THE PULP AND PAPER WASTEWATER BIOREFINERY
Potential for concomitant value recovery and wastewater treatment

Susan T.L. Harrison, Shilpa Rumjeet, Lesley D. Mostert, Charlotte Wessels, Sisanda Rini, Tendani Manenzhe, Nodumo Zulu, Thanos Kotsiopoulos

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Final Report

for the Water Research Commission

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Executive Summary

The need to utilise the world's natural resources more efficiently is increasingly recognised as critical for enhanced sustainability and ability to function within the envelop of the earth's resources. Resource efficiency requires the maximum use of available resources for products of social and economic value whilst minimising un-used resources, undesirable by-products, and waste, and thereby the associated environmental burden requiring assimilation. A key feature of this resource and product orientation in water-scarce South Africa includes the minimising of the water footprint and maximising of its re-purposing, including water recycle, re-use and return to the environment at appropriate quality, as well as beneficiation of the contaminants carried in wastewater. The WRC report K5/2380 (Harrison et al., 2017) conceptualised and reviewed the potential of the 3rd generation wastewater biorefinery as a vehicle to convert wastewater streams into resources of organic carbon, nitrogen, phosphorus, energy and water, thereby enhancing resource recovery and reducing waste assimilation burden, while ensuring maximum potential for re-purposing of fit-for-purpose water. This, building on WRC K5/2000 (Verster et al., 2014), introduced the wastewater biorefinery (WWBR) concept to target improved resource productivity while minimising pollution, environmental burden, and the carbon, nitrogen, energy and water footprints of anthropological activity. The pulp and paper industry was one of the industries identified in WRC K5/2380 as showing good potential for WWBR implementation. This potential is investigated in more detail through this project.

In addition to the potential of its wastewater, the pulp and paper industry is transitioning from a mature industry to re-define its product spectrum based on the potential of the 2nd generation woody biomass biorefinery. This makes it an opportune time to consider, simultaneously, the third generation WWBR.

As observed in the global examples presented in the report, solid waste and wastewater are treated separately in South African P & P mills. While van der Merwe-Botha, et al. (2017) observed improvements in the waste and wastewater management practices over the years, these improvements were limited to water saving and recycling along with improved sludge management. Valorisation is typically limited to the use of black liquor and bark as energy sources in the waste and wastewater sectors. However, there is increasing interest in the South African P & P industry to diversify its product portfolio by investigating product formation from residual holocellulose and lignin-rich waste streams. While some data collection from the South African P & P industry has occurred since 2010, the anonymity and inconsistency in the data make it challenging to investigate routes for value addition. Effluent data and characterisation are typically available after combined on-site wastewater treatment, preventing analysis of the full resource potential of the combined and/or individual wastewater streams.

In this project, we bring together data available on the in-depth characterisation of effluent streams from various pulp and paper mills, allowing typical characteristics of the sector in South Africa to be ascertained through an extensive literature analysis. In the P & P industry, the main resource present in wastewater streams before treatment is carbon in the form of lignocellulosic biomass or the hydrolysed hemicellulose, cellulose and lignin fractions or a combination. Lignocellulosic biomass is considered a solid waste and is removed or reclaimed throughout the operations of a P & P mill while the hydrolysed components are lost to wastewater treatment. In the WWBR, resource efficiency is fundamental. Maintaining separation of the wastewater streams at source may aid this. For example, owing to the high complexity of the bleaching effluents, they should be handled separately as much as possible. High concentration wastewater streams can be processed directly without dilution and increased complexity of mixing, as an example.

We employed a scoring exercise to identify promising streams within the plant for establishing a P & P WWBR and to guide selection of the most appropriate route for further valorisation. It further highlighted the potential benefit to investigate different valorisation routes for different processes. For example, where liquors are produced, it is beneficial to consider where these are potential feedstocks for

production of higher value-added products, rather than only energy products. We further examined the potential of combined or individual wastewater streams for valorisation and found pulping wastewater streams are better handled separately as opposed to wastewater streams for paper-making and recycling processes which demonstrate higher potential for a WWBR, when combined. There are also some streams such as the condensate streams in chemical pulping processes, which seem best suited for remediation purposes only. It is expected that the scoring exercise for local mills in South Africa will be basically similar to Table 4-43, as pulp and paper-making processes are generally well-established globally. Further, it is recommended that this approach be used within and across P & P plants nationally.

Due to the main resource being carbon in the context of a P & P WWBR, the focus is on a primary bacterial bioreactor to harness most of the carbon towards a valuable by-product. Among products highlighted for production as the anchor product of the WWBR are the platform products lactic acid and ethanol, as well as polymers. Depending on the residual resources contained within the water after the bacterial bioreactor, an informed decision can be made on the unit operations to further clean the water and the potential for additional products can be investigated to build an integrated process. The considerations that play the biggest role for product selection are the dilute nature of the wastewater, the downstream processing and byproduct generation. To this end, an approach for the selection of promising products, taking into account the characteristics of the wastewater, the locality, product demand, remediation potential and technology complexity, is presented. By implementing a multi-unit WWBR, both anchor product and water recovery and quality can be optimised simultaneously, potentially with additional products such as an energy product.

We use a case study approach for the compilation and assessment of potential wastewater biorefinery flowsheets, addressing specific challenges associated with these feedstocks and identifying potential products. Here we explore both complex streams requiring substantial pre-processing as well as a stream of low complexity, high volume and high concentration of organic material. In essence, wastewater streams with high volume, high concentration and low complexity are postulated to have the greatest potential as feedstocks for the WWBR to produce value-added products. Effluents which contain high pollutant quantities (VOCs, methanol, phenols and AOXs) should not be mixed with carbon-rich wastewater streams to ensure that pre-treatment costs are minimised. Remediation and bioenergy generation is investigated for streams where high value products are not feasible. Analysis of regional impact is also considered with the potential for clustering of wastewater biorefineries to service more than one plant where co-located, weighed up against management complexity and transport costs.

The novelty of the wastewater biorefinery concept rests with generating multiple products through the cascading use of resources contained within waste and wastewater streams while producing ‘fit-for-purpose’ water as an important product, which was demonstrated in this report through our case studies. The findings are examined to identify common elements to facilitate knowledge development towards the practice of industrial ecology through implementation of wastewater biorefineries across other sectors of importance in South Africa, to enhance resource efficiency while enabling re-purposing of ‘fit for purpose’ water, key steps towards enhancement of the sustainable development of our society through creation of social, environmental and economic value.

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Acronyms and abbreviations

ABR	Anaerobic baffled reactor
AD	Anaerobic digestion
AOX	Adsorbable organic halides
APMP	Alkaline peroxide mechanical pulping
AS	Activated sludge
ASB	Aeration Stabilisation Basins
AST	Activated Sludge Treatment
BCTMP	Bleached chemi-thermomechanical pulping
BD	Buffer dam
BOD	Biological oxygen demand
COD	Chemical oxygen demand
CTMP	Chemithermomechanical pulping
DAF	Dissolved air flotation
DSP	Downstream processing
EC	Evaporator condensate
FBR	Fluidised bed reactor
FSB	Facultative stabilization basin
LL	Landfill leachate
MBBR	Moving bed biofilm reactors
MBR	Membrane bioreactor
NSSC	Neutral sulphite semi-chemical pulping
RBC	Rotating biological contactor
RMP	Refiner mechanical pulping
SBR	Sequencing batch reactor
SHF	Separate hydrolysis and fermentation
SPF	Sludge press filter
SSF	Simultaneous saccharification and fermentation
ss	Sampling stations
TMP	Thermochemical pulping
TOC	Total organic carbon
TSS	Total suspended solids
UAF	Upflow anaerobic filter
UASB	Upflow anaerobic sludge blanket
VFA	Volatile fatty acids
WWBR	Wastewater Biorefinery
WWTP	Wastewater treatment plant

Glossary of Terms

Bio-based chemicals	Substitutes for petrochemicals or novel products derived from renewable biomass sources (recently fixed CO_2)
Bio-based economy	An economy that integrates the full range of natural and renewable biological resources and the processing and consumption of these bioresources
Bio-based products	Non-food products derived from biomass (plants, algae, crops, trees, marine organisms and biological waste from households, animals and food production)
Bioprocess	Specific process that uses microorganisms or enzymes to obtain desired products
Biorefinery	Integrative, multifunctional overarching concept that uses biomass as a diverse source of raw materials for the sustainable generation of a spectrum of intermediates and products while ensuring the minimisation of waste products
Circular economy	An alternative to a traditional linear economy (make, use, dispose) in which we keep resources in use for as long as possible, extract the maximum value from them while in use, then recover and regenerate products and materials at the end of each service life www.wrap.org.uk/about-us/about/wrap-and-circular-economy
Economy of scale	Reduction in cost-per-unit-produced resulting directly from increased size of production facility
Feedstock	Raw material used as the basis for an industrial process
Fine chemical	Complex, single, pure chemical substances produced in limited quantities in multipurpose plants by multistep batch chemical or biotechnological processes, identified according to chemical formula
Macrophyte	Aquatic plant (growing in or near water) – emergent, submerged or floating
Non-renewable resources	Natural resources of economic value that cannot be replaced by natural means on a level equal to consumption
Platform chemical	Used as feedstock in subsequent chemical or biochemical industrial processes to manufacture a range of consumer products
Resource recovery	Process of obtaining matter or energy from waste materials
Valorisation	Process of using chemical or biological methods to increase the value of a material by changing it – in particular here, producing products of value from a feedstock otherwise regarded as waste
Wastewater biorefinery	A biorefinery (see above) operating in the wastewater arena and designed to generate products of value-from-waste nutrients and simultaneously produce clean or “fit for purpose” water as the non-negotiable product

1 Introduction

1.1 Introducing the concept of the wastewater biorefinery in the pulp and paper industry

A move towards resource efficiency requires the maximum use of available resources for products of social and economic value while minimising unused resources, undesirable by-products, and waste, thereby minimising environmental burden requiring assimilation. A key feature of this resource and product orientation in water-scarce South Africa includes minimising the water footprint and maximising its repurposing, including recycling, reusing, and returning to the environment at an appropriate quality.

The WRC report K5/2380 (Harrison et al. 2017) reviewed the potential of the third-generation wastewater biorefinery as a vehicle to convert wastewater streams into resources of organic carbon, nitrogen, phosphorus, energy and water, thereby enhancing resource recovery and reducing waste assimilation burden. This, building on WRC K5/2000 (Verster et al. 2014), introduced the wastewater biorefinery (WWBR) concept to target improved resource productivity while minimising pollution, environmental burden, and the carbon, nitrogen, energy and water footprints of anthropological activity. The wastewater biorefinery is centred on the combined concepts of the industrial ecology in which wastes from one process are repurposed into raw materials for the next, and the circular economy in which resources are returned into the same process or function, or both, at end of use.

The pulp and paper industry was one of the industries identified in WRC K5/2380 as showing good potential for wastewater biorefinery implementation, motivating its investigation in more detail through this project. Here, the potential for value generation from the wastewater effluents generated in the pulp and paper industry with simultaneous remediation of the water resource to yield ‘fit-for-purpose’ water was targeted. The concomitant biotransformation of this resource for value generation and bioremediation of the effluent streams, with particular value placed on the water product, thus facilitating water recycling or repurposing, has been investigated.

1.2 Challenges in the pulp and paper industry and the need for an enhanced product portfolio

Prior to positioning this study on pulp and paper wastewater, it is valuable to set this in context with the industry as a whole. While the global demand for pulp and paper products has remained relatively stable, the increased use of digital media has resulted in reduced demand for printing products, notably printing paper, with an associated shift in product spectrum and balance within the industry. While the demand for paper and paperboard is still on the rise since it is a common material used in the packaging industry, Pätäri (2010) and Sabatier et al. (2012) describe the industry as a mature one where profitability is decreasing, fuelling the need for new and more diverse business models.

Large economies of scale have traditionally characterised the pulp and paper industry (PPI), focused on exploiting existing technological capabilities (Toivanen, 2004), and this motivates the potential for value from the large wastewater streams emanating. However, the narrow traditional product focus has constrained the industry as more and more companies are reporting the closure of mills and long-lasting profitability problems (Sorenson et al. 2007; van Horne et al. 2006). The common problem points towards a lack of value creation in the industry. Pätäri et al. (2011) investigated the trade-offs of economies of scale versus economies of scope for the PPI, as seen in Table 1-1, stipulating that the PPI should target economies of scope rather than economies of scale. Economies of scope have the potential to drive competitive advantage by allowing the PPI to use firm-specialised knowledge coupled with other resources and related capabilities to create new products and processes (Pätäri et al. 2011).

For example, South America has laid the foundation for economies of scope by investing significantly in eucalyptus fibre, which in turn attracted global investments (de Carvalho et al. 2004).

Table 1-1 Comparison of the main drivers for economies of scale versus economies of scope (Pätäri et al. 2011)

	Traditional economies of scale	Future of economies of scope
Main source of competitive advantage	Large investments in tangible assets and effective control over capital and markets	Ability to flexibly extend, modify and reconfigure internal and external intangible VRIN* resources with dynamic capabilities
Role of forests	Raw material to be used efficiently for large-scale pulp and paper production	Sustainable use of forests for both traditional and innovative end uses
Processes	Large-scale, cost-efficient processes making bulk products	Sound knowledge of manufacturing processes is adjusted for innovative and customised products
Products	Incremental innovations that spread fast across the industry Mass products (pulp, paper) for industrial buyers	Appropriability is built around innovations Traditional fibre-based products and innovative products (e.g. bioenergy, biofuels, information delivery, intelligent packaging, intangible forests, medical, polymers) for customised industry and consumer markets.
Required resources	Forest industry-specific assets with reliance on process efficiency	Specialised resources according to the strategic focus
Representative type of an organisation	Large, vertically integrated conglomerates	Focused and potentially networked organisation using outsourcing

*VRIN: valuable, rare, inimitable and non-substitutable

Pätäri et al. (2011) further devised a framework to inform the strategic steps needed to create a sustainable competitive advantage for the PPI:

- sensing the weak signals of the operational environment,
- formulating them as strategic options in order to capture their upside potential,
- hedging against the downside risks of the options,
- exercising these options is often related to imperfect intangible knowledge assets markets, and
- reconfiguring the existing knowledge base and capabilities to sustain the competitive advantage obtained.

