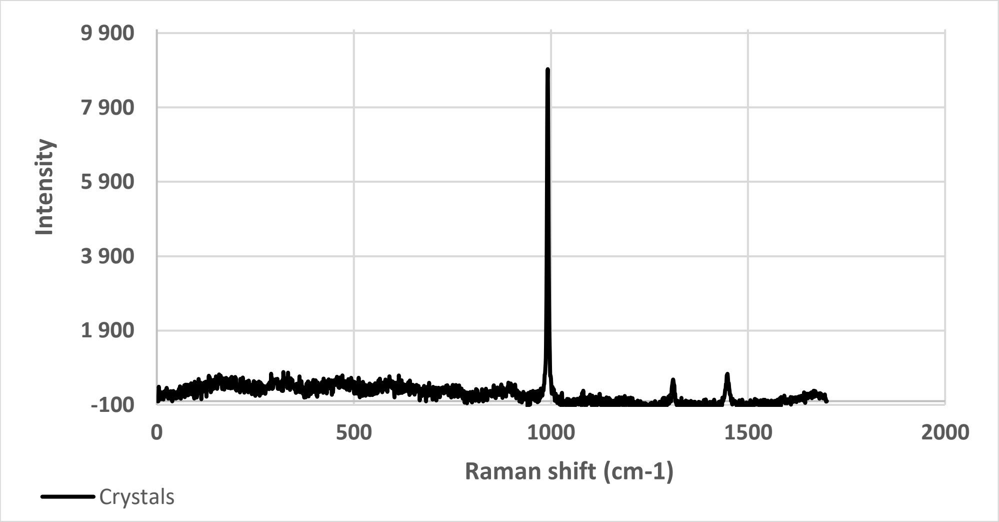


Figure 4-21 Raman spectrum for the crystal-like residue emerging from precipitation.

According to Lam et al., 2013, APS has been known to exhibit three primary peaks: 211 cm^{-1} (δm: deformational vibration of the S−O−O−S bridge), 835 cm^{-1} (νm: symmetric stretching vibration of the S−O−O−S bridge), and 1074 cm^{-1} (νs: symmetric stretching vibration of the S−O bond of the $SO_3{}^{-}$ group of the persulfate anion)(Lam et al., 2013). An aqueous ammonium sulphate (AS) solution exhibited a ν1($SO_4{}^{2-}$) band with only a small red shift from 981 to 977 cm^{-1} when the water−solid ratio decreased from 15.8 to 1.7. In Figure 4-20 and Figure 4-21, the peak observed at 973 cm^{-1} could be attributed to the presence of AS.

Analysis of the two solids precipitated out of solution using FTIR, revealed a lack of substantial comparability with pure APS, thereby corroborating and reinforcing the findings inferred from the earlier titration assays (Figure 4-22).

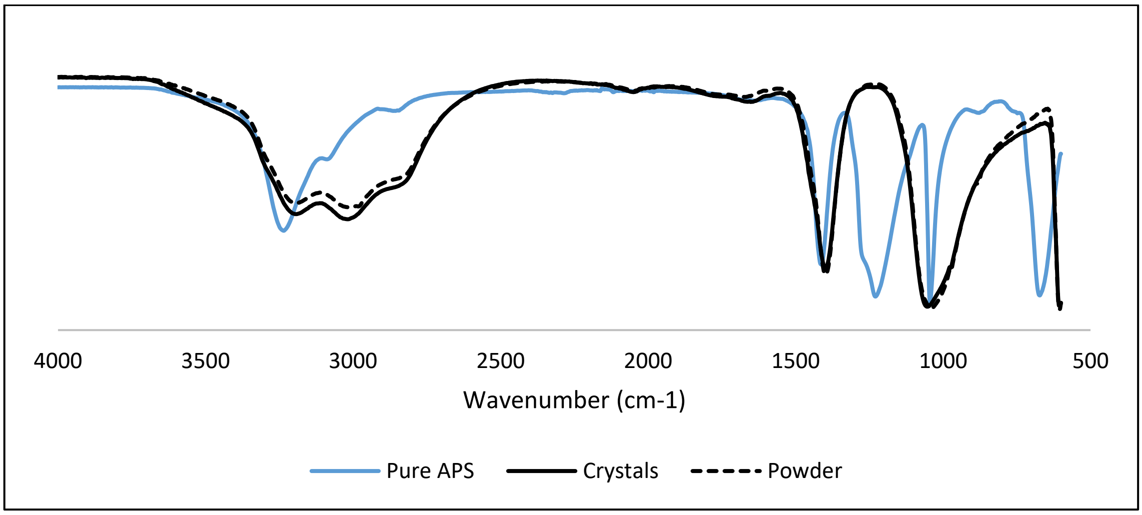


Figure 4-22 FTIR spectrum for the solids emanating from the precipitation experiment compared to pure APS.

Two layers of liquids were also found (Figure 4-23). Sulfuric acid is also believed to exhibit a ν1($SO_4{}^{2-}$) band at 982 cm^{-1}, with additional Raman bands at 890 cm^{-1} (ν(SOH): asymmetric stretching vibration of $HSO_4{}^{-}$) and 1040 cm^{-1} (ν1: symmetric stretching vibration of $HSO_4{}^{-}$ ions) (Lam et al., 2013). The intensity and frequency of these three peaks vary based on the acid concentration. Beyond 80 wt%, sulfuric acid typically exhibits only two distinct Raman peaks at approximately 910 (ν(SOH)) and 1050 cm^{-1} (νs) (Lam et al., 2013). Nevertheless, the intensity of the former peak diminishes with increasing H_2SO_4 concentration. This peak nearly disappears when the acid concentration exceeds 80 wt%, a condition where low water content hinders H_2SO4 from ionizing into H_3O+, and HSO_4 − or $2H_3O+$ and SO_4^{2-}. However, difficulties were experienced with generating a Raman spectrum for the liquids as they were found to exhibit high fluorescence and hence no analysis of the spectrum could be conducted.

Titration methods were used to identify the presence of sulphuric acid (Titrations.Info, 2009). 0.1M NaOH and Phenolphthalein indicator were used to identify the concentration of sulphuric acid. Liquid 1 showed a concentration of 0.028 M sulphuric acid whilst liquid 2 showed a concentration of 0.13 M sulphuric acid. Liquid 1 turned to a dark pink solution indicating a high presence of a basic solution when Phenolphthalein is added. Hence it is suspected that liquid 1 was the remaining ethanol or NH_4OH solution containing trace amounts of sulphuric acid.

Figure 4-23 Two layers of liquid emanating from the precipitation reaction filtrate.

FTIR analysis library search (Figure 4-24) revealed that liquid 1 could potentially be ethanol as also confirmed by the titration applied. The library search provided a 96% match for ethanol. Ethanol recovery is also possible in this case and is recommended for re-use in the precipitation process.

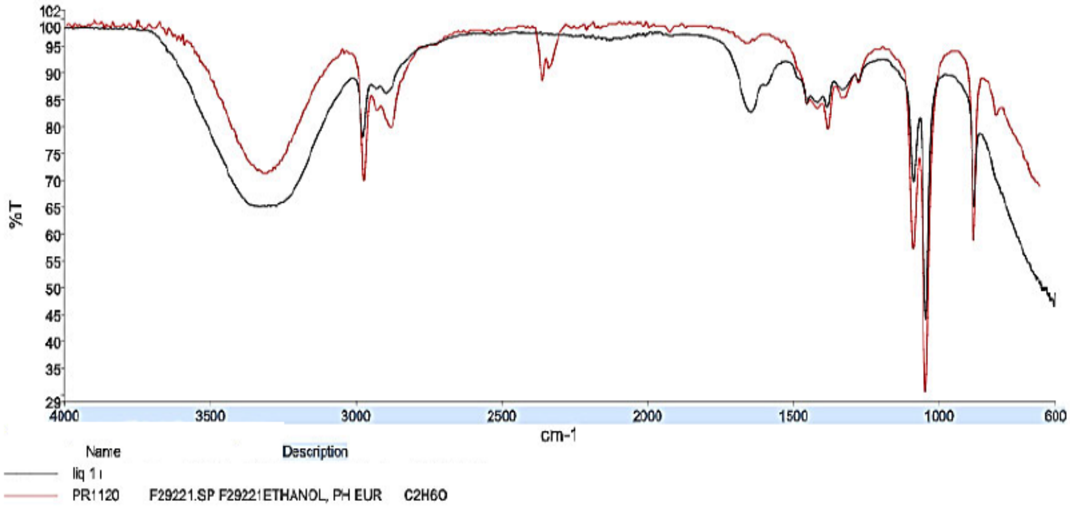


Figure 4-24: FTIR library search spectrum showing the best match for liquid 1

Ammonium sulphate and sulphuric acid can potentially be extracted as by-products from the waste liquid. The tests and simple calculations showed that approximately 16% of AS can be extracted, and this must be taken into consideration in the techno-economic study to understand if the extraction process is viable.

Both chemicals have significant value. According to available literature, AS finds widespread application in nitrogen (N)-based fertilizers for crop production, especially when both nitrogen and sulphur (S) are needed (Mosaic, 2023, Powlson and Dawson, 2022). Its high solubility makes it versatile for various agricultural applications (Mosaic, 2023). Beyond agriculture, AS is utilized by food companies as a dough conditioner for bread products, in fire extinguisher powder, and as a flame-proofing agent. It serves multiple purposes in industries such as chemicals, wood pulp, textiles, and pharmaceuticals (Mosaic, 2023, National.Library.of.Medicine, 2023, Power2SME, 2023). In the pharmaceutical sector, AS aids in water purification and vaccine manufacturing by facilitating the removal of excess proteins and contaminants. The chemical industry employs it for persulfate production, while the textile industry uses it as an additive in dye baths, wadding, and wicks. (Power2SME, 2023). Additionally, the wood pulp industry utilizes it in yeast and sulphite liquor production (National.Library.of.Medicine, 2023). Ammonium sulphate is also valued as a decontaminant in household products like detergents, toothpaste, shampoo, dental cleansers, and water softeners (Power2SME, 2023).

Conversely, sulfuric acid is incredibly versatile and is primarily employed in fertilizer production, contributing to the generation of phosphoric acid for phosphate fertilizers (Byjus, 2023). It serves various other purposes, including metal cleaning, impurity removal from oil, and the manufacturing of chemicals such as nitric acid, hydrochloric acid, dyes, drugs, and explosives. The wastewater industry utilizes sulfuric acid in water treatment processes, the textile industry incorporates it in rayon manufacturing, and the paper industry relies on it for producing aluminum sulphates (Byjus, 2023, Ecolink, 2023). In the medical field, sulfuric acid is used to damage the DNA of cancerous cells through the production of chemotherapy drugs and ointments for treating various skin infections. It is a fundamental component of topical ointments, like Debacterol, used in canker sore treatment (Byjus, 2023, LabProInc, 2022).

4.6.2 *Acid recovery (HCl)*

Large amounts of acid water are expected (to process 500 g o.d pulp, approximately 25 litres) due to the liquid-to-solid ratio being 50:1 for the acid hydrolysis process. For this reason, a suitable HCl regeneration process was considered. The proposed process (BetaControl systems, 2023) is useful since the water is also treated and can be recycled into the process. The concentration of HCl in the filtrate is unknown but it is assumed that a very high concentration exists since the pH is between 1-2. Recycling the acid and the water using the prescribed process can potentially enhance the economic viability of the process.