One way to move towards economies of scope is to widen the PPI array of products and services, through biorefining operations, including, for example, the production of renewable fuels, chemicals, bio-based fibrils and wood composite materials, amongst others (Toppinen et al. 2017). In the context of the PPI, a forest biorefinery can be defined as a processing plant where forest-based feedstocks such as wood, virgin and recycled fibres are converted into a spectrum of value-added products. In terms of the framework proposed by Pätäri et al. (2011), Table 1-2 highlights its application for the forest biorefinery

Table 1-2 Investigation biorefineries as a case study through the strategic options thinking, adapted from Pätäri et al. (2011)

Key steps in value creation	Case forest biorefinery
(i) Sensing weak signals	- Environmental treaties such as Kyoto Protocol - Corporate social responsibility among customers and society - Increasing global interest in forest-based raw material and biomass for the bioproducts business
(ii) Building strategic options capturing the upside potential	- Forming strategic partnerships (such as alliances and mergers) with, e.g. research institutes and energy industry companies to complement the resource base and to gain new knowledge - Making feasibility studies relating to the raw material, technology and markets - Investing in pilot plant – Understanding the global economy (energy regulation, subsidy policies, political risks, etc.)
(iii) Hedging the downside of strategic options	- Managing the options portfolio (scaling, waiting, abandoning) - Managing strategic partnerships with, e.g. contracts - Exercising learning and waiting options if first-mover advantages are not strong - Appropriating knowledge assets from the use of rivals through building up a strategic firewall by using legal means (e.g. patents, copyrights, trade secrets) or by keeping the valuable knowledge tacit - Committing and rewarding professionals in the company
(iv) Exercising the strategic options	- Investing in technology (forests, plants, distribution) - Investing in knowledge
(v) Reconfiguring the existing knowledge base and capabilities to sustain the competitive advantage obtained	- Managing human resources proactively - Enhancing learning - Orchestrating the global value chain - Managing strategic partnerships - Buying services from experts

The topic of biorefinery transition in the PPI has been discussed in the literature for several years (see Janssen and Stuart (2010a); Pätäri (2010); Hämäläinen et al. (2011); Näyhä et al. (2014); Stern et al. (2015); McGuire et al. (2017)).

The implementation of biorefinery facilities in the PPI presents significant potential and can drive various technological, environmental, economic and social benefits, as highlighted in Brunnhofer et al. (2020) in the following ways:

- Optimising existing value chains to generate additional value (Giurca and Späth, 2017; Näyhä et al. 2014).
- Maximising resource efficiency through the complete use of raw materials in order to reduce waste and close the material loop (Näyhä et al. 2014; Oliveira and Navia, 2017).
- Enhance profitability by a more diversified product portfolio and attracting new customers and markets (Hansen and Coenen, 2016; Hoher et al. 2016; Janssen and Stuart, 2010a).
- Create new jobs and contribute towards the revitalisation of rural areas where PPI mills are often located (Priefer et al. 2017).

Indeed, returning to the wastewater biorefinery concept introduced in Section 1.1, this expanding of the focus of the pulp and paper industry to include, alongside its traditional products, the forest biorefinery (second-generation) opens up the potential to exploit the wastewater biorefinery concept simultaneously owing to the opening up of the product spectrum under consideration. Through the wastewater biorefinery, the potential exists to reduce environmental burden, reduce water footprint, enhance product spectrum and, importantly, enhance resource efficiency of material emanating from the biomass feedstock, the chemicals used and the water itself. This wastewater biorefinery for the pulp and paper industry forms the central focus of this project.

1.3 Project scope, aims and objectives

This project focuses on the potential for value generation from the wastewater effluents generated in the pulp and paper industry with concomitant remediation of the water resource to yield 'fit-for-purpose' water. In this project, the concomitant biotransformation of this resource for enhanced resource efficiency and value generation concomitantly with bioremediation of the effluent streams and enhancing their potential for water recycling or repurposing is investigated using the industrial ecology-based approach of the wastewater biorefinery. The requirements and potential of the wastewater biorefinery for South Africa have been investigated in detail in the recent project WRC K5/2380 (Harrison et al. 2017). The objective of this project is to explore the applicability of concepts developed in Harrison et al. (2017) to a major industrial sector in South Africa through the pulp and paper sector and to explore the potential for demonstrating the possible implementation of a WWBR within this sector. This project provides an in-depth characterisation of effluent streams from the various pulp and paper mills in South Africa, allowing typical characteristics of the sector in South Africa to be ascertained. Analysis of regional impact is considered. Using case studies, compilation and assessment of potential wastewater biorefinery flowsheets are undertaken, addressing specific challenges associated with these feedstocks and identifying potential products. The findings of this report serve to facilitate knowledge development towards the practice of industrial ecology through the implementation of wastewater biorefineries across other sectors of importance in South Africa, to enhance resource efficiency while enabling the repurposing of 'fit-for-purpose' water, key steps towards improved resource efficiency and the enhancement of the sustainable development of our society through the creation of social, environmental and economic value.

The key aims addressed in this project report follow and are addressed in two overarching components of the report.

In Part 1, the potential to embed wastewater biorefineries in the pulp and paper industry is evaluated through a review of current knowledge and information. To achieve this, a rigorous overview of the potential for value recovery and value addition to the pulp and paper industry is provided using both global and national input. Building on this, we address the first two core aims:

- Building on the review of waste resources in South Africa conducted in WRC K5/2380, and the recent NATSURV report, a detailed mapping of the wastewater resource from the pulp and paper industry and its potential for value addition is provided. This includes the volume, concentration and complexity, hence the amount of each of the important resources (organic carbon, N, P, water, other) contained within the effluent streams, the regional proximity of the resources, the suitability of these streams as feedstocks to the WWBR and their associated challenges.
- Products of interest for generation in the WWBR are identified and include commodity products of relevance to the pulp and paper industry, bio-based commodity products with potential value (economic, social or environmental), energy products and fit-for-purpose water.

In Parts 2 and 3, case studies on selected pulp and paper wastewater streams are undertaken to evaluate further the potential for burden reduction, value recovery and enhanced resource efficiency. Here we have the following core aims:

- A framework for a pulp and paper wastewater biorefinery is built by exploring different production platforms to include in the wastewater biorefinery, thereby identifying critical components of the WWBR and the influence of site and stream complexity on the WWBR proposed.
- Case studies are explored based on specific wastewater streams and characteristics.

- Areas of critical new knowledge requirement are identified and explored. These include refinement of lactic acid (as a potential product) production from lignocellulosic waste streams, de-ashing requirements and specific recalcitrant wastewater streams.
- Development of process flowsheets to facilitate burden reduction and concomitant value recovery and resource efficiency enhancement from example wastewater streams are presented along with high-level techno-economic analysis to enable assessment of the feasibility of the WWBR approach and its potential for social, environmental and economic value.

1.4 Project outcomes and expected impacts

In this project, we summarise data available on the in-depth characterisation of effluent streams from the various pulp and paper mills in South Africa, allowing typical characteristics of the sector in South Africa to be ascertained. Analysis of regional impact allows the potential for clustering of wastewater biorefineries to service more than one plant where co-located, weighed up against management complexity, and transport costs to be assessed.

An approach for the selection of promising products, taking into account the characteristics of the wastewater, the locality, product demand, remediation potential and technology complexity, is presented. We use a case study approach for the compilation and assessment of potential wastewater biorefinery flowsheets, addressing specific challenges associated with these feedstocks and identifying potential products. Here we explore both complex streams requiring substantial pre-processing as well as a stream of low complexity, high volume and high concentration of organic material.

The findings of this report are examined to identify common elements to facilitate knowledge development towards the practice of industrial ecology through the implementation of wastewater biorefineries across other sectors of importance in South Africa, to enhance resource efficiency while enabling the repurposing of ‘fit-for-purpose’ water, key steps towards enhancement of the sustainable development of our society through the creation of social, environmental and economic value.

Several knowledge contributions arise from this study. Firstly, the characterisation of the effluent streams in the pulp and paper industry allows for quantification of the potential resource available as feedstocks to the WWBR biorefinery and additionally enables the assessment of these resources on a regional basis. Secondly, a range of products is identified for production through the WWBR, which can either be used in the pulp and paper industry itself or as value-added products to other processes in other industries. Thirdly the development of the pulp and paper WWBR framework and demonstration of the concept of the WWBR is expected to enable new technical knowledge on the application of bioconversion processes leading to the platform, polymer and other bio-based commodity products and bioenergy with the aim of producing sought-after products, for which production processes are already known, from pulp and paper effluents and of overcoming the recalcitrance of feedstocks and process inhibition, while designing for resilience to feedstock variability and dealing effectively with dilute feed streams. The recovery of ‘fit-for-purpose’ water is a non-negotiable outcome.

The potential socio-economic impacts involve the possibility of job creation through increased plant activities in the realisation of value from wastewater resources in the region surrounding the paper mills and factories. Improved water quality and ‘fit-for-purpose’ water as one of the products of the WWBR also provide societal benefits. The reduction in pollution load of the effluents and the associated environmental burden has the potential to provide a health benefit to both the people and aquatic life.

It is well-recognised that in water-scarce countries such as South Africa, access to and appropriate handling of water resources for both plant and community inform the plant’s legal and social licence to operate.

Part 1

Evaluating the potential of the pulp and paper industry to house wastewater biorefineries towards resource efficiency

2 Global Review of Value Recovery and Value Addition in the Pulp and Paper Industry

2.1 Opportunities and challenges with the implementation of biorefineries in the PPI

The changing paradigm in the pulp and paper industry over the past 10 to 15 years has led to a number of studies focusing on the "forest" biorefinery approach globally, with some extending beyond this to consider integration within the mill as well. Key examples are introduced in this chapter.

Owing to the high resource potential of wood, there are various ways in which one can adapt the current PPI to become more resource efficient. The work of Jansson et al. (2015) is informative with respect to the biorefinery potential of the traditional P&P mill. In their work, they proposed a roadmap for 2015 until 2025, where the prospect for product diversification was identified on a component basis (Table 2-1). The kraft pulp mill was used as a demonstration for value and energy recovery and coined the "Multi-Product Mill Biorefinery". Four main routes were identified for upgrading an existing kraft pulp mill:

- Route A: Upgrading cellulose pulp fibre to cellulose for higher-value products.
- Route B: Upgrading lignin into value-added products.
- Route C: Producing chemical intermediates and transportation fuels from forestry residues.
- Route D: Symbiotic processes for pulp mills and the food industry: production of fish and vegetables from waste streams using by-products.

In this context, the main product (cellulose pulp fibre) and associated by-products (black liquor, forest residues etc.) were further processed to produce value-added products. Additional upgrading and resource recovery from P&P wastewater were limited to anaerobic digestion of the sludge to produce biogas.

Table 2-1 Range of possible products from the pulp and paper industry (Jansson et al. 2015)

Component	Possible products
Cellulose	Textiles, fibres, non-woven textiles* (made of short and long fibres bonded together by heat, chemicals or pressure) and nanocellulose
Lignin	Used as raw material for carbon fibre, resins, gasoline, diesel, specialty chemicals and in chemical building blocks for bioplastics
Cellulose and hemicellulose	Used as chemical intermediates by the chemical industry
Forest residues	Processed to produce syngas and biogas, which can be further refined into transportation fuels and value-added chemicals
Pulp mill waste streams	Potentially used to produce biogas and algal-based chemicals

*The term is used in the textile manufacturing industry to denote fabrics, such as felt, which are neither woven nor knitted

While wood biomass is available in relatively large quantities, the total quantity is limited by the ability of companies to collect, transport and utilise this biomass, and this makes the procurement and logistics of wood biomass key success factors (Näyhä and Pesonen, 2012; Pätäri, 2010). Waste wood biomass is also mostly used for the production of bioenergy in mills, and this will limit the amount of biomass available for additional bio-based products, but this challenge can be mitigated by a company's strategic plan to diversify its classical portfolio to include both bioenergy and bio-based products (Chambost et al. 2008; Oliveira and Navia, 2017; Pätäri et al. 2011).

However, the PPI is traditionally known to be risk averse, which constitutes a significant barrier towards investing in second-generation biorefineries (Janssen and Stuart, 2010a; Näyhä and Pesonen, 2012;

Toppinen et al. 2017). The authors highlighted that the necessary resources to develop and implement new second-generation biorefinery technologies are often not present in the PPI, and cooperation with research institutes or universities or both is necessary to develop R&D and engage in the appropriate knowledge transfer. The latter is key since the ability to develop biorefineries (both second and third generation) in the PPI is present, but the transfer from theory to practice is lacking.

Another crucial factor which will determine the success or failure of establishing forest biorefineries is the identification of new value chains that will create new markets and attract new customers (Giurca and Späth, 2017; Toppinen et al. 2017). Political and governmental support also make a valuable contribution to mitigating the risks of new development and investment and thus play significant roles in biorefinery development (Giurca and Späth, 2017; Janssen and Stuart, 2010a; Stern et al. 2015).

Against this backdrop, the complexity of the multi-faceted nature of the resulting forest-based value chain has been recognised. Aggestam and Pulzl (2018) highlight the benefits of the circular economy approach to the forest value chain, of which the P&P industry is a subset, as well as the potential for contribution to reduced fossil fuel dependence and preservation of biodiversity. Benefits with potential to accrue from the forest value chain include opportunities for rural communities, competitiveness, and sustainability of the industry, contribution to mitigation of climate change and maintenance of ecosystem services, and contribution to the green economy. To maximise these, appropriate indicator systems are required and are under development for Europe (von Geibler et al. 2010).