4.7 Techno-economic evaluation

4.7.1 *Fixed capital costs*

The fixed capital costs (Table 4-15) were estimated and calculated using guidance and recommendations from various engineering plant design sources. Land costs were estimated as 8% of the total purchased equipment cost (Peters and Timmerhaus, 1991). Building capacity was estimated to accommodate adequate office space which supports a staff size of approximately 20-30 people, a large boardroom, kitchen, and canteen area, an adequately sized chemistry and pilot plant and quality control laboratories, ablutions (outside, office area and lab area), workshop, plant equipment floor area, control room area, packaging area, storage/warehousing, recycle and hazardous waste storage, yard space, parking area, reception area, security check area. Taking all the above areas into consideration with a 10% space clearance for passageways etc, a land floor size of approximately 4000 m^2 is required.

The equipment costs were estimated using the correlations per specific unit provided in Towler and Sinnott (2008) and then using the Chemical Engineering Plant Cost Index (CEPCI) for the quoted and the current year as well as incorporating the conversion factor for stainless steel. Installation costs were estimated using the installation cost factors provided for different units of equipment (Peters and Timmerhaus, 1991). Maintenance costs were estimated as 5% of the purchased equipment and installation costs (Towler and Sinnott, 2008). It was evident that certain costs remained uniform across all MCC products. However, equipment and resultantly installation, and maintenance costs for the MHW and SW processes are much higher due to an additional bleaching stage required in the process.

The costs for the chlorine dioxide (ClO_2) plant including installation and maintenance were calculated separately and added as an additional fixed cost. The costs of the wastewater treatment plant (WTTP) including installation and maintenance were also determined individually and added as an additional cost. Taxes were estimated using an online calculator for small industrial businesses. The tax was estimated at 28% of the gross income after deducting R608 013 using an online tax calculator. The SW process generates more revenue than the MHW process due to the higher yields and thus the tax implications are slightly higher resulting in higher overall costs.

Table 4-15: Summary of estimated fixed costs for all prepared MCC species.

Type of cost (R)	HW	MHW	SW
Land	6 698 227	6 914 581	6 849 949
Building (offices/lab facility)		8 400 000*	
Lab instruments and PCs		5 000 000*	
Office furniture		500 000*	
Plant equipment	83 727 841	86 432 267	85 624 366
ClO_2 plant (incl installation & maintenance)	5 937 865	5 937 865	6 102 661
Trucks		1 000 000*	
Bobcats		800 000*	
Installation	43 542 601	48 109 018	47 788 809
Maintenance	6 363 522	6 727 064	6 670 659
Taxes	67 029 756	59 637 756	67 029 756
WTTP (wastewater treatment plant)	23 867 956	23 867 956	23 867 956
Total	**252 867 768**	**253 326 508**	**259 634 156**

* The value applies to all species

Items such as lab instruments, vehicles, and office furniture were estimated based on a startup facility and were held constant and assumed to be the same for all three processes. It is important to note that fixed costs can easily be paid off if the process is economically viable.

4.7.2 *Running operational costs per month*

Operational costs (Table 4-16) are running costs endured over the monthly periods to ensure the smooth operation of the plant. Bond costs for the land were calculated using an online bond calculator using no initial deposit and an interest rate of 11.75% over ten years. Municipal property rates were estimated using an online calculator using the municipal rate value multiplied by a given rate for industrial property of 0.02560 divided by 12 months to obtain a monthly rate. Water and electricity costs were determined using the latest available and documented local municipality tariffs for small industrial businesses and the total requirement based on mass and energy balances carried out per process. Labour requirements were estimated as the same for all processes, assigning approximately 2-4 technical staff workers per process stage, to permit shifts if required or accommodate the absence of a staff member. The salaries were estimated based on an online pay scale. The ClO_2 process costs were calculated separately once again. Materials produced by the process that cannot be recycled or sold as by-products must be disposed of as waste (Towler and Sinnott, 2008). Hazardous waste disposal was estimated on the costs obtained from the pilot process and scaled up according to the mass balances.

Overheads and contingencies were roughly estimated as the same for all three processes. Once again, the MHW process exhibited higher monthly costs followed by the SW process due to higher utility and raw material consumption due to lower yields of the process. Although the MHW process required shorter delignification and acid hydrolysis times, the heating requirements were much more demanding for the raw material masses in a shorter period resulting in a higher electricity cost. Hence the SW process benefits electricity cost savings due to the longer processing times.

Table 4-16: Summary of estimated monthly operational costs for all MCC prepared species.

Type of cost (R)	HW	MHW	SW
Bond rate	95 135	98 207	97 289
Rates	14 290	14 751	14 613
Water Utilities	1 191 130	1 208 044	1 301 731
Electricity utilities	891 966	3 555 446	774 438
Raw materials	12 142 604	14 968 026	14 931 481
ClO_2 production	207 895	207 895	215 649
Labour	1 155200	1 155200	1 155200
Hazardous waste disposal	6 675176	6 675176	6 675176
Overheads (fuel & consumables etc.)		500 000*	
Contingencies		500 000*	
Total	**22 386 300**	**25 229 092**	**25 391 139**

* Figure applies to all species

4.7.3 *Market research*

To identify the market size of MCC in SA and determine the average production tonnage required per day, data retrieved from SARS over 3 years shown in section 2.10.1 was analysed and manipulated and used to calculate the average tonnage per day, and the three-year average was calculated to be approximately 0.55 tons per day in SA. It was decided that 1 ton of MCC would be produced per batch per day to also export some MCC potentially at competitive rates.

The average cost of MCC per kg is approximately R1500-2500 per kg (Ninelife, 2023, Ubuy, 2023, Wantitall, 2023). Hence for 25 tons produced per month, an expected revenue of approximately R25 million is calculated by offering a more competitive rate of R1000 per kg.

The economic parameters (Table 4-17) provide some insightful information on whether the processes would be economically viable. The plant is expected to operate at 25 days per month which equates to 300 days per year. Due to long reaction periods, it was decided that one batch per day would be reasonable. As a result of yields, the highest revenue obtained is by the HW and SW process with the MHW process lagging. An investment of R500 million rands was selected to compensate for the total fixed costs with a surplus of almost double the costs for any unplanned or costs not accounted for. These cash flows however are projections or expectations.

The ROI and IRR were calculated, over 10 years with a net income increase of approximately 10% on each progressive year, the result is similar for the SW and HW process and slightly lower for the MHW process. However, the PBP lies between 2-3 years for all processes meaning the invested money will be recuperated within similar time frames and the associated risk exposure is also over a short period. This is a result of the capital investment being set at a fixed amount for all processes. The ROI and IRR both provide insight into the performance of the project. ROI shows the total growth since the start of the project and has been represented as an average of 12 months, while IRR shows the annual growth rate. Over a year, the two numbers are roughly the same. The economic parameters discussed are indicative that the processes are indeed profitable and viable with the HW and SW process being more viable and offering a larger ROI and IRR than the MHW process.

Table 4-17: Summary of calculated economical parameters for all prepared MCC species.

	HW	**MHW**	**SW**
MCC yield after acid hydrolysis (% based on sawdust)	42	30	41
Selling price per kg (R)		800	
Production MCC per batch/day (kg)	1000	890	1000
Number of operational days per month		25*	
Number of operational days per year		300	

	HW	MHW	SW
Revenue per year (R)	240 000 000	213 600 000	240 000 000
TIC (Total invested capital) -R		500 000 000	
TDC (Total discounted capital)- R	247 132 232	246 673 492	240 365 844
Depreciation (R)	24 713 223	24 667 349	24 0365 84
Average ROI (%)	63.1	54.6	62.2
IRR- Internal rate of return (%)	56.2	49.9	55.5
PBP (payback period) in years		2-3*	

* Figure applies to all species

4.7.4 *Recovery considerations effect on fixed and operational cost and economic parameters*

Recovery considerations are always worth investigating to reduce the environmental footprint of the process by waste reduction and to ensure maximum revenue from the process. According to Towler and Sinnott (2008), determining the economic feasibility of byproduct recovery poses challenges, primarily in evaluating whether the additional processing costs justify the recovery. It is advisable to weigh the costs involved in recovering and purifying the byproduct against its value and the savings in waste disposal costs. A practical guideline for an initial assessment, especially in large plants, is to consider byproduct recovery economically viable when the net benefit surpasses $200,000 per year, equivalent to R3,614,000 per year (Towler and Sinnott, 2008).

The estimation of the AS recovery plant to recover AS from the APS filtrate waste from the delignification process was estimated separately and then incorporated into the total costing to identify if the techno economics were improved (Table 4-18).

The fixed costs of the recovery plant range between R35 and 65 million. Higher costs are expected for the MHW process due to a larger amount of waste filtrate expected from the process as a result of the lower yield. This results in a higher overall fixed cost for the respective processes (Table 4-18).

Table 4-18: Summary of estimated fixed costs adjusted according to AS recovery considerations for all prepared MCC species.

Type of cost (R)	HW	MHW	SW
Land	6 698 227	6 914 581	6 849 949
Building (offices/lab facility)		8 400 000*	
Lab instruments and PCs		5 000 000*	
Office furniture		500 000*	
Plant equipment	83 727 841	86 432 267	85 624 366
ClO_2 plant (including installation & maintenance)	5 937 865	5 937 865	6 102 661
AS recovery plant	35 632 748	64 742 755	37 407 748
Trucks		1 000 000*	

Type of cost (R)	HW	MHW	SW
Bobcats		800 000*	
Installation	43 542 601	48 109 018	47 788 809
Maintenance	6 363 522	6 727 064	6 670 659
Taxes	67 104 013	62 304 013	67 104 013
WTTP (wastewater treatment plant)	23 867 956	23 867 956	23 867 956
Total	**288 574 773**	**320 735519**	**297 116 161**

* Figure applies to all species

The monthly recovery costs once again are higher for the MHW process due to more utilities and raw materials and larger sized equipment required to handle the larger amount of filtrate. The monthly operational costs range between 18-27 million which results in a higher overall operational cost of the plant (Table 4-19).

Table 4-19: Summary of estimated monthly operated costs adjusted according to AS recovery considerations for all prepared MCC species.

Type of cost (R)	HW	MHW	SW
Bond rate	92 000	92 000	92 000
Rates	14 290	14 751	14 613
Water Utilities	1 559 425	1 208 044	1 301 731
Electricity utilities	701 943	3 555446	774 438
Raw materials	12 142 604	14 968 026	14 931 481
Clo2 production	207 895	207 895	215 649
AS recovery (Labour, raw materials & utilities)	18 850 379	26 861 222	19 141 685
Labour	1 155200	1 155200	1 155200
Hazardous waste disposal	6 675176	6 675176	6 675176
Overheads (fuel & consumables etc.)		500 000*	
Contingencies		500 000*	
Total	**42 398 912**	**55 737 760**	**45 301 973**

***** Figure applies to all species

The yield calculated for AS recovery through the processes described in section 4.6.1 is rather low (16%). AS typically sells for R87 per kg. The selling price is selected at a competitive rate of R80 per kg (Table 4-20). The largest quantity of AS is produced from the MHW process whilst the HW and SW process quantities are rather similar. Revenue generated per year ranges between 72-102 million per annum which is well over the prescribed amount of R3 614 000 per year (Towler and Sinnott, 2008). In addition, the hazardous waste costs of 6 675176 could be reduced significantly. This cost-saving is not incorporated in the costs in Table 4-20, however, it is evident that slight improvements in the ROI (78-84%), IRR (66-70%), and PBR (1-2 years) exist in comparison to the original configuration.