Sections 2.2, 2.3 and 2.4 explore how the pulp and paper industry in, respectively, Europe, Brazil and North America is diversifying their product portfolio. Section 2.5 then examines how our study fits within these global developments around value recovery and value addition in the industry.

2.2 The evolving European P&P industry

The PPI in Europe has been experiencing global competition due to lower production costs in South America (pulp production) and South East Asia (paper and packaging production) (CEPI, 2013). Declining growth and profitability are further compounded by the changing landscape of environmental policy in the European Union with a growing emphasis on climate change mitigation (Näyhä et al. 2014; Näyhä and Pesonen, 2012; Toppinen et al. 2017). Between 2000 and 2017, the number of companies and mills decreased by more than 30%, with the number of employees declining by 37% since 2000 (CEPI, 2018).

The Confederation of European Paper Industries (CEPI) positions the European paper industry as a benchmark model of resource efficiency, easily integrated into a circular economy (CEPI, 2015). The second-generation biorefinery concept is ubiquitous in their published reports: wood fibre is used to make pulp, chemicals are made from resins, and bark is used to produce energy. The carbon stored in the products is usually converted to bioenergy by the end of the product's lifetime. Figure 2-1 presents an overview of the range of products which can be synthesised from the three main components in wood.

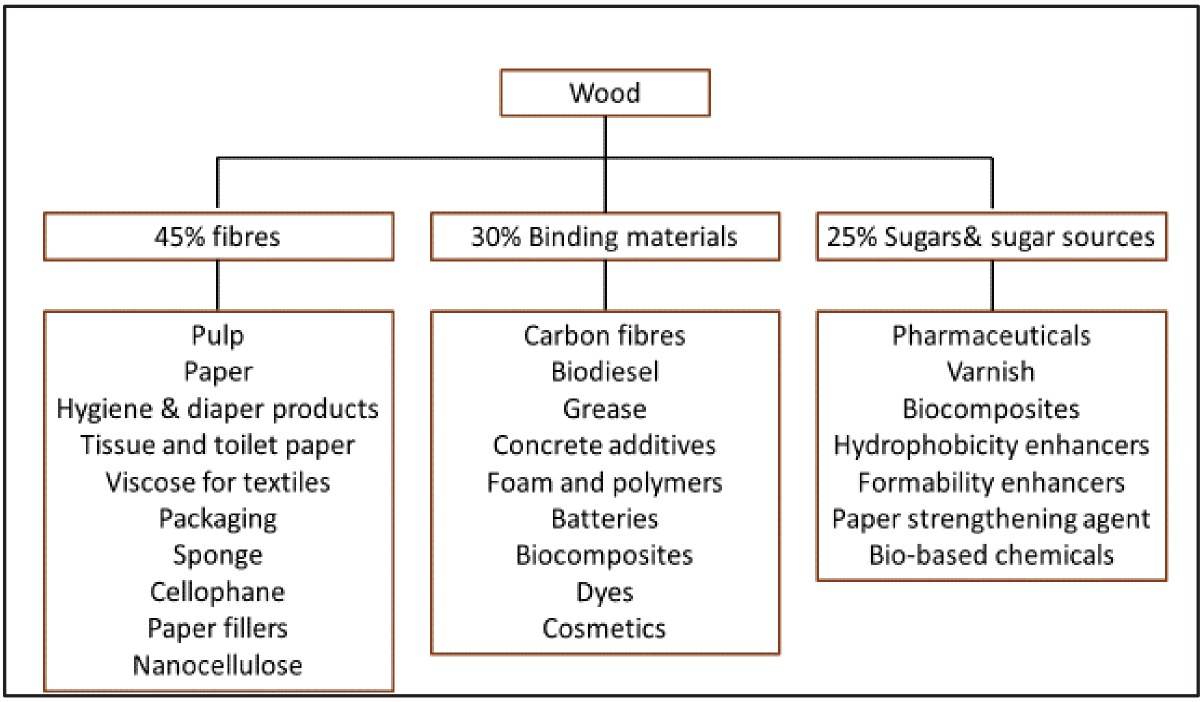

Figure 2-1 Range of possible products through the exploitation of wood components (CEPI, 2015)

In CEPI (2021), the first biorefinery study on the European forest industry was reported, where biorefineries were classified into three sub-categories:

- Category 1: Biorefineries based on chemical pulping operations to produce various existing or emerging bio-based products
- Category 2: Biorefineries using virgin pulp or recycled fibres or both to produce emerging bio-based products
- Category 3: Other biorefineries using lignocellulose as raw material to produce existing or emerging bio-based products

Bio-based products were further classified into five areas for commercial or internal use, with examples of current production given in Table 2-2:

- Materials
- Chemicals
- Fuels
- Food and feed
- Cosmetics and pharmaceuticals

Table 2-2 Production of non-traditional products in the P&P biorefineries in Europe, adapted from CEPI (2021)

Materials	Chemicals	Fuels	Food/feed
- Bio-composite - Cellulose nanofibres - Kraft lignin - Man-made fibres - Microfibrillated cellulose - Nanocrystalline cellulose - Powdered cellulose	- Biopolymer - Carbon dioxide - Dimethyl ether - Lignosulphonates - Methanol - Monoethylene glycol - Sulphuric acid - Tall oil products	- Biodiesel - Bioethanol - Biogas - Bio-oil - Lignin oil - Syngas	- Carboxymethyl cellulose - Microcrystalline cellulose - Vanillin

Note: Traditional products from P&P mills, such as chemical pulps, board and paper grades, were not included in the study. No products under the cosmetics/pharmaceuticals were identified.

A total of 139 biorefineries were identified across Europe, most of which are based on chemical pulping (84%). Most of the facilities are located in Sweden, Finland, Germany, France and Austria, producing common bio-based products such as man-made fibres, biodiesel, bio-naphtha, lignosulphonate and tall oil products.

2.2.1 Examples of product diversification by European P&P companies

2.2.1.1 Borregaard, Norway

One of the most advanced wood biorefineries is the Norwegian company, Borregaard. Their Sarpsborg mill produces a versatile speciality cellulose which can be used in the construction industry, the oil industry, the food industry, the cosmetics industry and the textile industry. Bioethanol is produced from sugars present in the wood. This company is also the only producer of vanillin, one of the most sought-after flavouring agents, using wood as raw material rather than traditional petrochemical raw materials (Borregaard, 2018). A summary of the applications for the products derived from wood components produced by Borregaard at the Sarpsborg mill is shown in Table 2-3.

Table 2-3 Areas of use of wood-derived products from Borregaard (Borregaard, 2018)

Wood-derived products	adhesives	animal feed	agriculture	battery	bioethanol	bioplastics	carbon black
ceramics	coatings	construction	dust control	emulsions	flavour	food	Fragrance
home care	industrial binders	industrial cleaners	oilfield	personal care	pharma	textiles	water treatment

2.2.1.2 UPM, Finland

The forest company UPM is a leading forest-based biorefinery in Finland (UPM Biochemicals, 2018). In addition to traditional P&P products, UPM produces three types of bioproducts: chemical building blocks (CBB), lignin products and biomedical products (UPM Biochemicals, 2018). Their lignin product is used in resins. For medical applications, the company produces wood-based cellulose, nanofibril hydrogel, biocompatible with human cells and tissues. Biodiesel and naphtha are made from the tall oil extracted in the pulping process and are produced at the UPM Lappeenranta biorefinery. This Finnish company also developed a wood-plastic composite from recycled paper and leftover paper labels, possessing the combined characteristics of cellulose and plastic (UPM Profi, 2018). Additional products include turpentine which can be used in the perfume industry, and pitch, used in energy generation and manufacturing (UPM Biofuels, 2018). Other CBBs are currently under development via their Biofore™ platform, which seeks the integration of bioindustry and forest industries (UPM Biochemicals, 2018).

One of the sustainable development targets of UPM mills is to achieve zero solid waste to landfill or incineration without energy recovery by 2030 in Finland. This has already been achieved in UPM Austria and seven UPM mills in Germany (UPM, 2016). In 2015, 67% of the fuel used by UPM was biomass-derived: from bark and logging residues as well as the fibre-rich solid waste from de-inking and wastewater treatment. The current usage or disposal methods for the main types of waste at UPM mills are shown in Table 2-4. Research is currently focused on the valorisation of the five most difficult components to recycle in Finland: mixed waste and wood residue that includes sand, sludge, dregs and ash (UPM, 2018).

Table 2-4 Solid waste valorisation in UPM mills(UPM, 2018)

Main waste fractions	Source	Usage or disposal
Ash	Power plants	Most of the ash is utilised in earthwork operations, as a fertiliser or in the cement and brick industry Only a small fraction is taken to landfills
Organic process waste such as bark, fibre residues and fibre sludge	Wood and recovered paper processing, effluent treatment	Mainly used as fuel by mill power plants Fibrous residues not incinerated are repurposed; for example, composted or used in soil improvement and earthworks
Other process waste, such as coating colour waste and green liquor dregs	Coating of paper Chemical pulping	Large proportion repurposed; for example, in the construction industry and soil improvement The rest is mainly landfilled
Other solid waste	Recovered paper processing, label production, packaging of incoming materials (mainly metal, board or plastic waste)	Sorted and utilised as a raw material where possible, e.g. for the wood-plastic composite Unusable waste fractions taken to landfill sites or municipal waste incineration plants
Hazardous waste	Maintenance (mainly oil or oil-contaminated equipment)	Forwarded to licensed hazardous waste treatment facilities Compliance with relevant statutory requirements documented

2.2.1.3 Stora Enso, Finland

The Stora Enso mill in Finland produces a high-purity kraft lignin, which is separated from Nordic softwood black liquor during the kraft pulping processing using the Lignoboost™ method (Section 0) (Stora Enso, 2018a). The product can act as a phenol replacement in industrial resins used in the manufacture of wood panels and engineered woods. Further research in expanding the applications of this lignin product is underway. Crude tall oil and turpentine are other products of their kraft pulping. Crude tall oil derivatives can be used in the adhesive, rubber and lubricant industries, while crude turpentine applications include solvents, thinners and adhesives, as well as flavours and fragrances for the food and cosmetic industries (Stora Enso, 2018b).

A strong focus is placed on recycling chemicals and using residual biomass, such as bark and wood waste, lignin, black liquor and wastewater sludge, to produce heat and power, leading to around 98% of their waste being reused either in their facilities or by external parties (Stora Enso, 2018c). The Stora Enso mill has also acquired an extraction and separation technology from US Company Virdia to extract sugars and lignin from lignocellulosic material, leading to three different processing platforms–xylose (C5 sugars), cellulose or glucose (C6 sugars) and lignin (Granström, 2015). This will allow the company to develop its biorefining capabilities with a focus on producing both sugar-derived and lignin-based products from lignocellulosic biomass (Stora Enso, 2018d). Granström (2015) explains that the properties of the lignin, which can be extracted via the biorefinery platform, are different from the kraft lignin mentioned above and thus can offer a wider range of applications, particularly in the automobile and construction industries.

2.2.1.4 Other European P&P mills

The Italian producer Favini uses agro-industrial waste from oranges, nuts, corn and olives as raw materials for paper production. Sappi's European mills make use of waste sludge as animal bedding material and in the manufacture of bricks or cement (Sappi, 2018a). The Svenska Cellulosa AB's (SCA) Lilla Edet mill in western Sweden uses the ash from the burning of sludge as a construction material for roads, as a binder in asphalt and a pH control agent for farm soil. The Metsä forest in Finland supplies ash (rich in potassium and phosphors) to forest owners for use as fertiliser. Residues from the pulping process are used for soil restoration in Portugal and in maintaining the health of forestlands. The Saica paper mill in Spain has anaerobic digesters which transform organic waste into biogas (CEPI, 2015).

2.2.2 European Union's Horizon 2020

European Commission (2018) describes Horizon 2020 as the biggest EU Research and Innovation Programme with funding of close to € 80 million spanning seven years (2014–2020). There are two main projects dedicated to the P&P biorefinery–the Bioforever and Zelcor projects. The Bioforever project, an acronym for bio-based products from forestry via economically viable European routes, aimed to investigate the feasibility of using lignocellulosic biomass to produce chemical building blocks and high-value-added products. Over the project's course (2016–2019), processing technologies were investigated and selected for pre-industrial-scale operations, after which commercialisation routes for the most promising value chains were presented (Bioforever, 2018). The Zelcor (zero-waste lignocellulosic biorefineries by integrated lignin valorisation) is a 3-year project (2016–2019) focused on harnessing the potential of recalcitrant side streams in a lignocellulosic biorefinery towards the production of high-value-added bio-based products, including fine chemicals (Zelcor, 2018). The main three recalcitrant streams under investigation are lignocellulosic residues from ethanol production, lignin dissolved during the pulping process, and lignin-like humins formed by sugar conversions. The objective is to facilitate these bioconversions through a combination of chemical and biological processes (Zelcor, 2018).

2.2.3 Overview of European facilities focused on process and product research within the P&P industry

LignoCity is a joint venture among Innventia, Nordic Paper and Paper Province where the companies can develop and upscale processes and technology related to lignin-based products such as fuels, chemicals and materials (RISE, 2018a). A plant in Bäckhammar was set up in 2007 to demonstrate the LignoBoost™ process, where lignin is precipitated from black liquor by acidification (using CO_2) and filter pressed (Tomani, 2010). An R&D service is offered to clients who wish to investigate the potential of their black liquor for the production of lignin-based products. Incidentally, in 2011, a nanocellulose pilot plant with a capacity of 100 kg/day was opened at LignoCity, where the R&D conducted on-site showed that upscaling is possible. With additional funding, a movable demo plant for nanocellulose was built in 2017 to allow paper mills to test the production of nanocellulose in their facilities. The nanocellulose can be used as an additive in paper machines to improve the qualities of paper and cardboard (RISE, 2018b). The centre also has a testing facility for extruding lignin into fibres (filaments) and converting them to carbon fibres via several heat treatments (RISE, n.d.).

Stora Enso mill in Finland established an innovation centre dedicated to the R&D of biomaterials. Current research includes the production of cost-competitive carbon fibre from a mixture of lignin and cellulose (The renewable materials company, 2018).

2.3 Brazilian P&P industry

In Brazil, the P&P industry is mostly concentrated in the central south, with Fibria, Suzano and Klabin being the largest companies in terms of revenue(Business Sweden, 2014). All three companies have a strong focus on water reuse:

- Fibria recirculates its captured water 4. 2 times before disposal through plant sections such as the cooling tower and backwash circuits for filtered fibre (Fibria, 2018);
- Suzano water reuse rate is approximately 35% (Suzano Pulp and Paper, 2018);
- Klabin's recycled water is put to the following uses: producing glue, cleaning in its packaging sector, irrigation, the papermaking process, cooling hot water and condensate return(Business Sweden, 2014). Five of Klabin's production units use 100% of its factory effluents, and their WWTPs have a BOD removal of 85.5%.

Suzano is investing in lignin production as part of the diversification of its operations to include biorefining in its portfolio(Suzano Papel e Celulose, 2016).

2.4 North American P&P industry

2.4.1 United States

The US has a dedicated Forest Products Laboratory based in Madison, Wisconsin(USDA, n.d.). One of their research portfolios is the forest biorefinery focused on using woody biomass to produce biofuels (Forest Products Laboratory, 2018). The State University of New York (SUNY)College of Environmental Science and Forestry (ESF) in Syracuse, New York, developed a hot water extraction process to be used as pre-treatment before the chemical pulping or burning of wood chips (Amidon and Liu, 2009). The hot water extraction technology was further used to develop a value-optimisation pathway from woody biomass (the ABS^{TM} process) and is on the path to commercialisation, facilitated by a private company based in New York, Applied Biorefinery Sciences LLC (Amidon et al. 2011). The resulting multi-product portfolio is depicted in Figure 2-2. It is important to note that this research was focused on valorising the hemicellulose rather than the cellulose and lignin fractions. The rationale was that cellulose has a high current commodity value as fibres, and lignin has a heating value, thus, the hemicellulose potential is what remains significantly untapped.

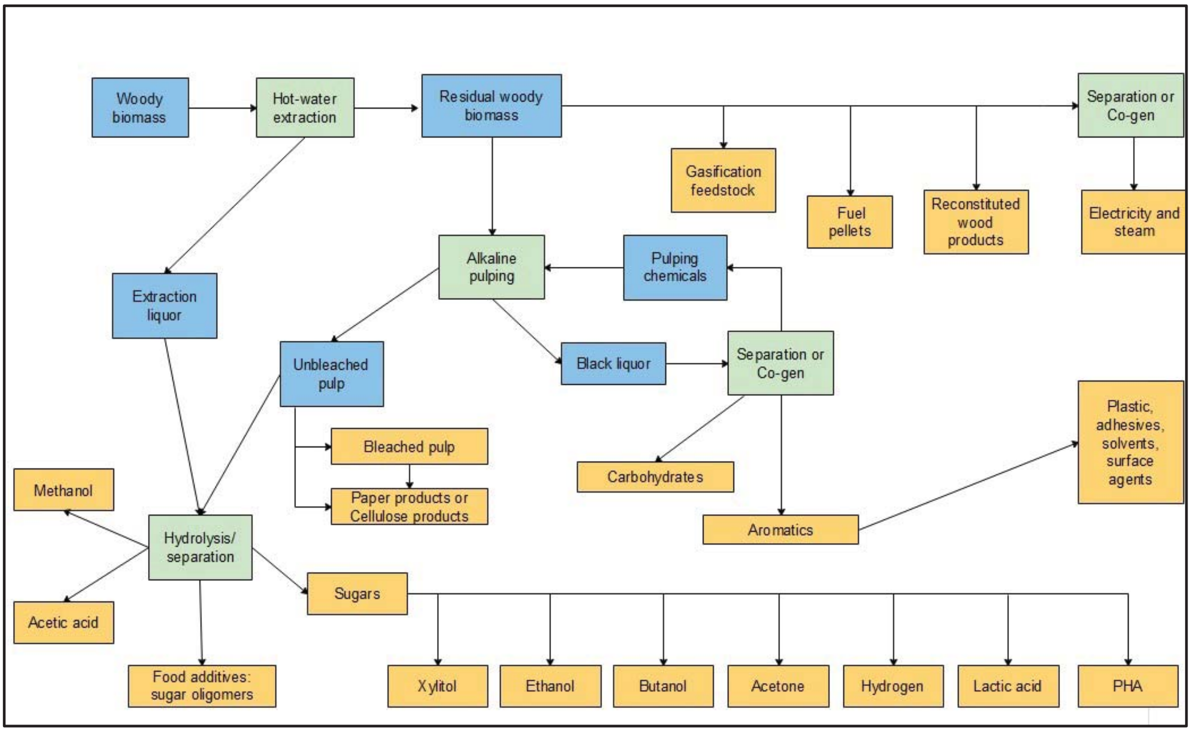

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Figure 2-2 Multi-product pathways developed for the hot water extraction process by Amidon and Liu (2009)

2.4.2 Canada

The governmental commercial and industrial innovation framework in Canada focuses on energy-oriented R&D for existing Canadian plants with the aim of increasing industrial energy efficiency by 20% or more (Natural Resources Canada, 2018a). They have a dedicated project to investigate the potential of forest biorefineries across three biorefinery technologies, as illustrated in Figure 2-3: 1) lignin extraction and processing, 2) hemicellulose extraction and processing, and 3) biomass gasification. While the Canadian forest biorefinery is similar to the European one, they are taking a more cautious approach by focusing on the integration of the various interlinked systems for energy generation, steam and water usage, heat recovery techniques, greenhouse emissions, and the economic outlook of existing plants. A decision-support tool will be put together to offer biorefinery solutions to existing mills (Natural Resources Canada, 2018b). A trial will be implemented in an existing kraft pulp mill.

A partnership was announced in 2017 between the Neste Corporation, a renewable fuels company and Bioenergy La Tuque (BELT) to investigate the production of biodiesel from forest harvest residues in La Tuque, Canada (Neste, 2017). This project is considered a large-scale forest biorefinery utilising the thermochemical pathway to produce biofuels in the short term and other bioproducts in the long term (Delcroix and Mangin, 2016).

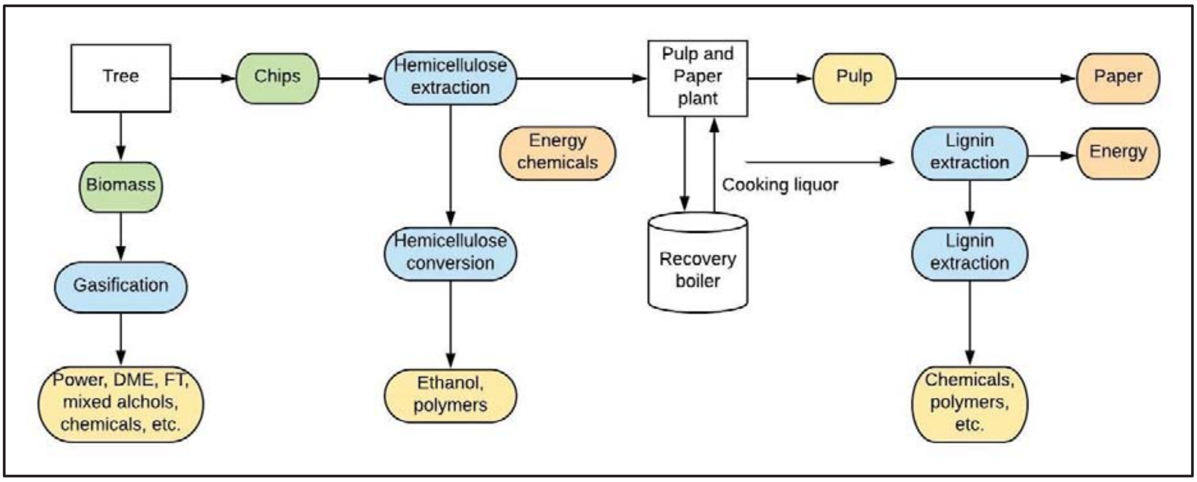


Figure 2-3 Schematic of a Canadian Integrated Forest Biorefinery, a project adapted from (Natural Resources Canada, 2018b)

2.5 Identifying the opportunity for a pulp and paper wastewater biorefinery

The concept of an integrated biorefinery in the PPI has already been applied to existing chemical pulping technologies in the P&P industry - kraft, sulphite and soda where the main product is a paper product (cellulosic fraction), and secondary products are the energy products from the residual black liquors (lignin-rich fraction) and bioproducts such as tall oil, turpentine, crude oil and lignosulphonates(Drahansky et al. 2016; Suhr et al. 2015).

Globally, there is a now strong focus on implementing the P&P biorefinery within the context of second-generation biorefineries, whereby the feedstocks are in the form of lignocellulosic biomass and non-food crop biomass. The Europeans are focusing on maximising the use of woody material for developing hemicellulose- and cellulose-based products and lignin-based products. There is a drive for more sustainable practices with regard to handling solid waste. A key observation is that the value of lignin is being extended beyond its traditional use as a fuel. Thus it is estimated that with 1 m^3 of wood, 2.38 times more products and energy arise from the cascading use of wood instead of its single-use (Mautau, 2012). Cascading use refers to how different wood components are used by different sectors and how the waste and residue from one sector are used by another, as depicted.

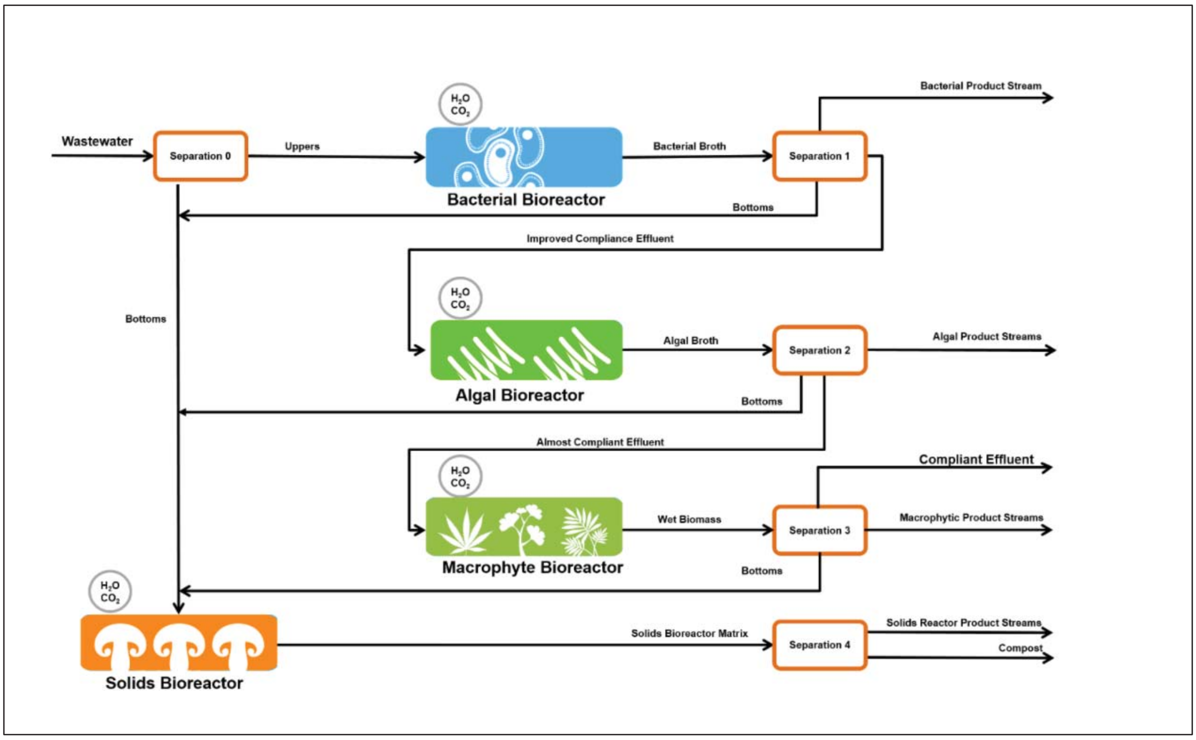


Figure 2-4 Example of cascading use of wood adapted from Essel et al. (2014) and reported in Babuka et al. (2020)

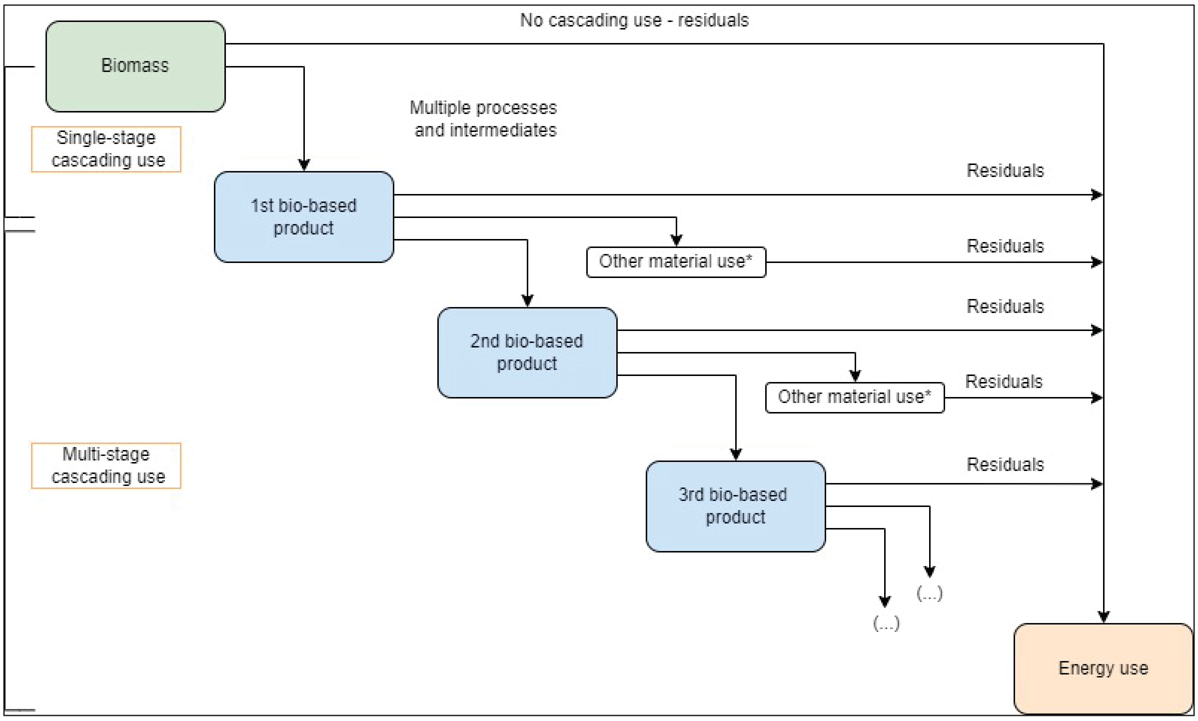


Figure 2-5 Wastewater biorefinery concept developed by Harrison et al. (2017a)