Over the projected lifespan of the plant, various assumptions may change, including potential increases in raw material and energy prices, overestimation of product uniqueness, actions by competitors, and insufficient patent protection, which might not materialise or have consequences in the project's initial years (Wagenmakers, 2017). Short Payback Periods (PBPs) serve to minimize such risks, enhancing the economic appeal of a project. In the chemical industry, a PBP of typically no more than 3 years is often sought (Wagenmakers, 2017). The MHW promises a slightly higher ROI and IRR as a result of the additional revenue obtained from the larger quantity of the AS product.

Table 4-20: Summary of calculated economical parameters adjusted according to AS recovery considerations for all prepared MCC species

	HW	**MHW**	**SW**
Yield of AS (%)		16*	
Selling price per kg (R)		80*	
Production AS per month (kg)	3032	4245	3106
Number of operational days per month		25*	
Number of operational days per year		300*	
Revenue per year for AS (R)	72 775 017	101 885 023	74 550 017
Combined Revenue per year (R)	312 775 017	341 885 023	314 550 017
TIC (Total invested capital) -R		500 000 000*	
TDC (Total discounted capital)- R	211 499 484	181 930 737	202 958 096
Depreciation (R)	21 149 948	18 193 074	20 295 810
Average ROI–Return on investment (%)	78.7	84.0	78.2
IRR- Internal rate of return (%)	67.1	70.3	66.6
PBP (payback period) in years		1-2*	

* Figures apply to all species

Another recovery process worth considering for improving the techno-economic viability of the process is the recovery of HCl from the acid hydrolysis process. Large quantities of HCl are utilised in the acid hydrolysis process due to the significantly large liquid-to-solid ratio of 50:1 as well as the high concentrations of 4 and 6 M. For this reason, high concentrations are expected in the acid wastewater. It is recommended that the HCl be recovered and recycled to the acid hydrolysis process, thereby reducing the raw material costs required to purchase fresh acid.

The recovery of HCl is a well-documented and researched process and hence calculations were conducted using estimates adapted or recommended for the selected process described in the recovery considerations chapter. Evaporative recovery systems are believed to cost between US$6 and US$10 per metric ton of Spent Pickle Liquor to operate (Cullivan and Cullivan, 2023). Hence operating costs were estimated based on R181 per metric ton (Table 4-21). Fixed costs for the recovery plant which include equipment costs, installation costs, and maintenance costs were estimated as calculated previously. The total monthly cost of purchasing fresh HCl for each run was used as a basis to determine if recovery of HCl is more viable. An assumption of 31% HCl recovery was made based on a study (Cullivan and Cullivan, 2023).

Table 4-21 Costs associated with HCl recovery plant inclusion.

	HW	**MHW**	**SW**
HCl required per month (Tons)	1724	1407	1940
Cost for purchasing HCl per month (R)	3 575 460	2 989 553	6 155 879
Fixed cost for recovery plant (R)	66 540 900	59 754 312	70 931 232
Operational costs per month (R)	311 428	254 269	350 606
Disposal of hazardous waste per month cost (R)	51703675	58207925	42213975
Cost for purchasing HCl per month after recovery plant installed (R)	1 009 456	728 221	2 248 057

The fixed cost to erect a recovery plant can be compensated within the R500 million capital investment. The SW HCl requirement is much higher due to the large quantity required at a concentration of 6 M. In addition, the recovery costs are also higher for SW as there is a larger quantity of HCl to treat and recover. However, the operational costs of running the recovery plant for all processes are much lower than the cost of purchasing fresh HCl per month. Significant savings can be made by reducing the dependency on fresh HCl by even 31% if not more. In addition, significant reductions in waste disposal costs can be achieved through the recommended process since the estimated costs of disposing of the hazardous filtrate with transportation monthly as shown in Table 4-21 is almost the same as the fixed cost plant investment. A very slight reduction in ROI and IRR is observed by consideration of erecting an HCl recovery plant (Table 4-22). PBP is also not affected significantly.

Table 4-22: Summary of economical parameters after HCl recovery plant considerations.

	HW	**MHW**	**SW**
TIC (R)		500 000 000*	
TDC (R)	144 958 584	122 176 426	132 026 864
Depreciation (R)	14 495 858	12 217 643	13 202 686
Combined Revenue per year (R)	313 481 781	316 191 787	315 256 781
Average ROI–Return on investment (%)	79.3	76.9	79.2
IRR- Internal rate of return (%)	66.3	64.1	66.0
PBP (payback period) in years		1-2*	

* Figure applies to all species

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Raw material preparation

The analysis of the three sawdust samples showed significant differences in their chemical composition. These differences, in turn, may influence the subsequent downstream processing stages. Consequently, it was anticipated that product quality stemming from the different wood species would show distinct variations, which was evident throughout the subsequent stages.

In certain instances, physical attributes such as size reduction, as in the case of pin chips, or screening to eliminate irregular or oversized particles, may be amenable to alteration. However, the chemical composition remains an immutable attribute, necessitating the adjustment of process parameters to align with the specific characteristics of the raw material.

5.2 Delignification

The application of the proposed prehydrolysis treatment did not show any advantage in terms of milder delignification conditions (i.e., shorter reaction times and lower APS concentration). Consequently, it was not recommended as an initial pre-treatment step for the proposed pilot-scale process. Subsequent avenues of exploration may encompass the evaluation of alternative prehydrolysis techniques such as acidic, alkaline, or organic prehydrolysis before delignification, with the intent of ascertaining the compatibility of these methods with the delignification stage. Such endeavours may enable the enhancement of hemicellulose fractionation, consequently contributing further to the techno-economic viability of the overall process. However, this pursuit necessitates a comprehensive study, including the optimization of time, temperature, and chemical concentrations which is beyond the scope of this study.

The designated delignification parameters, notably temperatures ranging from 60 to 70 °C and reaction durations spanning 3 to 6 h, markedly deviate from the traditional PHK and AS processes, conventionally operated at elevated temperatures of 160 to 170 °C. This disparity underscores substantial cost savings inherent to the proposed approach. Furthermore, the streamlined single chemical application in the cooking processes represents a departure from traditional methodologies, which frequently entail multiple stages. Additionally, the process exhibits notable flexibility in accommodating diverse wood raw materials, a contrast to traditional methods tailored to specific wood species.

Specific chemical characteristics measured highlighted ISO brightness improvements, reduced hemicellulose content, and a substantial reduction in lignin content, conveying the efficacy of the delignification process. The results also implied that subsequent bleaching requirements could be less stringent while remaining effective in targeting residual lignin and hemicelluloses to enhance brightness. However, a noteworthy concern emerged in the form of significantly diminished intrinsic viscosity and

DP, indicating a potential occurrence of cellulose degradation. Endeavours to introduce a cellulose protector (CP) as a potential inhibitor of cellulose degradation during delignification were pursued, yet these attempts encountered limitations, as CPs proved incompatible with the APS oxidizing agent employed in the delignification stage.

It was deduced that the resultant pulp, given its inherent limitations in DP and intrinsic viscosity enhancement, did not align with the criteria of a grade of dissolving wood pulp (DWP) suitable for viscose production. Notwithstanding this, the primary objectives of the benchtop experiments, namely the identification of optimal conditions for the delignification process, were duly accomplished. Pulp samples with negligible or minimal instances of rejects were successfully achieved across the HW, MHW, and SW species. It was concluded that the established conditions could be seamlessly transitioned to pilot-scale operations, wherein the production of microcrystalline cellulose (MCC), predicated on the utilization of low DP pulp was considered suitable.

5.3 Bleaching

The objectives set forth within the framework of the bleaching trials were duly met. The outcome aligns with the anticipated trajectory, attributed to the superior quality inherent in the unbleached pulp. The DEpD sequence emerged as the most fitting course for HW substrates, while the DEDP regimen exhibited superior suitability for SW and MHW.

The discernment of these conditions was strategically guided by the dual imperatives of achieving elevated brightness levels and concurrently ensuring that the DP outcomes approximated a value of < 400. It is prudent to underscore that, if deemed necessary, the attained brightness levels of 86-88% could be elevated to the desired threshold of 90%. This augmentation could be effectuated through the incorporation of an additional stage, such as the H-stage, or calibrated enhancements in the chemical dosages.

Some imbalances were noted with total sugar composition during HPLC measurements. These were attributed to potential underestimations in glucose or other monosaccharides. It is assumed that this could be associated with analytical errors, losses of sample during sample preparation or errors in the method. It is therefore recommended that for future work, careful attention be drawn to HPLC measurements to improve accuracy due to the sensitivity around analysis.

Furthermore, to fulfil the specific requisites pertinent to MCC production, it was decided that the DP could be selectively refined through a process of controlled mild acid hydrolysis. This strategic modulation held the potential to achieve further reductions, specifically targeting values below 148 for intrinsic viscosity and 400 for DP, in alignment with the exigencies of MCC production protocols.

5.4 MCC production

The successful demonstration of MCC production from sawdust at the benchtop scale presents a promising avenue for the creation of a versatile and utilitarian material. The procedural methodologies have been elucidated, laying the groundwork for the transition to a pilot scale operation, which is imperative for a comprehensive evaluation of process feasibility.

In the context of acid hydrolysis, the attained yields spanned a range of 90-98%. Substantial losses incurred primarily emanated from the handling and washing stages of the product, and these aspects offer potential avenues for refinement. In aggregate, the MCC yield percentages, based on the sawdust, realized through benchtop testing manifested as 45, 34, and 44% for MCC-derived HW, MHW, and SW, respectively.

Further analysis has pinpointed the MCC produced from HW as the optimal contender for large-scale MCC production. This designation is substantiated by several compelling factors, encompassing milder processing conditions denoted by reduced time and temperature requisites for delignification (60 °C and 4 hours), augmented yield, a three-stage bleaching regimen, and a truncated acid hydrolysis duration (5 minutes). These attributes collectively contribute to the realization of a desired final product quality characterized by diminished hemicellulose content, a DP below 400, a proximity to commercial MCC evident in Fourier transform infrared spectroscopy (FTIR) analysis, and a crystallinity index (CrI) as verified by XRD analysis.

5.5 Pilot scale production

The pilot-scale experimentation has demonstrated the successful transferability of the technology, with anticipated disparities attributed to equipment variations and scaled-up quantities. Notably, the outcomes underscore the pronounced influence of the unbleached pulp's quality stemming from the delignification phase upon the resultant quality of MCC, as well as the parameters governing the bleaching and acid hydrolysis stages. To attain the desired MCC quality parameters, minor adjustments were deemed requisite, particularly concerning brightness and DP.

A comprehensive spectrum of commercial MCC grades exists, each characterized by significant variations in attributes. This notwithstanding, it is well understood that subsequent processing can effectively modulate physical attributes such as particle size and brightness. In the context of the proposed investigation, the prepared MCC closely approximated the properties of Avicel PH101 commercial MCC. Notably, it is essential to acknowledge that Avicel PH101 is predominantly employed in pharmaceutical applications, thereby necessitating a stringent evaluation encompassing standard health and safety tests before ascertaining its suitability for such utilization.

For further optimization, the application of spray drying, or ball milling is recommended to achieve the requisite reduction in particle size as necessitated by the intended applications for the prepared MCC grades. This approach aligns with tailoring the material to fulfil specific performance criteria.