Regarding wastewater, the general approach is to maximise its reuse through recycling and managing the pollutants within. There is no explicit work being done on the possible valorisation of the wastewater streams in an integrated system where wastewater treatment is achieved in tandem with bioproducts formation from the resources contained with the wastewater. Such practice will fall under the implementation of third-generation biorefineries; this is the classification of the WWBR under consideration in the study described in this report. In short, our conceptualisation of the wastewater biorefinery (WWBR), depicted in Figure 2-5, has the ability to maximise cascading use of the woody feedstock in the PPI, thereby increasing resource efficiency and products of value while also increasing the water efficiency in the industry. Thus, this study is positioned within the realm of industrial ecology with a focus on resource recovery and resource efficiency. The concept presented interfaces well with the move to application of the second-generation biorefinery in the PPI in Europe, Brazil, the USA and Canada, in which the product spectrum is expanded with new value chains considered. Integration of the second-generation biorefinery with the WWBR stands to provide maximum benefit.

The WWBR concept within the South African P&P industry is investigated and explored in subsequent chapters.

3 Overview of the Pulp and Paper Industry in South Africa from a Waste Management Perspective

In order to investigate the possible implementation of the wastewater biorefinery concept within the South African PPI, we need a status quo of the current waste and wastewater management practices in the industry. Additionally, we need to investigate the raw materials used, products made, the type of pulping and papermaking technologies and whether the industry is already embarked on an approach towards the diversification of its product portfolio or, if not, whether it is open to doing so.

3.1 Current status of the South African pulp and paper industry

Both hardwood and softwood trees species are used for pulping in South Africa, with eucalyptus (*Eucalyptus grandis*) and acacia (*Acacia mearnsii*) being the most commonly used hardwoods and pine (*Pinus patula*), the more prevalent softwood as seen in Table 3-1, with a focus on their different features. In terms of non-wood cellulosic materials, recycled wastepaper and bagasse are predominantly used. All three main pulping processes (chemical, mechanical and semi-chemical) are employed in the South African pulp and paper industry, as detailed in Table 3-2, with a general estimate of their yield ranges(Adu-Poku, 2015; Mokebe, 2007).

Table 3-1 Types of wood cellulosic raw materials used in South Africa (Adu-Poku, 2015)

	Softwoods	Hardwoods
Wood species	mainly *P. patula*	mainly *E. grandis* and *A. mearnsii*
Fibre dimensions	long and thin fibres	short and thick fibres
End-products	low opacity	high opacity
Pulping characteristics	high lignin content, high extractive content	Low lignin content, low extractive content

Table 3-2 Common pulping processes used in South Africa (Mokebe, 2007)

Classification	Process name	Wood used	Yield range (%)
Chemical	Kraft	Hardwood and softwood	40–50
	Sulphite	Hardwood and softwood	45–55
	Soda	Hardwood	45–55
Mechanical	Groundwood	Softwood (mostly)	90–95
	Thermo-mechanical	Softwood	90 -96
Semi-chemical	NSSC	Hardwood	65–80
	SASAQ	Hardwood	50–65

Economic pressures experienced in South Africa in the last decade have led to the conversion or closure of a number of paper production facilities. While the demand for newsprint and office paper has decreased, there has been an increase in demand for recyclable paper bags and paper-based packaging owing to increasing environmental awareness and new legislations such as the extended producer responsibility (EPR) (Molony, 2021; Research and Markets, 2020). Molony (2021) reports a four-year average recovery rate of 70% in the country, making paper the second most recovered material in South Africa. There is a surplus of waste paper due to higher collection rates locally, which has led P&P companies to find new markets and uses for waste paper (Research and Markets, 2020).

The PPI in South Africa is the largest contributor to wastewater generation, as reported by van der Merwe et al. (2009) and Cloete et al. (2010), accounting for more than 60% of industrial effluents in the country, as depicted in Figure 3-1.

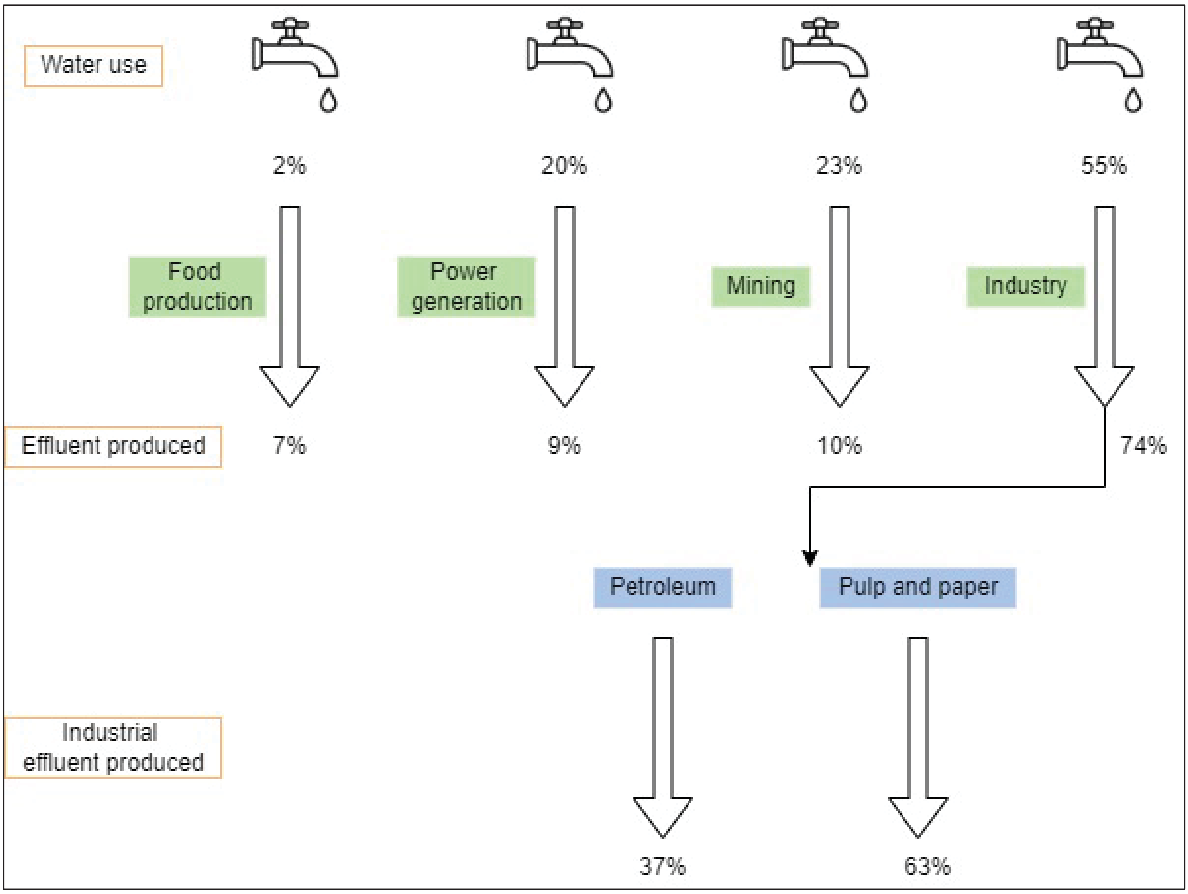


Figure 3-1 Water use and effluent production in South Africa adapted from Cloete et al. (2010) and reported in Steyn et al. (2021)

In terms of product portfolio diversification, Molony (2021) mentioned dissolving pulp and cellulose as wood-based products already in circulation and highlighted some additional promising wood-based products such as xylitol, biocomposites, nanocellulose, xylitol and alternate fuels from lignin. This demonstrates that the South African PPI is adopting a similar approach to that globally and working towards diversifying the revenue streams of a traditional P&P mill using a second-generation biorefinery approach. To this end, CSIR has partnered with the University of KwaZulu-Natal and established the CSIR Biorefinery Industry Development Facility, led by Prof. Sithole, to develop technologies for maximising the use of the woody biomass to up to 90% by focusing on the production of numerous value-added chemicals (CSIR, n.d.). The facility is investigating the extraction and production of products from sawdust waste, such as hemicellulose sugars, pine oils and nanocrystalline cellulose. Paper mill sludge is also being investigated as a feedstock for the production of bio-bricks and biopolymers (Sithole, 2017).

In terms of PPI players, Sappi is focused on expanding its product portfolio and has commissioned a second-generation biorefinery demonstration plant at its Ngodwana dissolving pulp mill in the Mpumalanga province. The demonstration plant is focused on the extraction and separation of sugars from a pre-hydrolysate liquor stream in the dissolving pulp process. Sappi is also investigating a selection of sugar-derived products, namely xylitol (a sugar substitute), furfural (to be used as a solvent), lactic acid (for the production of the biodegradable plastic polylactic acid) and glycols (for the production of PET bottles and resins) (Sappi, 2021, 2018b). The process for the manufacture of furfural and derivatives from sugar has been developed and implemented at the biorefinery at their Sezela plant in South Africa by the sugar company Illovo.

While the second-generation biorefinery approach constitutes various advantages, as highlighted in Chapter 2, the focus of this report is to explore the third-generation biorefinery approach focused on wastewater valorisation and repurposing and on whether it can be applied in the context of the South African PPI with the aim being to concomitantly manage the waste and wastewater challenges of the industry and develop a resilient and diverse product portfolio to harness the maximum potential of the resources contained within the waste streams (solid and liquid) in the industry and optimise resource efficiency.

3.2 Water and waste management in the South African paper and pulp industry

3.2.1 NATSURV report

As a starting point to explore resource efficiency in the waste sector of the PPI, the recently released NATSURV 12 on water and waste management, compiled by van der Merwe-Botha et al. (2017), was consulted and examined. The main purpose of this study was to investigate the PPI in South Africa with respect to their production capacity, specific water use, effluent production, energy use and best available techniques for the industry. The study identified 29 operational pulp and paper mills in South Africa, of which 22 participated in the survey. The five largest manufacturers are Kimberly-Clark, Mondi, Mpact, Sappi and the Twinsaver group.

Table 3-3, Table 3-4 and Table 3-5 were compiled to summarise the information obtained on each of the 22 mills. The water intake and effluent generation are dependent on the raw materials used, the process technology, the type of products produced and the age of the facility. At the time of their investigation, van der Merwe-Botha et al. (2017) reported the Cape kraft Sappi mill and Enstra Sappi mill to be still under Sappi ownership, but by the end of 2015, Sappi concluded the sales of the two mills–Cape kraft mill to the New Era Holdings and Enstra mill to the Corruseal Group (Sappi, 2016, 2015).

The water sources for each of the 22 mills are listed in Table 3-4. Raw water intake for the manufacturing process is taken from either a water source or the local municipality. The specific water intake per air-dried ton of product (SWI) for the participating sites was in the range of 11. 9–76. 1 m^3/Adt for the paper and pulp mills and 3. 5–38. 8 m^3/Adt for paper mills. The main effluent treatment technologies are clarification, activated sludge dissolved air flotation (DAF) and belt presses, as seen in Table 3-5. The specific effluent volume (SEV) was in the range of 10. 5–84. 5 m^3/Adt for the pulp and paper mills and 0. 08–38. 2 m^3/Adt for paper mills (van der Merwe-Botha et al. 2017). Treated effluents are either discharged into the environment or recycled within the process. The authors collected additional data from each of the 22 mills and anonymously reported their specific effluent volume per air-dried ton of product (m^3/Adt) and effluent composition. However, due to the anonymised data and confidentiality clauses, the authors were unable to share individual mill data with our team. Therefore, for this report, we focus on the upper and lower bounds, as well as the average values for the effluent data reported in the NATSURV 12 report, which are shown in Table 3-6 and Table 3-7. It is observed that P&P mills have higher effluent volume than paper mills, which is expected due to high water use during pulping processes. A look at the range and average values demonstrate that both specific effluent volume and the effluent composition vary significantly across the mills. In the case of the composition, the difference in characteristics of the treated effluents can also be attributed to different wastewater treatment facilities present in the different mills.

Table 3-3 South Africa mills data detailing location, type of plant, products and production capacity, adapted from Van der Merwe-Botha et al. (2017)

Name	Area	Province	Type of plant	Products
Kimberly-Clark	Enstra, Springs	Gauteng	Paper	toilet tissue, facial tissue and paper towel products
Mondi	Merebank	KwaZulu-Natal	integrated mechanical (TMP) and recycled paper and pulp mill	i) uncoated wood-free paper (260,000 t/a); (ii) newsprint 120,000 t/a
Mondi	Richards Bay	Northern KwaZulu-Natal	integrated kraft paper and pulp mill	bleached chemical pulp and white top linerboard at total production of 750,000 t/a
Mpact	Felixton	Northern KwaZulu-Natal	integrated paper and pulp mill	packaging material; Production capacity of paper machine is 165,000 t/a
Mpact	Piet Retief	South eastern part of Mpumalanga	integrated paper and pulp production facility	linerboard and fluting 132,000 t/a
Mpact	Springs	Gauteng	paper mill only	Packaging board production' 175,000 t/a on board 6 and 35,000 on board machine 3
New Era Holdings	Milnerton, Cape Town	Western Cape	paper mill only	fluting, 30,000 t/a; linerboard, 30,000 t/a)
Corruseal Group	Enstra, Springs	Gauteng	non-integrated paper mill	uncoated office paper; 200,000 t/a; fluting and linerboard grades
Sappi	Ngodwana, west of Mbombela	Mpumalanga	integrated pulp and paper mill	405,000 t/a total pulp; 370,000 t/a total water
Sappi Saiccor	Umkomass	KwaZulu-Natal	dissolving pulp mill	800,000 t/a elemental chlorine
Sappi	Stanger	KwaZulu-Natal	integrated paper and pulp mill	30,000 - 60,000 t/a uncoated paper; 30,000 t/a tissue
Sappi Tugela	Madeni	KwaZulu-Natal	integrated paper and pulp mill	210,000 t/a fluting paper and liner board packaging
Twinsaver	Bellville	Western Cape	tissue manufacturer	25,000 t/a tissue paper
Twinsaver	Klipriver	Gauteng	tissue manufacturer	24,000 t/a of tissue paper
Twinsaver	Verulam	KwaZulu-Natal	tissue manufacturer	10,000 t/a tissue wadding
Corell Tissue (independent)	Phoenix	KwaZulu-Natal	tissue manufacturer	10,000 t/a of tissue paper
Green Tissue (independent)	Bellville	Western Cape	tissue manufacturer	22-27 t/d of tissue paper
Sam's Tissue products (independent)	Langlaagte	Gauteng	tissue manufacturer	6000 t/a toilet tissue
Gayatri (independent)	Germiston	Gauteng	paper mill; packaging	
Huhtamaki (independent)	Springs	Gauteng	paper mill; packaging	
Huhtamaki (independent)	Atlantis	Western Cape	paper mill; packaging	
Lothlorien	Alberton	Gauteng	paper mill; packaging	

Table 3-4 South African mills data detailing location, type of plant, water source adapted from van der Merwe-Botha et al. (2017)

Name	Area	Province	Type of plant	Water source
Kimberly-Clark	Enstra, Springs	Gauteng	Paper	Fresh water supplied by municipality; fresh uptake is 19-24% of total monthly water requirements
Mondi	Merebank	KwaZulu-Natal	integrated mechanical (TMP) and recycled paper and pulp mill	From Durban Water recycling plant designed to treat 45,000 m/d of domestic and industrial ww
Mondi	Richards Bay	Northern KwaZulu-Natal	integrated kraft paper and pulp mill	Fresh water used is supplied as treated raw water by Mnlathuze Water
Mpact	Felixton	Northern KwaZulu-Natal	integrated paper and pulp mill (soda pulping)	(i) Raw water from Mhlathuze River (ii) potable water from adjacent Tongaat Hulett Sugar mill
Mpact	Piet Retief	South eastern Mpumalanga	integrated paper and pulp production facility	Water is extracted from Hlelo River; treated by flocculation to suitable quality for process use
Mpact	Springs	Gauteng	paper mill only	Fresh water from municipality
New Era holdings	Milnerton, Cape Town	Western Cape	paper mill only	Potable water and treated WW from municipality
Corruseal Group	Enstra, Springs	Gauteng	non-integrated paper mill	(i) Potable water from Rand Water (ii) treated municipal WW
Sappi	Ngodwana, west of Mbombela	Mpumalanga	integrated pulp and paper mill	Water from Ngodwana River stored in Ngodwana dam (owned and managed by SAPPI)
Sappi Saiccor	Umkomass	KwaZulu-Natal	dissolving pulp mill	Water from Umkomass River is pumped, flocculated and clarified, then used as domestic and process water; on-site de-mineralisation plant
Sappi	Stanger	KwaZulu-Natal	integrated paper and pulp mill	Water from Umvoti River and Mbozambo lake (filtered before used as process water); on-site de-mineralisation plant
Sappi Tugela	Madeni	KwaZulu-Natal	integrated paper and pulp mill	Water from Tugela River is flocculated and clarified before being sent to the Mill reservoir
Twinsaver	Bellville	Western Cape	tissue manufacturer	Potable water from municipality
Twinsaver	Klipriver	Gauteng	tissue manufacturer	(i) water from borehole (ii) potable water from Rand Water
Twinsaver	Verulam	KwaZulu-Natal	tissue manufacturer	uses a combination of fresh water (?) and recycled process water
Corell Tissue (independent)	Phoenix	KwaZulu-Natal	tissue manufacturer	uses a combination of fresh and recycled water (from where?)
Green Tissue (independent)	Bellville	Western Cape	tissue manufacturer	Water from municipality
SAMS Tissue products (independent)	Langlaagte	Gauteng	tissue manufacturer	uses a combination of fresh and recycled water (from where?)
Gayatri (independent)	Germiston	Gauteng	paper mill; packaging	Municipal water from Ekurhuleni municipality
Huhtamaki (independent)	Springs	Gauteng	paper mill; packaging	Municipal water
Huhtamaki (independent)	Atlantis	Western Cape	paper mill; packaging	Municipal water for supplemented groundwater
Lothlorien	Alberton	Gauteng	paper mill; packaging	Municipal potable water supplemented with groundwater

Table 3-5 South African mills data detailing location, plant type, effluent and solids treatment adapted from Van der Merwe-Botha et al. (2017)

Name	Area	Province	Type of plant	Effluent	Solids
Kimberly-Clark	Enstra, Springs	Gauteng	Paper	Only primary treatment of effluent is done via single-stage clarification 8600 - 11500 m^3/d	
Mondi	Merebank	KwaZulu-Natal	integrated mechanical (TMP) and recycled paper and pulp mill	Drainage system in place to collect WW on-site and re-direct to WW treatment; portion sent off to DWP and the rest to sea outfall	settled solids are sent for de-watering and sent off to Multi-Fuel Boiler
Mondi	Richards Bay	Northern KwaZulu-Natal	integrated kraft paper and pulp mill	All effluents generated are combined are routed to a 2-stage treatment plant; clarified effluent is sent to sea outfall	Activated sludge is settled out in secondary clarifier
Mpact	Felixton	Northern KwaZulu-Natal	integrated paper and pulp mill	Effluent and black liquor are combined, pre-treated on-site by clarification and then released to a marine outfall pipeline	
Mpact	Piet Retief	South eastern Mpumalanga	integrated paper and pulp production facility	Effluent produced in the mill is treated by dissolved air flotation and reused in paper machines; effluent from other areas sent off to clarifier where water and fibre are separated	Sludge is sent to landfill; product water from clarifier used for irrigation; black liquor is burnt to produce salt cake which is used as a makeup chemical in kraft mills
Mpact	Springs	Gauteng	paper mill only	Treated effluent is recycled internally, and excess is discharged from the municipality	TDS and SS are monitored
New Era Holdings	Milnerton, Cape Town	Western Cape	paper mill only	Effluent is treated by means of a dissolver air flotation (DAF) and clarification	
Corruseal Group	Enstra, Springs	Gauteng	non-integrated paper mill	Effluent is treated in two stages in WW plant	
Sappi	Ngodwana, west of Mbombela	Mpumalanga	integrated pulp and paper mill	All effluent streams report to the general effluent flume before going to treatment plant; strong black liquor is used as renewable energy source	Bark is used as a renewable energy source
Sappi Saiccor	Umkomass	KwaZulu-Natal	dissolving pulp mill	Effluent systems consist of three main channels	
Sappi	Stanger	KwaZulu-Natal	integrated paper and pulp mill	Effluent is pumped to primary clarifier, aeration lagoon and secondary clarifier before being discharged to the Ntshaweni river	
Sappi Tugela	Madeni	KwaZulu-Natal	integrated paper and pulp mill	Effluent is treated in a second clarifier and discharged into Tugela River	
Twinsaver	Bellville	Western Cape	tissue manufacturer	Effluent is treated on-site and recycled for reuse; excess clarified water is disposed of in municipal sewer	Solids are separated by centrifugation and disposed

Name	Area	Province	Type of plant	Effluent	Solids
Twinsaver	Klipriver	Gauteng	tissue manufacturer	Effluent is treated by clarification, removing part of COD and a portion of treated water is reused in the process; the rest is disposed of in municipal sewer	
Twinsaver	Verulam	KwaZulu-Natal	tissue manufacturer	Effluent is treated by means of a dissolver air flotation (DAF). Treated effluent and sand filters are recycled and reused in the paper machine. Excess process water is discharged to the eThekwini municipal sewer	
Corell Tissue (independent)	Phoenix	KwaZulu-Natal	tissue manufacturer		
Green Tissue (independent)	Bellville	Western Cape	tissue manufacturer	treats and reuses effluent on-site	
SAMS Tissue products (independent)	Langlaagte	Gauteng	tissue manufacturer	mill has installed an effluent treatment plant	
Gayatri (independent)	Germiston	Gauteng	paper mill; packaging	Effluent is treated and water is reused as washing water and any excess is discharged into municipal sewer system	Suspended solids are removed by a DAF unit; solids that are skimmed off are returned to process
Huhtamaki (independent)	(i) Springs	(i) Gauteng	paper mill; packaging	facility is operated as a closed loop with minimal effluent generated, once a year cleaning and flushing of system; effluents are released into municipal sewer	
Huhtamaki (independent)	(ii) Atlantis	(ii) Western Cape	paper mill; packaging	facility is operated as a closed loop with minimal effluent generated, once a year cleaning and flushing of system; effluents are released into municipal sewer	
Lothlorien	Alberton	Gauteng	paper mill; packaging	Liquid effluent is treated by screening; a portion is reused on-site and excess is released to municipal sewer	

Table 3-6 Specific effluent volume for pulp and paper mills which participated in the NATSUV12 adapted from van der Merwe-Botha et al. (2017)

	Range	Average
Specific effluent volume per air-dried ton of product (m^3/Adt) for pulp and paper mills	10.5–84.5	37.5
Specific effluent volume per air-dried ton of product (m^3/Adt) for paper mills	0.08–38.2	12.2

Table 3-7 Treated effluent characteristics for pulp and paper mills which participated in the NATSUV12 adapted from van der Merwe-Botha et al. (2017)

	Range	Average
COD (mg/l)	165–3853	1773
Conductivity (µS/cm)	210–4970	2070
SS (mg/l)	38–2260	561
pH	6.5–8.5	7.5
N (mg/l)	0.1–1.2	0.4
P (mg/l)	0.1–0.27	0.2
SO_4 (mg/l)	16–565	234
Cl (mg/l)	11–340	151
Na (mg/l)	10–582	293

3.2.2 Data challenges in the industry

Additional reports were consulted to get more localised and detailed information on P&P effluents. Table 3-8 was compiled by Harrison et al. (2017) using data from Burton et al. (2009), CSIR (2010), Cloete *et al.* (2010) and Hagelqvist (2013) to categorise the available wastewater data for the P&P industry based on volume, concentration and complexity.

Harrison et al. (2017)further proposed a data standardisation for the concentrations of C, N and P from the COD, TKN, ammonia, nitrate, nitrite and PO_4^{3-} concentrations.

$$Concentration\ of\ C\ (mg/l) = 3\ x\ COD\ (mg/l) \quad \text{Equation 3-1}$$

$$Concentration\ of\ N\ (mg/l) = (14/62)\ x\ NO_3^- - N(mg/l)\ or\ (14/18)\ x\ NH_4^- - N(mg/l) \quad \text{Equation 3-2}$$

The total Kjeldahl nitrogen (TKN) is the sum of organic nitrogen, ammonia (NH_3) and ammonium (NH_4^+) in the sample. Organic nitrogen consists of protein, urea and nucleic acids. The total nitrogen (TN) is the sum of TKN, nitrate (NO_3^-)-N and nitrite (NO_2^-)-N

$$Concentration\ of\ P\ (mg/l) = (31/95)\ x\ PO_4^{3-}(mg/l) \quad \text{Equation 3-3}$$

To obtain more perspective, the data reported by Harrison et al. (2017) was decoupled into two main sources: Table 3-9 for the data obtained from Burton et al. (2009)and Table 3-10 from Cloete *et al.* (2010). Burton et al. (2009) were able to get data on combined wastewaters before any on-site treatment from four pulp and paper mills only: Mondi at Richards Bay (flow, COD, pH), Felixton (flow, COD), Piet Retief and Springs (flow, COD). Data shown for the remaining mills' data, shown in Table 3-9, was sourced from open literature and estimated using the pulp and mills production figures. The COD (mg/L) was converted to the estimated C content (mg/L) using Equation 3-1. The data from Cloete *et al.* (2010) was obtained directly from the P&P mills and reported anonymously for confidentiality. The wide range of measured parameters in the P&P industry is expected, given the significant differences in the various raw materials and types of pulp production and papermaking/recycling operations.

While previous reports provided a detailed overview of the P&P industry in South Africa, characteristics of raw waste and wastewater before treatment are missing, and this data is crucial for exploring the feasibility and development of a P&P WWBR.