5.6 Recovery and by-product consideration

While considerable attention has been directed toward exploring potential avenues for the retrieval of by-products from waste streams, it is paramount to understand that the methods of application and identification of the products are qualitative approaches and hence only provide an estimated value. In cases where challenges were experienced with quantification such as of the APS concentration in the filtrate, suggestions are made to further dilute the filtrate and attempt the titration method. Suitable measurements and instrumentation for identifying and quantifying the products are highly recommended before drawing conclusions. In addition, a complete environmental impact assessment (EIA) is recommended for such a process should it be considered for commercialisation. This comprehensive evaluation will serve as an indispensable requisite to holistically appraise the potential ramifications and ecological footprint of such an operational endeavour.

The avenues for the recuperation and reutilization of acid waste, as well as the recycling of ethanol, stand firmly grounded in well-established research paradigms, lending themselves as prudent augmentations to the operational schema. These integrations hold the promise of amplifying the techno-economic feasibility of the process, thereby endorsing the ethos of greener production via the reclamation and redirection of waste streams.

The ultimate determination of whether to effectuate the neutralization and responsible disposal of the involved chemicals as hazardous waste or pursue strategies for recovery, regeneration, or other by-product valorisation is a multifaceted question. This quandary necessitates a thorough techno-economic assessment to unveil a conclusive perspective on the practicability and inherent value of the envisaged pursuits.

5.7 Techno-economic evaluation

There isn't a universally superior criterion for the economic assessment of projects. Each company employs its preferred methods and establishes criteria for the minimum performance required to secure project funding. The design engineer must exercise caution to ensure that the chosen method and assumptions align with company policy, facilitating a fair comparison of projects.

While projects should be compared using the same economic criterion, they don't necessarily have to be evaluated on identical bases. In a global economy, regional advantages in feed and product pricing, capital costs, financing, or investment incentives may significantly vary. Alongside economic performance, numerous other factors warrant consideration in project evaluation. These encompass safety, environmental concerns (waste disposal), political considerations (government policies), the location of customers and suppliers (supply chain), the availability of labour and supporting services, corporate growth strategies, and the company's experience in technology.

The techno-economic evaluation has shown the HW process to be the most economically viable process in terms of ROI and IRR. However, with AS recovery consideration, the MHW process leads to the most viable process in terms of ROI and IRR. The PBP reduces by an average of 1 year when AS recovery is considered. In addition, HCl recovery and recycling shows even more promising cost savings for all processes by eliminating the total dependency on the purchase of fresh acid per batch and addresses waste disposal costs and thus overall operational costs. Both recovery processes also promote sustainability and green practices.

Although AS recovery shows promising cost savings. Recommendations are made for further work to potentially convert AS into APS by an established electrochemical process to recycle APS into the process and thus reduce the costs of purchasing fresh APS. A techno-economic evaluation is recommended to identify the viability of such a process and whether it would enhance the techno-economic viability of the current process

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CHAPTER 7 APPENDICES

Appendix A

Table A1: Screening experimental design tests for delignification benchtop trials using Minitab trial version per wood species

Std Order	Run Order	Pt Type	APS CONCENTRATION (M)	TEMPERATURE (℃)	L: W RATIO	PULP
5	1	2	3	80	7.5	-1
14	2	2	2	80	10	-1
17	3	2	1	70	5	-1
2	4	2	2	60	5	-1
12	5	1	1	60	10	-1
6	6	2	1	60	7.5	-1
21	7	1	1	80	5	-1
1	8	2	2	80	10	-1
10	9	1	1	80	10	-1
8	10	1	1	80	5	-1
18	11	2	3	80	7.5	-1
7	12	1	3	60	10	1
11	13	1	3	80	5	0
15	14	2	2	60	5	-1
24	15	1	3	80	5	-1
3	16	2	3	70	10	1
23	17	1	1	80	10	-1
19	18	2	1	60	7.5	-1
25	19	1	1	60	10	-1
26	20	0	2	70	7.5	0
22	21	1	3	60	5	0
4	22	2	1	70	5	-1
9	23	1	3	60	5	-1
13	24	0	2	70	7.5	0
16	25	2	3	70	10	1
20	26	1	3	60	10	1

Pulp response factor levels	Meaning
-1	Unpulped
0	Semi pulped
1	Pulped, little to no rejects

Table A2: Optimisation experimental design tests for delignification benchtop trials using Minitab trial version per wood species

StdOrder	RunOrder	Temperature (°C)	Time (h)	Pulp
8	1	60	4	-1
13	2	60	3	-1
14	3	60	4	-1
6	4	70	6	
4	5	70	3	1
12	6	70	6	
5	7	70	4	
17	8	70	4	
16	9	70	3	1
10	10	70	3	1
7	11	60	3	-1
3	12	60	6	1
15	13	60	6	1
11	14	70	4	
2	15	60	4	-1
9	16	60	6	1
1	17	60	3	-1
18	18	70	6	

🟥	Not tested as pulped achieved in shorter time in screening experiments

Table A3: Standard errors for duplicate or triplicate measurements

Sawdust

	SE	HWE	ASL	AIL	Ash	Siefert cellulose	HPLC			PSD
							Xylose	Mannose	Glucose	
HW	±0.01	±0.01	±0.005	±0.11	±0.00	±0.07	±0.08	±0.00	±0.05	±0.7
MHW	±0.01	±0.02	±0.003	±0.01	±0.02	±0.04	±0.01	±0.03	±0.03	±0.1
SW	±0.01	±0.01	±0.01	±0.01	±0.00	±0.04	±0.00	±0.00	±0.00	±0.4

Prehydrolysis

	SE	HWE	ASL	AIL	Ash	Siefert cellulose	HPLC				
							Arab	Galact	Xylose	Man	Gluco
HW (150 ℃, 45 mins)	±0.02	±0.02	±0.05	±0.03	±0.01	±0.19	±0.00	±0.01	±0.14	±0.00	±0.03
HW (170 ℃, 45 mins)	±0.01	±0.02	±0.00	±0.03	±0.03	±0.22	±0.00	±0.00	±0.01	±0.00	±0.08
HW (150 ℃, 90 mins)	±0.01	±0.02	±0.00	±0.01	±0.00	±0.59	±0.01	±0.01	±0.02	±0.00	±0.11

Delignification benchtop

	Yield	ASL	AIL	Ash	HPLC					ISO brightness (%)	Intrinsic viscosity (ml/g)	DP
					Arab	**Galac**	**Xylose**	**Mannose**	**Glucose**			
HW	±0.1	±0.01	±0.55	±0.17	±0.00	±0.00	±0.09	±0.00	±0.04	±0.3	±0.00	±0.00
MHW	±0.1	±0.02	±1.43	±0.11	±0.00	±0.00	±2.61	±2.80	±3.16	±0.3	±0.00	±0.00
SW	±0.1	±0.04	±1.75	±0.27	±0.00	±0.00	±0.64	±0.00	±0.69	±0.3	±0.00	±0.00

Bleaching benchtop

	Yield	HPLC			ISO brightness (%)	Intrinsic viscosity (ml/g)	DP
		Xylose	**Mannose**	**Glucose**			
91α DWP	-	±0.01	±0.00	±0.00	±0.3	±0.00	±0.00
HW	±0.11	±0.10	±0.00	±0.47	±0.3	±0.00	±0.00
MHW	±0.11	±1.72	±0.00	±3.15	±0.3	±0.00	±0.00
SW	±0.11	±0.05	±0.12	±0.03	±0.3	±0.00	±0.00

Acid hydrolysis benchtop

	HPLC			ISO brightness (%)	Intrinsic viscosity (ml/g)	DP
	Xylose	Mannose	Glucose			
MCC commercial	±0.02	±0.03	±0.01	±0.3	±0.00	±0.00
HW	±0.02	±1.97	±0.01	±0.3	±0.00	±0.00
MHW	±0.00	±0.11	±0.23	±0.3	±0.00	±0.00
SW	±0.00	±0.11	±0.22	±0.3	±0.00	±0.00

Delignification Pilot

	ISO brightness (%)	Intrinsic viscosity (ml/g)	DP
HW	±0.3	±0.00	±0.00
MHW	±0.3	±0.00	±0.00
SW	±0.3	±0.00	±0.00

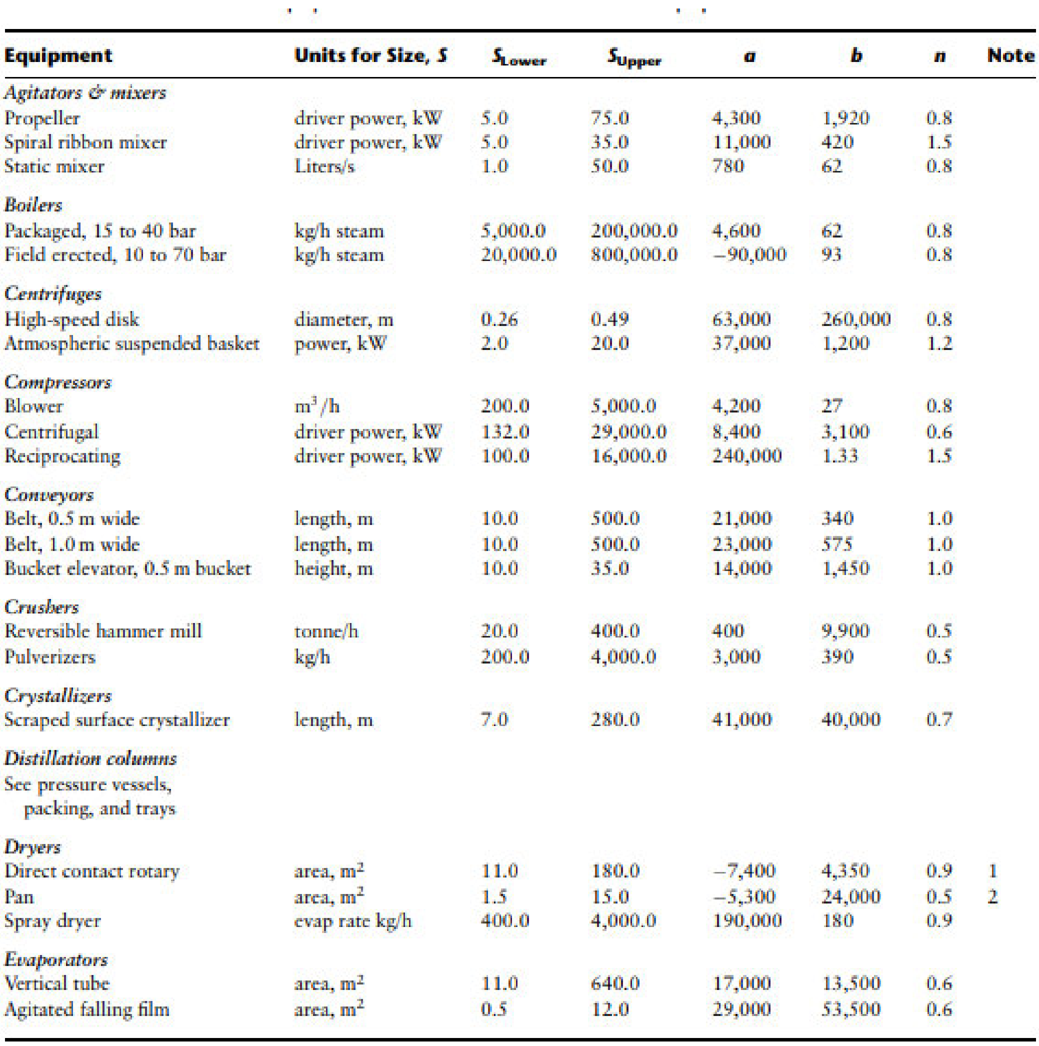
Bleaching Pilot

	Yield	ISO brightness (%)	Intrinsic viscosity (ml/g)	Degree of polymerisation (DP)
91α DWP	-	±0.3	±0.00	±0.00
HW	±0.10	±0.3	±0.00	±0.00
MHW	±0.10	±0.3	±0.00	±0.00
SW	±0.10	±0.3	±0.00	±0.00

Acid hydrolysis pilot

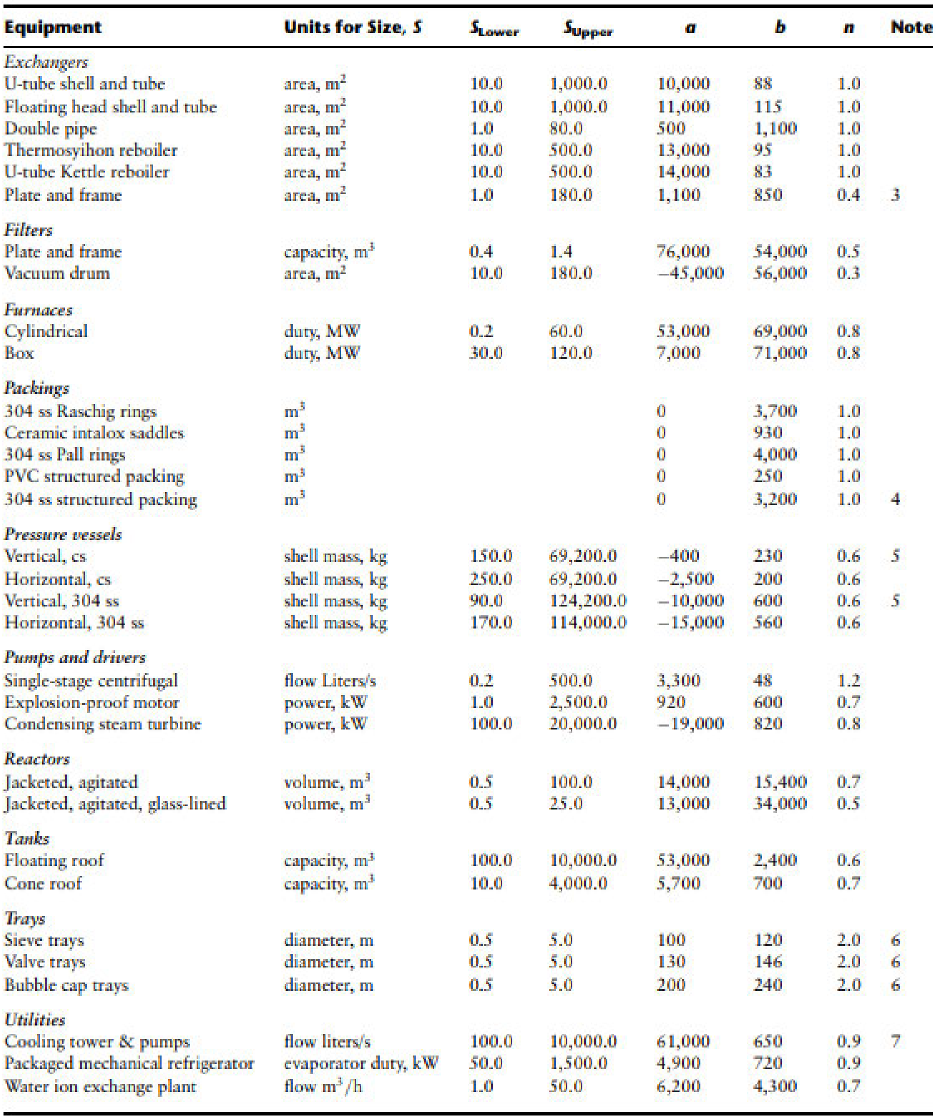
	Yield	HPLC			Intrinsic viscosity (ml/g)	Degree of polymerisation (DP)
		Xylose	Mannose	Glucose		
MCC commercial	-	±0.03	±0.04	±0.02	±0.00	±0.00
HW	±0.58	±0.03	±0.04	±0.31	±0.00	±0.00
MHW	±0.40	±0.02	±0.04	±0.01	±0.00	±0.00
SW	±0.88	±0.02	±0.04	±0.02	±0.00	±0.00

Table A4: Purchased equipment costs for common plant equipment (Towler and Sinnott, 2008)



Equipment	Units for Size, S	S_{Lower}	S_{Upper}	a	b	n	Note
Agitators & mixers							
Propeller	driver power, kW	5.0	75.0	4,300	1,920	0.8	
Spiral ribbon mixer	driver power, kW	5.0	35.0	11,000	420	1.5	
Static mixer	Liters/s	1.0	50.0	780	62	0.8	
Boilers							
Packaged, 15 to 40 bar	kg/h steam	5,000.0	200,000.0	4,600	62	0.8	
Field erected, 10 to 70 bar	kg/h steam	20,000.0	800,000.0	−90,000	93	0.8	
Centrifuges							
High-speed disk	diameter, m	0.26	0.49	63,000	260,000	0.8	
Atmospheric suspended basket	power, kW	2.0	20.0	37,000	1,200	1.2	
Compressors							
Blower	m^3/h	200.0	5,000.0	4,200	27	0.8	
Centrifugal	driver power, kW	132.0	29,000.0	8,400	3,100	0.6	
Reciprocating	driver power, kW	100.0	16,000.0	240,000	1.33	1.5	
Conveyors							
Belt, 0.5 m wide	length, m	10.0	500.0	21,000	340	1.0	
Belt, 1.0 m wide	length, m	10.0	500.0	23,000	575	1.0	
Bucket elevator, 0.5 m bucket	height, m	10.0	35.0	14,000	1,450	1.0	
Crushers							
Reversible hammer mill	tonne/h	20.0	400.0	400	9,900	0.5	
Pulverizers	kg/h	200.0	4,000.0	3,000	390	0.5	
Crystallizers							
Scraped surface crystallizer	length, m	7.0	280.0	41,000	40,000	0.7	
Distillation columns							
See pressure vessels, packing, and trays							
Dryers							
Direct contact rotary	area, m^2	11.0	180.0	−7,400	4,350	0.9	1
Pan	area, m^2	1.5	15.0	−5,300	24,000	0.5	2
Spray dryer	evap rate kg/h	400.0	4,000.0	190,000	180	0.9	
Evaporators							
Vertical tube	area, m^2	11.0	640.0	17,000	13,500	0.6	
Agitated falling film	area, m^2	0.5	12.0	29,000	53,500	0.6	

Table A4 continued: Purchased equipment costs for common plant equipment continued (Towler and Sinnott, 2008)

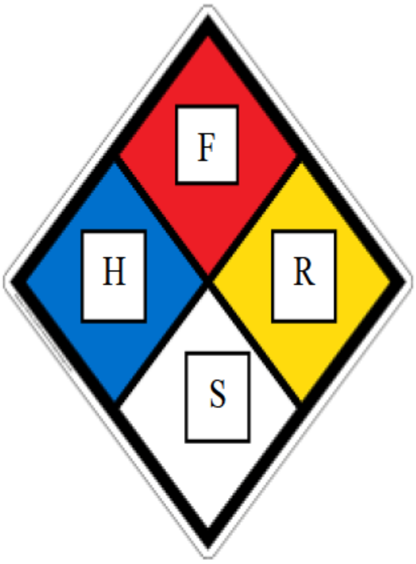


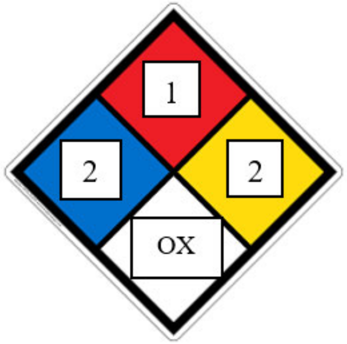
Equipment	**Units for Size, *S***	**S_{Lower}**	**S_{Upper}**	***a***	***b***	***n***	**Note**
Exchangers							
U-tube shell and tube	area, m^2	10.0	1,000.0	10,000	88	1.0	
Floating head shell and tube	area, m^2	10.0	1,000.0	11,000	115	1.0	
Double pipe	area, m^2	1.0	80.0	500	1,100	1.0	
Thermosyihon reboiler	area, m^2	10.0	500.0	13,000	95	1.0	
U-tube Kettle reboiler	area, m^2	10.0	500.0	14,000	83	1.0	
Plate and frame	area, m^2	1.0	180.0	1,100	850	0.4	3
Filters							
Plate and frame	capacity, m^3	0.4	1.4	76,000	54,000	0.5	
Vacuum drum	area, m^2	10.0	180.0	−45,000	56,000	0.3	
Furnaces							
Cylindrical	duty, MW	0.2	60.0	53,000	69,000	0.8	
Box	duty, MW	30.0	120.0	7,000	71,000	0.8	
Packings							
304 ss Raschig rings	m^3			0	3,700	1.0	
Ceramic intalox saddles	m^3			0	930	1.0	
304 ss Pall rings	m^3			0	4,000	1.0	
PVC structured packing	m^3			0	250	1.0	
304 ss structured packing	m^3			0	3,200	1.0	4
Pressure vessels							
Vertical, cs	shell mass, kg	150.0	69,200.0	−400	230	0.6	5
Horizontal, cs	shell mass, kg	250.0	69,200.0	−2,500	200	0.6	
Vertical, 304 ss	shell mass, kg	90.0	124,200.0	−10,000	600	0.6	5
Horizontal, 304 ss	shell mass, kg	170.0	114,000.0	−15,000	560	0.6	
Pumps and drivers							
Single-stage centrifugal	flow Liters/s	0.2	500.0	3,300	48	1.2	
Explosion-proof motor	power, kW	1.0	2,500.0	920	600	0.7	
Condensing steam turbine	power, kW	100.0	20,000.0	−19,000	820	0.8	
Reactors							
Jacketed, agitated	volume, m^3	0.5	100.0	14,000	15,400	0.7	
Jacketed, agitated, glass-lined	volume, m^3	0.5	25.0	13,000	34,000	0.5	
Tanks							
Floating roof	capacity, m^3	100.0	10,000.0	53,000	2,400	0.6	
Cone roof	capacity, m^3	10.0	4,000.0	5,700	700	0.7	
Trays							
Sieve trays	diameter, m	0.5	5.0	100	120	2.0	6
Valve trays	diameter, m	0.5	5.0	130	146	2.0	6
Bubble cap trays	diameter, m	0.5	5.0	200	240	2.0	6
Utilities							
Cooling tower & pumps	flow liters/s	100.0	10,000.0	61,000	650	0.9	7
Packaged mechanical refrigerator	evaporator duty, kW	50.0	1,500.0	4,900	720	0.9	
Water ion exchange plant	flow m^3/h	1.0	50.0	6,200	4,300	0.7	