Table 3-8 Volume, concentration and complexity of the SA pulp and paper industry (Harrison et al. 2017)

Effluent volume in South Africa	total estimated effluent volume in South Africa	ML/year	339300
	Days of operation	days	365
	total estimated effluent volume in South Africa	ML/day	929.6
Distribution of number of plants (data obtained from Burton et al. 2009)	TOTAL		18
	Micro	< 0.5 ML/day	0
	Small	0.5–2 ML/day	8
	Medium	2–10 ML/day	3
	Large	10–25 ML/day	2
	Macro	> 25 ML/day	5
Concentration	estimated average carbon content	mg/L	2850
	estimated average nitrogen content	mg/L	9.04
	estimated average phosphorus content	mg/L	1.3
	pH		6–8
	Conductivity	mS/m	1.5–348
	solids component (TSS)	mg/L	6000
	toxic compounds		absorbable organic halogens (AOX)
	Metals		-
Complexities	complex organics		chlorinated lignosulphonic acids, chlorinated resin acids, chlorinated phenols and chlorinated hydrocarbons, chlorinated organics such as chloroform, chlorate, phenols, catechols, guaiacols, furans, dioxins, syringols, vanillins
	other valuable components		cellulose

Table 3-9 Annual combined wastewater data before on-site treatment adapted from Burton et al. (2009)

Mill	Wastewater (ML)	COD (mg/L)	estimated C content (mg/L)
Mondi			
Merebank	10264	470–1659	1410-4977
Richards Bay	21361	1399	4197
Felixton	1933	22842	68526
Piet Retief	566	6021	18063
Springs	1046	1940	5820
Sappi			
Saiccor	33320	615–3073	1845–9219
Stanger	6248	319–1175	957–3525
Enstra	7586	578–1929	1734–5787
Adamas	506	848–3221	2544–9663
Ngodwana	10413	1219–4607	3657–13821
Tugela	15470	358–1305	1074–3915
Cape kraft	428	592–4167	1776–12501
Nampak			
Bellville	655	733–2443	2199–7329
Kliprivier	506	711–2372	2133–7116
Riverview	208	721–2404	2163–7212
Rosslyn	298	671–4698	2013–14094
Kimberly-Clark			
Enstra	803	897–2989	2691–8694
New Era			
Gayatri	-	625–4375	1875–13125
Other	-	789–3116	2367–9348

Table 3-10: Wastewater data from Cloete et al. (2010)

	COD (mg/L)	Ammonia (N) (mg/L)	Nitrite/ Nitrate (N) (mg/L)	Phosphate (P) (mg/L)	TSS (mg/L)	pH
Paper industry effluent 1 (Cape Town)	1461	-	-	-	-	6
Paper industry effluent 2 (Cape Town)	5898	-	-	-	-	6
Paper industry effluent three for the year 2002 (location anonymous)	6328	-	-	-	18.5	-
Paper recycling effluent (Tshwane)	14225	8.7	1.52	4	-	8
Carton recycling and manufacturing effluent (Tshwane)	3667	0	3	6	-	8

N.B: The authors did not specify whether the reported data is for treated or untreated effluent

3.3 A look at the geographical clusters of South African pulp and paper mills

A preliminary mapping of the participating 22 pulp and paper mills from the NATSURV 12 was undertaken. Referring to Figure 3-2, four main clusters can be identified based on their regional proximity. The rationale behind geographically clustering the mills is to analyse the possibility of collaboration between mills which are geographically co-located on the potential for implementation of the WWBR concept. In order to identify the type of wastewater within each cluster, the data was compiled to showcase the process description of each mill as described by van der Merwe-Botha et al. (2017).

Furthermore, with wastewater having generally diluted concentrations of nutrients for a successful biological conversion to potential products, the wastewater of the P&P mills can be mixed with the wastewater from surrounding facilities to generate a more robust source of carbon, nitrogen and phosphorus.

Figure 3-2 Preliminary mapping of pulp and paper mills in South Africa

Table 3-11 Process description of mills with respect to their regional clustering

Mills in Gauteng cluster	Process description
Kimberly-Clark, Enstra	- de-inking plant on-site for processing of waste paper etc. - pulp is bought from other mills for production of virgin tissue - waste paper of different grades is bought un for recycled fibre tissue - Tissue manufacturing includes pulping, blending, refining, screening, formation and drying - Recycled fibre plant includes pulping, bulk screening, coarse screening, fine screening, washing, flotation, bleaching and wetlap formation via a press
Corruseal Group (previously Sappi Enstra)	- non-integrated mill using bleached pulp and both recycled and virgin unbleached pulp
Twinsaver, Klipriver	- de-inking on-site - Hardwood and softwood pulps are re-pulped in a high-intensity pulper
Sam's tissue	
Gayatri	- packaging producer; producers kraft liner and fluting from 100% recycled paper
Huhtamaki	- packaging producer; pulping of waste paper to producer packaging material
Lothlorien	- packaging producer; produces brown paper from recycled fibres
Mpact	- packaging board production facility; uses recycled paper and imported pulp
Mills in KwaZulu-Natal cluster	**Process description**
Mondi, Merebank	- mechanical pulping and recycled paper and pulp mill
Mondi, Richards Bay	- Kraft pulping and paper mill
Mpact	- soda pulping to produce bagasse pulp, paper mill
Sappi, Saiccor	- dissolving pulp mill for the production of specialised cellulose
Sappi, Stanger	- soda pulping to produce bagasse pulp, paper mill
Sappi, Tugela	- unbleached kraft and semi-chemical, uses a combination of wood and waste paper, paper mill
Twinsaver	- pulper, stock preparation equipment and paper machine for tissue production
Corell tissue	- tissue manufacturer
Mills in Mpumalanga cluster	**Process description**
Mpact	- semi-chemical alkaline sulphite anthraquinone, paper production
Sappi	- Kraft pulping process, paper production
Mills in Western Cape cluster	**Process description**
Twinsaver	- tissue production from recycled fibre and virgin pulp
Green tissue	- tissue production
Sappi cape kraft (sold to Golden Era Group)	- paper mill only, re-pulps waste paper to produce paper products
Huhtamaki	- pulping of waste paper, packaging

3.3.1 Gauteng cluster: wastewater type and location distance

Figure 3-3 shows the Gauteng cluster for the pulp and paper mills. The green area (A: 821 km^2) represents the tissue manufacturers, while the pink area (A: 88.5 km^2) shows the paper packaging plants. Grouping similar manufacturing plants in sub-categories allows for the selection of similar wastewater types. However, the tissue manufacturers are quite distant from each other, with the closest distance being between Twinsaver Klipriver and Kimberly-Clark at around 40 km. The packaging companies Mpact and Huhtamaki are less than 1 km away from each other, and the Corruseal Group is 3 km away from Mpact, while the Gayatri plant is 6 km away from Lothlorien. Thus, potential partners for collaboration are Mpact-Huhtamaki, Corruseal Group-Mpact and Corruseal Group-Kimberly-Clark.

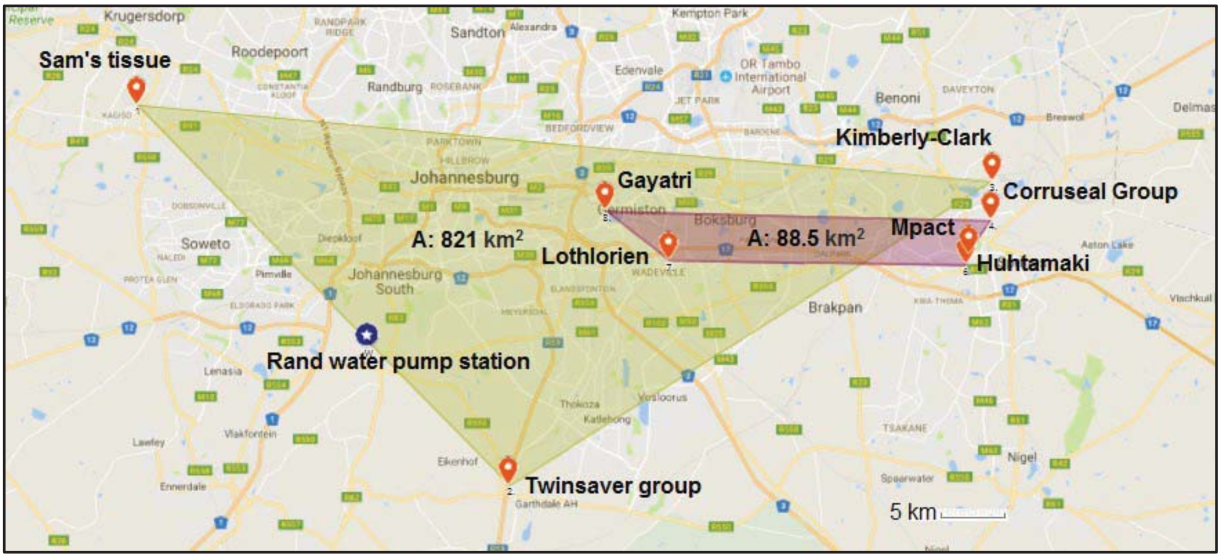


Figure 3-3 Gauteng cluster of pulp and paper mills

3.3.2 KwaZulu-Natal cluster: wastewater type and location distance

The mills in this cluster have mostly different manufacturing operations, as seen in two exceptions - Mpact and Sappi Stanger mills have similar soda pulping processes; Twinsaver Riverview and Corell tissue are tissue manufacturers. However, the distance between the mills, represented in Figure 3-4, at an estimated 82 km and 11 km, respectively, will not facilitate potential collaboration. Also, Mpact and Sappi are well-established plants with significant large production facilities and their own primary and secondary wastewater treatment.

Figure 3-4 KwaZulu-Natal cluster of pulp and paper mills

3.3.3 Mpumalanga cluster: wastewater type and location distance

The two mills in this cluster have different manufacturing processes and are over 150 km apart, as seen in Figure 3-5, and this makes collaboration highly unlikely.

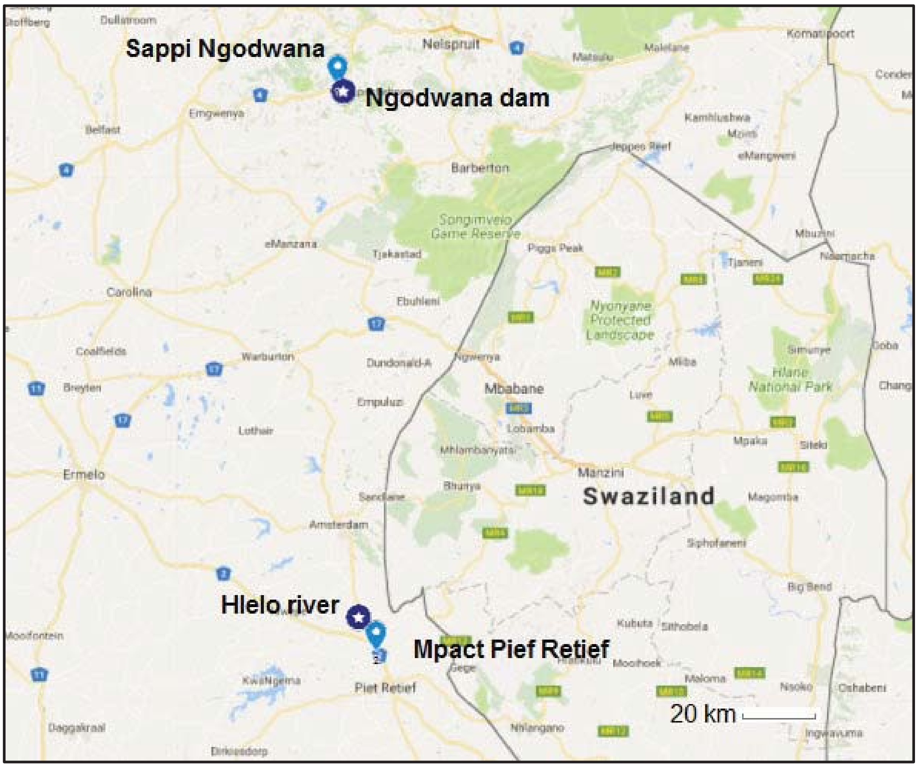


Figure 3-5 Mpumalanga cluster of pulp and paper mills

3.3.4 Western Cape cluster: wastewater type and location distance

There are two tissue manufacturers and two paper packaging manufacturers in this cluster. Referring to Figure 3-6, there is a significant distance (29.6 km) between Huhmataki and Golden Era, while the tissue companies Twinsaver Bellville and Green Tissue are less than 1 km apart, making a potential collaboration possible.

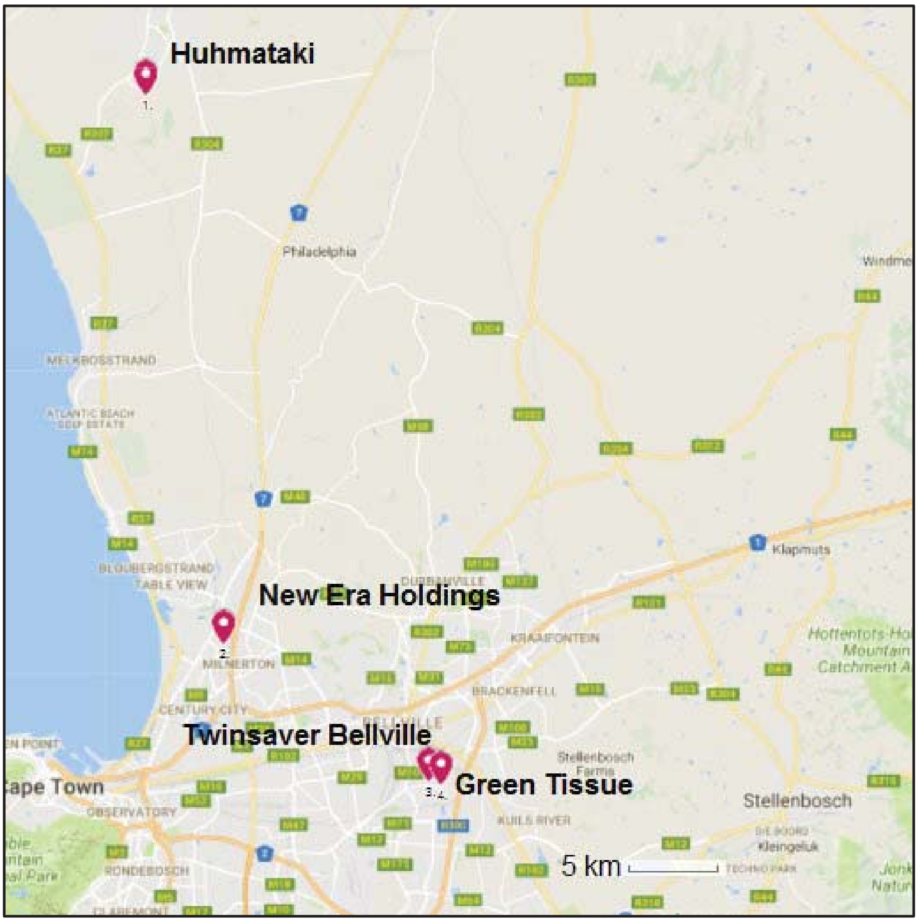


Figure 3-6 Western Cape cluster of pulp and paper mills

3.3.5 Supply chain challenges for regional clusters

While collaboration can be feasible within the Gauteng cluster and the Western Cape cluster, a well-designed and well-managed supply chain is essential, especially in the context of using wastewater as biorefinery feedstocks. One major challenge lies in the vested interests of the different stakeholders involved, who are focused on achieving their own targets because organisations in supply chain networks are often independent and geographically distributed, as seen in the clustering exercise (Long and Zhang, 2014).