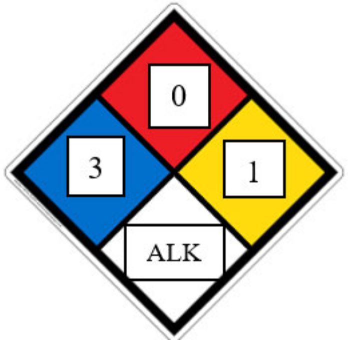
Appendix B

HAZOP PART 1

A. SUMMARY OF CHEMICAL HAZARDS

	F: Flammability H: Health R: Reactivity S: Speciality hazard	0: None 1: Low 2: Medium 3: High 4: Extreme

Chemical name	**Potential Hazard**	**Severity**	**Preventative control measure**
Ammonium persulphate	• May intensify fire; oxidizer (OX) • Harmful if swallowed • Causes skin irritation • Causes serious eye irritation • May cause an allergic skin reaction • May cause allergy or asthma symptoms or breathing difficulties if inhaled • May cause respiratory irritation		• Wash face, hands, and any exposed skin thoroughly after handling • Do not eat, drink, or smoke when using this product • Wear protective gloves/protective clothing/eye protection/face protection • Avoid breathing dust/fume/gas/mist/vapours/spray • In case of inadequate ventilation wear respiratory protection • Contaminated work clothing should not be allowed out of the workplace • Use only outdoors or in a well-ventilated area • Keep away from heat/sparks/open flames/hot surfaces. - No smoking • Keep/Store away from clothing/ other combustible materials • Take any precautions to avoid mixing with combustibles

Sodium hydroxide (Neutralisation)	• Causes eye burns. May cause blindness, chemical conjunctivitis, and corneal damage. • Causes skin burns. May cause deep, penetrating ulcers of the skin. • May cause severe and permanent damage to the digestive tract. Causes GI tract burns. May cause perforation of the digestive tract. Causes severe pain, nausea, vomiting, diarrhoea, and shock. • Irritation may lead to chemical pneumonitis and pulmonary edema. Causes severe irritation of upper respiratory tract with coughing, burns, breathing difficulty, and possible coma. Causes chemical burns to the respiratory tract. • Prolonged or repeated skin contact may cause dermatitis. Effects may be delayed.		• Eyes: Wear chemical splash goggles and face shields. • Skin: Wear butyl rubber gloves, apron, and/or clothing. • Clothing: Wear appropriate protective clothing to prevent skin exposure. • Respirators: Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149-approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced. • Store in closed containers under normal conditions. • Avoid moisture, contact with water, exposure to moist air or water, prolonged exposure to air. • Avoid incompatible materials: Water, metals, acids, aluminum, zinc, tin, nitromethane, leather, flammable liquids, organic halogens, wool. • Facilities storing or utilizing this material should be equipped with an eyewash facility and a safety shower. • Use adequate general or local exhaust ventilation to keep airborne concentrations below the permissible exposure limits.

B. RISK ANALYSIS

Hazard Classification

Chemical: 3 M ammonium persulphate

1. Toxicity data

Exposure limit: **(TLV-TWA, OEL-CL, OEL-RL)**	TWA: 0.1 mg/m3		
Toxicity (oral LD_{50}):	689 mg/kg	**Animal:**	Rat
Odour threshold:	odourless (no information available)		
Target organ and effects:	Respiratory system, skin (corrosion and irritation), oral toxicity, eye contact (damage and irritation)		

2. Hazard classification

Make a cross in the appropriate square

Toxicity **Oral (LD_{50}, mg/kg)**	(Extremely toxic) ≤ 5		(Highly toxic) 5-50		(Toxic or unknown) 50-500	x	(Non-toxic) >500	
Sensitisation	Extreme	x	Moderate∏ severe		Unknown ∏ mild		Non-sensitising	
Irritation/Corrosion			Corrosive, severely irritating	x	Unknown, moderately irritating		Non- or mildly irritating5000	
Carcinogenicity	A1 or 2		A3		A4		A5	x

Hazard Classification	Extreme Hazard		High Hazard	x	Medium Hazard		Non-Hazardous	

3. Exposure assessment

Value	**0**	**1**	**2**	**3**	**Score**
Quantity	< 0.1 kg	0.1 - 0.5 kg	0.5 - 1 kg	> 1 kg	3
Solid - dust level	waxy or big particles (no dust)	small particles (>1 mm, <5 mm)		fine powder (dusty <µm)	3
Liquid-vapour pressure @ 20°C		low (<20 mmHg)	medium	high (> 30 mmHg)	0
Gas				@ room temp	0
Toxicity **Oral LD_{50}, mg/kg**		>500	50-500	<50	2
Warning properties	Good (odorous, irritating)		Fair	Poor Unknown	0
Concentration **M/V (sol), V/V (liq)**		<25%	25-75%	>75%	2
Duration of exposure	<15 min	15 min- 1 hour	1-4 hrs	> 4 hours	3
Frequency of use		1 day/week	2-3 days/week	>4 days/week	3
	<1 week	1-2 weeks	2-4 weeks	> 4 weeks	1

Value	**0**	**1**	**2**	**3**	**Score**
Routes		ingestion, injection	absorption	inhalation	3
Hazard Warning	non-classified laboratory chemical	harmful, irritant, corrosive, flammable, oxidizing	very toxic, toxic, explosive, pyrophoric, lachrymator	**carcinogen,** teratogen, potential mutagen	1
Pressure	ambient		vacuum	>1 atm	2
Temp.	ambient		25 - 100°C	> 100°C	2
TOTAL (sum of above columns)					25
LOW RISK < 6		**MEDIUM RISK 6 - 14**		**HIGH RISK > 14**	

ACTIONS RESULTING FROM RISK ANALYSIS:

RISK	**NEED FOR HAZARD STUDY**	**CONTROL MEASURES** **Engineering**
Low		
Medium		
High	**Advisable/compulsory**	- Use PPE (Lab coat/overall, safety boots, gloves, goggles, and 3 M half-face respirator) when handling chemical - Weigh and make up solution under a lined fume hood. Ensure adequate ventilation, avoid dust formation - Filtration of product must occur under a lined fume hood - Ensure a suitable scrubber is used to vent any fumes when slight pressure build-up occurs - Protocol for containment and clean-up - Avoid inhalation, contact with skin, and contact with eyes - Ensure that eyewash station and safety showers are functional and close to weighing station and fermentation laboratory

Control Measures and PPE

Lab coat	X	Nitrile gloves	X	Safety glasses		Safety shoes	X	Face shield	
Overall		4 H gloves		Safety goggles	X	Respirator	X	Apron	
Other (specify)	Can use double gloves if required when handling chemical								

4. <u>Chemical hazard data</u>

Physical state	**Quantity (inventory or throughput)**
Solid	**6.846 kg in 7.326 L deionised water**

Flammability and Explosion Hazards

Fire	Oxidizer: Contact with combustible/organic material may cause fire. Slightly flammable to flammable in presence of open flames and sparks, of heat, of reducing materials, of combustible materials.
Deflagration / Detonation	NA
Static Discharge	NA
Reactivity Hazards	
Reactivity	Strong oxidiser. Moisture sensitive. May decompose on exposure to moist air or water. May be shock-sensitive and thermally unstable. Decomposes when heated. Incompatible with powdered aluminum, iron, sodium peroxide.

Stability	The product is chemically stable under standard ambient conditions (room temperature). May decompose on exposure to moist air or water.
Products of decomposition	Nitrogen oxides (NOx) Sulphur oxides Ammonia. Release of oxygen- due to fire Ambient fire may liberate hazardous vapours
Health Hazards – acute	
Carcinogen	No information available
Inhalation Toxicity	Hazardous in the case of inhalation (lung irritant, lung sensitizer). Over-exposure by inhalation may cause respiratory tract irritation. May cause chemical pneumonitis and pulmonary edema, inflammation, edema of bronchi and larynx.
Ingestion Toxicity	Harmful if swallowed
Other forms of Toxicity	Hazardous in the case of eye contact (serious irritant) and skin (irritant). Acute Potential Health Effects: Skin: Causes skin irritation. May cause skin sensitization, an allergic reaction, which becomes evident upon re-exposure to this material. Eyes: Causes eye irritation. Ingestion: Causes gastrointestinal (digestive) tract irritation with nausea, vomiting, and diarrhoea. May be harmful if swallowed. Inhalation: Causes respiratory tract irritation. May cause chemical pneumonitis and pulmonary edema, inflammation, edema of bronchi and larynx.
Irritant / Corrosive	Irritant and corrosive
Sensitizer	Skin sensitisation: May cause an allergic skin reaction Respiratory sensitisation: May cause allergy or asthma symptoms or breathing difficulties if inhaled.
Health Hazards – chronic	

Carcinogen	No information available
Other	Chronic Potential Health Effects: Repeated or prolonged skin exposure may cause allergic reactions in sensitive individuals. Repeated or prolonged exposure by inhalation may affect respiration and metabolism.
Other Health Hazards	
Odour	Odourless
Radiation	None
Environmental Hazards	
Water / Air / Ground	Toxicity to aquatic life

5. Chemical means of handling data

Storage	Keep container tightly closed in a cool dry place away from direct sunlight or heat source. Keep locked up or in an area accessible only to qualified or authorized persons. Do not store near combustible materials. Storage class (TRGS 510): 5.1B: Oxidizing hazardous materials
Transport	According to Hazard class 5.1 (oxidisers), packing group 3
Problems in handling	Wear personal protective equipment/face protection. Avoid dust formation. Do not breathe dust. Do not get in eyes, on skin, or on clothing. Keep away from clothing and other combustible materials. Pay attention to flashback.
Process conditions	Use in well-ventilated area during reaction. Use appropriate equipment and tools. Work under fume hood for reactant preparation, neutralisation of filtrate and filtration of product.
Materials of construction	NA
Gaseous emissions	NA
Quality control	Avoid contamination of the reactants
Area classification	5.1B: Oxidizing solid hazardous material

6. General Safety

(Mark with a cross in the appropriate box and comment or specify if necessary)

Fire Hazard

None		Negligible		Flammable	x	Highly flammable		Explosive	
Comments	Slightly flammable to flammable in presence of open flames and sparks, of heat, of reducing materials, of combustible materials. Contact with combustible/organic material may cause fire.								

Extinguish media

Sand		Water	x	Carbon dioxide	x	Dry chemical	x	Foam	x
Comments	Oxidizing material. Avoid contact with organic materials. Suppress (knock down) gases/vapours/mists with a water spray jet. Prevent fire extinguishing water from contaminating surface water or the ground water system. Can use CO2, dry chemical, or foam for extinction.								

Storage

Toxic		Harmful	x	Non-harmful		Flammable	
Acid		Bases		Oxidant		Reductant	
Incompatibilities	Strong oxidising agents, strong acids, excess heat						
Comments							

Disposal

Acid		General organic		Halogenated		Toxic	x	Solid	

Other (specify)	Should not be released into the environment. Neutralisation with sodium hydroxide to a pH of 7 and then dump down a designated drain at facility
Comments	Applicable for any solution that contains APS

Spill/Leak

Evacuate area		Add sand		Add Absorbent	x	Neutralise with		Sweep up	x
Comments	Keep combustibles (wood, paper, oil, etc) away from spilled material. Do not touch spilled material. Prevent entry into sewers, basements or confined areas, dike if needed. Keep solid/liquid in suitable, closed containers for disposal. Solid: Sweep up and shovel into suitable containers for disposal. Avoid dust formation. Keep substance damp using water spray. Liquid: Soak up with inert absorbent material.								

7. First aid

(Mark with a cross in the appropriate box and comment or specify if necessary)

Ingestion

Give water	x	Give milk		Induce vomiting		Keep warm		Get medical attention	x
Comments	Loosen tight clothing such as a collar, tie, belt, or waistband.								

Inhalation

Give water		Give oxygen		Keep warm		Perform CPR if necessary		Remove to fresh air	x	Get medical attention	x

Comments	Do not use mouth-to-mouth method if victim ingested or inhaled the substance; If not breathing give artificial respiration with the aid of a pocket mask equipped with a one-way valve or other proper respiratory medical device. If breathing is difficult, give oxygen.

Eye contact

Wash with water for at least 15 minutes	x	Get medical attention	x
Comments	Rinse immediately with plenty of cold water also under the eyelids. Check for and remove any contact lenses.		

Skin contact

Wash with water (> 15 minutes)	x	Wash with Soap (> 15 minutes)		Get medical attention	x
Comments	Remove contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used. Wash clothing before reuse.				

Chemical: Sodium hydroxide/Caustic soda

1. Toxicity data

Exposure limit: **(TLV-TWA, OEL-CL, OEL-RL)**	TWA: 2 mg/m^3		
Toxicity (oral LD_{50}):	4090 mg/kg	**Animal:**	Rat
Odour threshold:	odourless (no information available)		
Target organ and effects:	Respiratory tract, skin (corrosion and irritation), eye contact (damage and irritation)		

2. Hazard classification

Make a cross in the appropriate square

Toxicity **Oral (LD_{50}, mg/kg)**	(Extremely toxic) ≤5		(Highly toxic) 5-50		(Toxic or unknown) 50-500		(Non-toxic) >500	x
Sensitisation	Extreme		Moderate∏ severe		Unknown ∏ mild		Non-sensitising	x
Irritation/Corrosion			Corrosive, Severely irritating	x	Unknown, moderately irritating		Non- or mildly irritating5000	
Carcinogenicity	A1 or 2		A3		A4		A5	x
Hazard Classification	Extreme Hazard		High Hazard	x	Medium Hazard		Non-Hazardous	

3. Exposure assessment

Value	**0**	**1**	**2**	**3**	**Score**
Quantity	< 0.1 kg	0.1 - 0.5 kg	0.5 - 1 kg	> 1 kg	3
Solid - dust level	waxy or big particles (no dust)	small particles (>1 mm, <5 mm)		fine powder (dusty <µm)	0
Liquid-vapour pressure @ 20°C		low (<20 mmHg)	medium	high (> 30 mmHg)	1

Value	**0**	**1**	**2**	**3**	**Score**
Gas				@ room temp	0
Toxicity **Oral LD_{50}, mg/kg**		>500	50-500	<50	1
Warning properties	Good (odorous, irritating)		Fair	Poor Unknown	0
Concentration **M/V (sol), V/V (liq)**		<25%	25-75%	>75%	1
Duration of exposure	<15 min	15 min- 1 hour	1-4 hrs	> 4 hours	2
Frequency of use		1 day/week	2-3 days/week	>4 days/week	3
	<1 week	1-2 weeks	2-4 weeks	> 4 weeks	1
Routes		ingestion, injection	absorption	inhalation	3
Hazard Warning	non-classified laboratory chemical	harmful, irritant, corrosive, flammable, oxidizing	very toxic, toxic, explosive, pyrophoric, lachrymator	**carcinogen,** teratogen, potential mutagen	1
Pressure	ambient		vacuum	>1 atm	0
Temp.	ambient		25 - 100°C	> 100°C	0
TOTAL (sum of above columns)					16
LOW RISK < 6	**MEDIUM RISK 6 - 14**		**HIGH RISK > 14**		

ACTIONS RESULTING FROM RISK ANALYSIS:

RISK	**NEED FOR** **HAZARD STUDY**	**CONTROL MEASURES** **Engineering**
Low		
Medium		
High	**Advisable/compulsory**	- Use PPE (Lab coat/overall, safety boots, gloves, goggles and 3 M half face respirator) when handling chemical - Conduct neutralization in fume hood - Maintain overheat stirrer speed to avoid splashing - Ensure adequate ventilation, avoid dust formation - Protocol for containment and clean-up - Avoid inhalation, contact with skin, and contact with eyes - Ensure that eyewash station and safety showers are functional and close to weighing station and fermentation laboratory

Control Measures and PPE

Lab coat	X	Nitrile gloves	X	Safety glasses		Safety shoes	X	Face shield	
Overall		4 H gloves		Safety goggles	X	Respirator	X	Apron	
Other (specify)	Can use double gloves if required when handling chemical								

Chemical hazard dat

Physical state	**Quantity (inventory or throughput)**

Solid	**3.4 kg in 17 kg of APS filtrate**

Flammability and Explosion Hazards

Fire	Direct fire hazard: Non-combustible. Indirect fire hazard: Reactions involving a fire hazard; Reacts violently with many compounds: heat release resulting in increased fire or explosion risk. Violent exothermic reaction with water (moisture): release of corrosive mist. Reacts exothermically on exposure to water (moisture) with combustible materials: risk of spontaneous ignition.
Deflagration / Detonation	NA
Static Discharge	NA
Reactivity Hazards	
Reactivity	May be corrosive to metals. Absorbs the atmospheric CO2. Violent to explosive reaction with (some) acids. Reacts violently with many compounds: heat release resulting in increased fire or explosion risk. Violent exothermic reaction with water (moisture): release of corrosive mist. Reacts exothermically on exposure to water (moisture) with combustible materials: risk of spontaneous ignition.
Stability	Stable at ambient temperature but can become unstable at elevated temperatures and pressures. Hygroscopic. Unstable on exposure to air.
Products of decomposition	No decomposition if used and stored according to specification. Can decompose violently in contact with organic substances and hydrogen sulphide. Decomposition products: Sodium oxide, hazardous vapours.
Health Hazards – acute	
Carcinogen	No information available

Inhalation Toxicity	When processed: Dry/sore throat. Coughing. Irritation of the respiratory tract. Irritation of the nasal mucous membranes. On continuous exposure/contact: Respiratory difficulties. Following symptoms may appear later: Possible oedema of the upper respiratory tract. Possible laryngeal spasm/oedema. Risk of lung oedema.
Ingestion Toxicity	Dry/sore throat. Nausea. Abdominal pain. Blood in vomit. Difficulty in swallowing. Possible oesophageal perforation. Burns to the gastric/intestinal mucosa. Bleeding of the gastrointestinal tract. Shock.
Other forms of Toxicity	Hazardous in the case of eye contact (serious irritant) and skin (irritant). Burning sensation, Cough, wheezing, laryngitis, Shortness of breath, spasm, inflammation and edema of the larynx, spasm, inflammation and edema of the bronchi, pneumonitis, pulmonary edema.
Irritant / Corrosive	Irritant and corrosive
Sensitizer	No information available
Health Hazards – chronic	
Carcinogen	No information available
Other	Material is extremely destructive to tissue of the mucous membranes and eyes. On continuous/repeated exposure/contact: Dry skin. Skin rash/inflammation. Possible inflammation of the respiratory tract. Gastrointestinal complaints.
Other Health Hazards	
Odour	Odourless
Radiation	None
Environmental Hazards	
Water / Air / Ground	Prevent from reaching drains, sewers, and waterways. Harmful to crustacea. Harmful to fishes. Groundwater pollutant. pH shift.

4. Chemical means of handling data

Storage	Store in a dry area. Keep container tightly closed in a well-ventilated place. No metal containers. Keep locked up. Unauthorized persons are not admitted. Keep only in the original container. Meet the legal requirements. Protect from freezing and physical damage. Avoid storage near extreme heat, ignition sources, or open flame. Store away from foodstuff, oxidizing agent. Store with corrosives.
Transport	According to Hazard Class 8 (corrosive substances).
Problems in handling	Avoid raising dust. Avoid contact of substance with water. Measure the concentration in the air regularly. Carry operations in the open/under local exhaust/ventilation or with respiratory protection. Comply with the legal requirements. Remove contaminated clothing immediately. Clean contaminated clothing. Keep the substance free from contamination. Use corrosion-proof equipment. Thoroughly clean/dry the installation before use. Do not discharge the waste into the drain. Do not mix with acid. Apply good hygiene when handling.
Process conditions	Use in well-ventilated area. Use corrosion-proof equipment. Work under fume hood for neutralisation of filtrate.
Materials of construction	NA
Gaseous emissions	NA
Quality control	Avoid contamination
Area classification	Class 8 (corrosive substances)

5. General Safety

(Mark with a cross in the appropriate box and comment or specify if necessary)

Fire Hazard

None	x	Negligible		Flammable		Highly flammable		Explosive	
Comments									

Extinguish media

Sand		Water	x	Carbon dioxide		Dry chemical			Foam
Comments	Cool tanks/drums with water spray/remove them into safety. When cooling/extinguishing: no water in the substance. Take account of toxic fire-fighting water. Use water moderately and if possible, collect or contain it. If in a laboratory setting, follow laboratory fire suppression procedures. Use appropriate fire suppression agents for adjacent combustible materials or sources of ignition.								

Storage

Toxic		Harmful	X	Non-harmful		Flammable	
Acid		Bases	X	Oxidant		Reductant	X
Incompatibilities	Combustible materials, metals, strong acids, organic materials, and strong oxidizers. Protect from moisture and heat sources. Aluminum, brass, metal alloys, Zinc, Tin.						
Comments							

Disposal

Acid		General organic		Halogenated		Toxic	x	Solid	
Other (specify)	Do not discharge into drains or the environment. Remove waste following local and/or national regulations. Hazardous waste shall not be mixed with other waste. Different types of hazardous waste shall not be mixed if this may entail a risk of pollution or create problems for the further management of the waste.								
Comments	Refer to disposal of APS above for filtrate containing sodium hydroxide								

Spill/Leak

Evacuate area		Add sand	x	Add Absorbent	x	Neutralise with	x	Sweep up	x

Comments	Respiratory protection may be advisable. Avoid contact with eyes, skin and clothing. Wash hands after handling. Under controlled conditions: neutralize leftovers with dilute acid solution. Possible violent reaction if you neutralize. Carefully collect the spill/leftovers. Clean contaminated surfaces with an excess of water. Take collected spill to manufacturer/competent authority Liquid: Dike and contain spill. Cover with powdered limestone or dry sand, earth, vermiculite. Absorb spillage to prevent material damage due to corrosiveness to metals. Solid: Scoop solid spill into closing containers

6. First aid

(Mark with a cross in the appropriate box and comment or specify if necessary)

Ingestion

Give water	x	Give milk		Induce vomiting		Keep warm		Get medical attention	x
Comments	Rinse mouth thoroughly. Make victim drink water (two glasses at most), avoid vomiting (risk of perforation). Call a physician immediately. Do not attempt to neutralise.								

Inhalation

Give water		Give oxygen	x	Keep warm		Perform CPR if necessary		Remove to fresh air	x	Get medical attention	x
Comments	Move exposed individual to fresh air. Loosen clothing as necessary and position individual in a comfortable position. Seek medical advice is discomfort or irritation persist. If breathing difficult, give oxygen.										

Eye contact

Wash with water for at least 15 minutes	x	Get medical attention	x

Comments	Protect unexposed eye, then rinse immediately with plenty of water for 15 minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Do not apply neutralizing agents. Take victim to an ophthalmologist.

Skin contact

Wash with water (> 15 minutes)	x	Wash with Soap (> 15 minutes)		Get medical attention	x
Comments	Wipe off dry product from skin. Remove clothing before washing. Wash immediately with lots of water (15 minutes)/shower. Do not apply (chemical) neutralizing agents. Do not remove clothing if it sticks to the skin. Cover wounds with sterile bandage. Consult a doctor/medical service. If burned surface > 10%: take victim to hospital.				

C. CHEMICAL INTERACTION DATA

Legend: d=desired reaction

K = known reaction

- = no hazards

x = chemicals will not be used in the same reaction

	Chemicals	A	B
A	Ammonium persulphate	■	d
B	Sodium hydroxide	d	■

D. MATERIAL COMPATIBILITIES

Chemicals	A	B
Materials of construction		

Glass	-	-
Plastic	-	-
Metal	k	k
Rubber	-	-
316 stainless steel	-	-

HAZOP PART 2

A. SEQUENCE TABLE

Process: Delignification of biomass		
Step No.	**Sequence Description**	**Activities**
1	APS solution preparation	Weigh out media ingredients and make-up solutions
2	Loading of bioreactor	Transferring reactants to the reactor
3	Delignification	Transfer reactants to vessel. Set stirrer speed 300 rpm, Temp: 60/70 ℃, Time: 3/4/6 hrs
4	Harvesting	Cooling of reactor to 25℃. Harvesting of pulp slurry
5	Filtration	Transporting of pulp slurry from the lab to the filtration station and slurry washing under vacuum
6	Neutralisation	Neutralisation of filtrate to pH 7 using sodium hydroxide

B. HAZARD & OPERABILITY STUDY

BATCH PROCESS													
ENGINEERING LINE DIAGRAMS (PID)													
OPERATING/PROCESS STEPS													
SEQUENCE STEP NUMBER		**1**			**2-3**			**4**			**5-6**		
KEY ACTIVITY OR STATES IN STEP		APS solution preparation			Reactor loading and Delignification			Harvesting			Filtration/Neutralisation		
GW	**Deviation**	**Yes**	**No**	**Act**	**Yes**	**No**	**Act**	**Yes**	**No**	**Act**	**Yes**	**No**	**Act**
More	**Excessive/over**												
	Long Duration		**x**		**x**		**17**		**x**			**x**	
	Late Starting		**x**			**x**			**x**			**x**	
	Fast Rate	**x**		**1**	**x**		**1**		**x**		**x**	**1**	**1**
	Increased Temperature		**x**		**x**		**18**		**x**		**x**		**18**
	Increased Pressure		**x**		**x**		**19**		**x**			**x**	
	Higher Concentration	**x**		**2**		**x**			**x**		**x**		**2**
	Vapour	**x**		**3**	**x**		**3**	**x**		**3**	**x**		**3**
Less	**Little/under**												
	Short Duration		**x**		**x**		**20**		**x**			**x**	
	Sooner Starting		**x**			**x**			**x**			**x**	
	Slow Rate		**x**		**x**		**21**		**x**			**x**	
	Decreased Temperature		**x**		**x**				**x**			**x**	
	Decreased Pressure		**x**			**x**			**x**			**x**	
	Lower Concentration	**x**		**4**		**x**			**x**		**x**		**4**
None No Not	**Electrical supply**	**x**		**5**	**x**		**5**		**x**		**x**		**5**
	Water supply	**x**		**6**	**x**		**6**		**x**		**x**		**6**
	Ventilation- (extractor/ fumehood)	**x**		**7**	**x**		**7**	**x**		**7**	**x**		**7**
	Pulping		**x**		**x**		**22**		**x**			x	
Part of	**Spill - Material**	**x**		**8**	**x**		**8**	**x**		**8**	**x**		**8**
	Lose/gain - Heat/rate		**x**		**x**		**23**		**x**			**x**	
	Incomplete Execution	**x**		**9**	**x**		**9**		**x**	**9**	**x**		**9**
	Contamination	**x**		**10**	**x**		**10**		**x**			**x**	
	Effervescence/runaway reaction		**x**		**x**		**24**		**x**		**x**		24
	Failure:												
	Instrumental/ equipment trips	**x**		**11**	**x**		**11**	**x**		**11**	**x**		**11**
	Mechanical/electrical	**x**		**12**	**x**		**12**		**x**		**x**		**12**
	Operator error	**x**		**13**	**x**		**13**	**x**		**13**	**x**		**13**

BATCH PROCESS													
ENGINEERING LINE DIAGRAMS (PID)													
OPERATING/PROCESS STEPS													
SEQUENCE STEP NUMBER		1			2-3			4			5-6		
KEY ACTIVITY OR STATES IN STEP		APS solution preparation			Reactor loading and Delignification			Harvesting			Filtration/Neutralisation		
GW	Deviation	Yes	No	Act	Yes	No	Act	Yes	No	Act	Yes	No	Act
	Pressure relief valve		x		x		25		x			x	
As Well As	Both/together/alongside												
	Wear-Corrosion/abrasion		x		x		26		x			x	
	Pollution (Air, water)		x		x		27	x		27	x		27
	Emission (Toxic, noise)	x		14	x		14	x		14	x		14
	Radiation (Heat, nuclear)		x			x			x			x	
Other Than	Direction/route												
	Wrong material/step	x		15	x		15		x		x		15
	Instead:	x		16	x		16	x		16	x		16
	Maintenance/checking												

C. DEVIATION - CAUSE - CONSEQUENCE SHEET

Ref No	Deviation	Causes	Consequences	Safeguards	Recommendations
1	**Fast rate- (APS preparation, delignification and neutralisation)**	Stirrer speed too high, human error	Splashing of liquid, minor burns, skin irritation, eye irritation	PPE, fume hood,	Ensure full PPE used, work under fume hood
2	**High concentrations of reactants (APS preparation & Neutralisation)**	Human error, instrumental error	Undesired reaction	SOP	Ensure that SOP has correct quantities and staff is trained, calibrate scale

Ref No	**Deviation**	**Causes**	**Consequences**	**Safeguards**	**Recommendations**
3	**Release hazardous vapours (All steps)**	Not working under fumehood, pressure build-up, human error	Exposure to hazardous vapours. Health effects- respiratory irritation	Respirators, Working under a fumehood, scrubber, proper ventilation in lab (extractor)	Ensure suitable respirator worn as per SOP, fumehood, and extractor inspection
4	**Low concentration- (APS preparation & Neutralisation)**	Human error, instrumental error	Undesired reaction	SOP	Ensure that SOP has correct quantities and staff is trained, calibrate scale
5	**No electrical supply (APS preparation, delignification and neutralisation)**	Loadshedding, electrical fault, power trip due to overload	No reaction due to overhead stirrer not functioning or reactor not operating	Back-up power supply-generator	If no backup supply, check load-shedding schedule, UPS to prevent effects of power surges
6	**No water supply**	Water restrictions or shut-off, valve failure	No reaction, no cooling water supply to reactor for maintaining the temperature	None	Flow meter to indicate no water supply in reactor
7	**No ventilation (All steps)**	Extractor malfunction, fumehood malfunction	Exposure to hazardous vapours- health effects (respiratory, eye)	PPE-respirator	To open windows, service extractors and fumehood
8	**Spill of reactants/product (all steps)**	Human error, leaks, splashing	Exposure to hazardous chemicals- minor burns, eye and skin irritation, physical injury from slips and falls	SOP, PPE, Spill kit	Operator training on SOP
9	**Incomplete execution**	Human error, equipment malfunction, power	No reaction	Back-up power supply, SOP	Operator training, check loadshedding schedule, UPS to prevent effects of

Ref No	**Deviation**	**Causes**	**Consequences**	**Safeguards**	**Recommendations**
		failure			power surges
10	**Contamination of reactants (APS preparation, reactor loading and delignification)**	Human error	Undesired reaction, low quality products	None	Operator training, SOP, sterilize containers
11	**Failure: Instrumental/ equipment trips (all steps)**	Power failure, electrical fault	No reaction, no operation	Back-up power supply	UPS
12	**Failure: mechanical/ electrical**	Faulty motor driver, faulty temperature, and pressure transmitter	No reaction	Back-up instruments or equipment	Maintenance of the equipment
13	**Operator error (all steps)**	Negligence	No reaction, unsafe working environment	SOP, PPE	Operator training
14	**Toxic emissions (all steps)**	Pressure relief valve leak, reactor opened at temperatures > 25ºC	Exposure to hazardous vapours, health effect (respiratory, eye)	Fume hood, extractor, scrubber, PPE	SOP, operator training
15	**Wrong material/step (APS preparation, delignification, neutralisation)**	Human error	No pulping or undesired reaction, poor product quality	SOP, clear labelling of biomass samples and chemicals	Operator training
16	**Maintenance/ checking**	Negligence	No operation, undesired product, unsafe working environment	None	Maintenance plan, random inspections of instruments and equipment
17	**Long duration (Delignification)**	Human error	Degradation of cellulose, undesired product	SOP	Operator training, log start time, use a stopwatch with alarm

Ref No	Deviation	Causes	Consequences	Safeguards	Recommendations
18	**Increased temperature (Delignification, neutralisation)**	Poor temperature control, pressure relief valve fails, no cooling water supply, human error	Pressure build-up, explosion, undesired product, exposure to hazardous vapours, minor burns from neutralisation	Pressure relief valve, ventilation (extractor), PPE	Operator training, maintenance of temperature controller and pressure relief valve, high temperature alarm
19	**Increased pressure (Delignification)**	High temperature, pressure relief valve fails, uncontrolled reaction, air inlet left open	Explosion, exposure to hazardous vapours	Pressure relief valve, ventilation (extractor), PPE	High pressure alarm, operator training, regular pressure testing
20	**Short duration (Delignification)**	Human error, power failure, equipment malfunction	Undesired product	SOP	Operator training, Log start time and use a stopwatch with alarm
21	**Slow rate (Delignification)**	Equipment malfunction, human error, speed controller faulty	Undesired product	SOP	Operator training, maintenance of equipment
22	**No pulping (delignification)**	Human error, equipment malfunction, power failure	Accumulation of solid hazardous waste	SOP, backup power supply	Operator training, UPS to assist with power surges, regular maintenance of equipment
23	**Loss of heat (Delignification)**	Poor temperature control, no steam supply	Undesired product	None	Low temperature alarm
24	**Effervescence /runaway reaction (Delignification and neutralisation)**	High temperature, high pressure, air inlet left open, human error	Explosion, exposure to hazardous vapours and liquids, health effects, minor burns	SOP, PPE	Operator training, high temperature/ pressure alarm

Ref No	Deviation	Causes	Consequences	Safeguards	Recommendations
25	**Pressure relief valve failure (Delignification)**	Poor maintenance, blockage of line	Pressure build-up, explosion, exposure to hazardous vapours	PPE, ventilation (extractor)	Regular inspection of valve
26	**Corrosion/abrasion (Delignification)**	Continuous long-term exposure to 3 M APS (months), high APS concentration	Long term damage to digester, leaks	316 Stainless reactors being used, corrosion suitability testing conducted for 316 SS	Pressure testing before and after use of the reactor after a few runs
27	**Pollution air/water (All steps)**	Release of hazardous vapours, human error, incorrect disposal, incompatibility of materials, spillages	Health and environmental effects	SOP, PPE, spill kit, scrubber, ventilation, waste disposal protocol, correctly labelled waste bins	Operator training, for large spillages contact HAZMAT team