The benefits and demands of the level of integration required in such integrated and interdependent industrial ecology approaches are well recognised. Espinoza Pérez et al. (2017) explored the key challenges for sustainable and industrialised biorefinery supply chain design and management and highlighted the major roadblocks which need to be tackled by biorefinery investors and decision-makers; these are detailed in Table 3-12.

Table 3-12 Biorefinery supply chain uncertainties adapted from Kim et al. (2011); Sharma et al. (2013), and Espinoza Pérez et al. (2017)

Classification	Uncertainties
Cost	- Cost of transporting biomass/feedstock - Operation cost for conversion processing - Cost of transporting intermediate products - Cost of transporting final products - Acquisition cost for each biomass/feedstock type - Annualised capital cost of conversion processing - Expansion plans
Profits (value)	- Value of each intermediate product at the conversion processing site - Sale price of each final product
Production process	- Yield of final product from intermediate product at conversion processing - Yield of intermediate product from biomass/feedstock at conversion processing
Extern	- Demand fluctuations - Natural or human disasters - Weather - Technology availability - Change in regulations and policies
Nature of biomass/feedstock	- Availability - Physical and chemical properties

Espinoza Pérez et al. (2017) further presented five dimensions of analysis which should be considered to ensure the design of a feasible supply chain network:

(i) Economic:

A biorefinery must be self-sustaining by having the necessary profitability and not relying on governmental assistance or re-investments. One way to ensure this is to focus on product diversification and the sale of valuable by-products (You et al. 2012).

(ii) Social:

Social dimensions can include a number of factors–employment generation, social welfare, social acceptability and promotion of responsible working conditions (Bautista et al. 2016).

(iii) Environmental:

Environmental impacts with regards to relevant impacts (e.g. air, soil, water quality, waste and wastewater management, the balance of greenhouse gases, conservation and protection of biodiversity and wildlife) must be measured.

(iv) Technological:

This refers to existing and upcoming production technologies and trends in the use and production of bio-based products.

(v) Political:

The political dimension in the biorefinery supply chain can be considered to be the most important because the policies in place will either promote or restrict the market for bio-based products through subsidies, tax exemptions and compulsory consumption (Bautista et al. 2016). Countries such as Columbia, Brazil, Argentina, Peru and the European Union (European Parliament, 2009)have established enabling policies for the industry emergence of biofuels and bio-based products.

3.4 Opportunities and Challenges: Overall perspective of the South African pulp and paper industry

While van der Merwe-Botha et al. (2017)did notice improvements in the waste and wastewater management practices over the years, these improvements seem to be limited to water saving and recycling practices along with better sludge management. Valorisation to date has been limited to the use of black liquor and bark as energy sources in the waste and wastewater sectors of the PPI in South Africa. It is noteworthy to highlight that even though it is not reflected in the NATSURV12 report because production has not attained commercial scale, Sappi is investigating the valorisation of a side waste stream of its dissolving pulp process for the production of value-added bioproducts (Sappi, 2018b). As was observed in the global examples in Chapter 2, solid waste and wastewater are treated separately in South African P&P mills. The novelty of our wastewater biorefinery concept is the possibility of generating multiple products through the cascading use of resources contained within waste and wastewater streams while concomitantly producing fit-for-purpose water.

As presented in the previous sections, data collection on wastewater from the South African P&P industry has taken place over the years; however, the anonymity and inconsistency in the data make it challenging to analyse and investigate routes forward for value addition in the industry rigorously. Effluent data and characterisation often happen after combined on-site wastewater treatment, and the data do not represent the full resource potential of the combined or individual wastewater streams. Access to these data or to collecting the data has been challenging during the course of this project. Harding et al. (2020) investigated the challenges and shortcomings in acquiring South African industrial wastewater characterisation data and highlighted the need to enforce trust and transparency among industry, government and research bodies in order to fully harness the potential of wastewater streams for both reuse purposes and resource recovery.

The preliminary clustering exercise offered insights into the four main regions in which P&P plants are found and their potential for collaborating clusters by highlighting similar process technologies and distance between facilities. While collaboration can be feasible within the Gauteng and Western Cape clusters, a well-designed and well-managed supply chain will be essential, underpinned by the appropriate economic, social, environmental, technological and political dimensions.

4 Valorisation and Resource Recovery Potential from Pulp and Paper Wastewater Streams

4.1 Characterisation of wastewater streams for biorefinery application

The wastewater biorefinery concept is based on industrial ecology and aims at closing open-loop systems by implementing single or, more typically, multi-unit processes for recovering valuable resources from effluents of complex nature while improving water quality. Therefore, the effluent streams of the mill become the feedstock to its wastewater biorefinery. To implement and operate a successful wastewater biorefinery requires characterising and understanding key components with regards to feedstocks, products and available bioconversion technologies. Therefore, the characterisation of mill effluent streams in terms of physicochemical properties provides the key starting point. For a multi-product integrated mill, it may be difficult to separate different process wastewater since they are usually mixed prior to water treatment; however, use in the WWBR prior to mixing may provide a distinct advantage. Suhr et al. (2015) give an overview of the normal operating conditions of mills that influence the emissions of wastewater and must be included while calculating the load of wastewater:

- Chemical pulp mills: operation conditions include or impact spillages from pulping or recovery line, change of production output, change of wood raw material, change of product quality such as brightness (ISO%), regular routine maintenance and cleaning.
- Mechanical pulp mills: operation conditions include or impact the change of refining targets and wood raw material used, change of product quality such as brightness (ISO%), regular routine maintenance and cleaning.
- RCF mills: operation conditions impact the change of quality of the paper for recycling used.
- Paper mills: operation conditions include or impact the change of paper grades and qualities, paper breaks, stopping and start-up of the paper machine or other parts of the process due to paper breaks, regular routine maintenance and cleaning of equipment, tanks, pipes, chests and floors.

4.2 Introducing the analysis of pulp and paper wastewater

To assess the potential of the pulp and paper wastewater streams (Sections 4.3 and 4.5), a deeper understanding is needed of the composition of individual wastewater streams and the potential value of maintaining separate wastewater streams to facilitate valorisation (Cherubini and Strømman, 2011). Allowing for wastewater streams to enter the biorefinery at different points could yield higher value products at improved efficiencies and potentially a higher quality water product. While the South African data available is largely focused on the combined wastewater across all processes in the mill, there is a limited body of global literature from which a more detailed analysis can be attempted. However, assessing the wastewater biorefinery potential remains a challenge due to the complexity and lack of homogeneity in published data. This reflects the variations in the composition of individual streams between different mills. It may also indicate a likely fluctuation in composition over time within the same stream in the same mill, depending on raw materials and operating conditions.

Table 4-1 shows the main sections of an integrated pulp and paper mill, with an indication of the volumes of wastewater across each stage and its probable contamination. Table 4-2 and Table 4-3 expand on this information with concentration levels for organic material.

Table 4-1 Wastewater volume and pollution load in the papermaking process adapted from Ali and Sreekrishnan (2001), Pokhrel and Viraraghavan (2004), Tewari *et al.* (2009) and Saadia and Ashfaq (2010)

Process stage	**Wastewater volume**	**Pollution load**	**Typical effluent characteristics**
Raw material preparation	Low	Low	Suspended solids, including bark particles, fibre pigments, dirt, grit, BOD and COD
Pulping	Low	High	Colour, bark particles, soluble wood materials, resin acids, fatty acids, AOX, VOCs, BOD, COD, and dissolved organics
Pulp washing	Low	High	Usually similar in nature to the pulping effluents, with the final wash containing the least pollutants
Bleaching	High	High	Dissolved lignin, colour, COD, carbohydrate, inorganic chlorines, AOX, EOX, VOCs, chlorophenols and halogenated hydrocarbons
Papermaking	Depends on the extent of recycling	Low	Particulate wastes, organic and inorganic compounds, COD and BOD
Chemical recovery (in case of chemical pulping)	Low	High	Methanol, phenols, terpene, sulphides, sulphites, resin acids

Table 4-2 and Table 4-3 give us an indication of the organic content in the different unit operations in terms of COD concentration. The COD load tends to be higher for chemical pulps than for mechanical pulps owing to the combined effects of lower pulping efficiency in the case of chemical pulps and the chemical degradation of the woody material. This is also reflected in Table 4-4, where we see a higher oxidisable organic content for chemicals than mechanical pulping, with bleaching also increasing this organic load relative to effluents from non-bleaching processes. However, additional information is needed to evaluate the nature of the organic compounds present, their availability and potential valorisation.

The highest flow and levels of contaminants are found in the bleaching section, which also accounts for 60 to 85% of the total effluent volume (Cabrera, 2017; Saadia and Ashfaq, 2010). Evaporator condensate effluent, present in chemical pulping processes, also contributes significantly to the pollutant load (Makris, 2003; Suhr et al. 2015).

Table 4-2 Overview of selected wastewater streams in the pulp and paper industry with organic composition and COD characteristics (Srivastava and Singh, 2015)

Wastewater	COD (g/L)	Organic composition	% of COD	Potential inhibitory compounds
Wet debarking	1.3–1.4	Tannins: Monomeric phenols: Simple carbohydrates: Resin compounds:	30–55 10–20 30–40 5	Tannins, resin acids
Sulphite spent liquor	120–220	Lignosulphates: Carbohydrates:	50–60 15–25	Not reported
Sulphite evaporator condensates (SEC)	7.5–50	Acetic acid: Methanol Fatty acids	33–60 10–25 < 10	Sulphur, organic sulphur
Chlorine bleaching	0.9–2	Chlorinate lignin polymers: Methanol:	65–75 1–27	Chlorinated phenols, resin acids
Kraft Evaporator Condensate (KEC)	1–33.6	Methanol:	60–90	Sulphur, resin acids, fatty acids, volatile terpenes
TMP effluent	1–5.6	Carbohydrates:	25–40	Resin acids
CTMP effluent	2.5–13	Polysaccharides: Lignin: Organic acids:	10–15 30–40 35–40	Resin acids, fatty acids, sulphur

Table 4-3 Overview of selected wastewater streams in the pulp and paper industry adapted from Kamali and Khodaparast (2015), which covers the complete operation from raw material preparation to bleaching and thus includes cleaning, washing and thickening operations

Unit operations	pH	COD (mg/l)	BOD$_5$ (mg/L)	BOD$_5$/COD	TSS (mg/L)	Reference
Woodyard and chipping[1]	7	1275	556	-	7150	(Avşar and Demirer, 2008)
Thermo-mechanical pulping	4–4.2	3349–4250	-	-	330 - 510	(Qu et al. 2012)
Chemical thermo-mechanical pulping[2]	7.43	7521	3000	-	350	(T. Liu et al. 2011)
Kraft cooking section[3]	13.5	1670	460	0.27	40	(Wang et al. 2007)
Pulping process operations[4]	5.5	9065	2440	-	1309	(Avşar and Demirer, 2008)
Bleaching[5]	8.2	3680	352	-	950	(Kansal et al. 2008)
Paper machine	6.5	1116	641	-	645	(Avşar and Demirer, 2008)
Integrated pulp and paper mill	6.5	3791	1197	-	1241	(Avşar and Demirer, 2008)
Recycled paper mill	6.2–7.8	3380–4930	1650–2565	0.488–0.52	1900 - 3138	(Zwain et al. 2013)

[1] Pulpwood storage, debarking and chipping

[2] Alkaline peroxide mechanical pulping (apmp)

[4] Pulping, pulp screening, pulp washing and thickening, bleaching and kraft re-pulping

[3] Wheat as raw material

[5] A combination of chlorination and alkaline extraction stages from an agro-based paper mill

Table 4-4 Oxidisable material in common effluents in the pulp and paper industry before treatment (FAO, 1996)

Process	Oxidisable material (kg/t of pulp)
Mechanical	10
Unbleached kraft	15
Thermo-mechanical	30
Bleached kraft	50
Chemi-thermo-mechanical	50
Semi-chemical	90
Bisulphite	110

Based on the nature of operations, a pulp mill promotes natural separation processes, with the most obvious separation being organic partitioning. Processes which promote organic separation, in the case of chemical pulping, include leaching or evaporation in the woodyard, pulping, turpentine and tall oil collection, brownstock washing, alkaline extraction, acid washing, evaporation and primary and secondary treatment of effluents (Makris, 2003).

The natural components present in pulp and paper wastewater streams include polysaccharides, lignin, extractives and inorganics. The wood extractives are dependent on the tree species processed and include terpenoids, steroids, fats, waxes, phenolics and inorganics; the last includes metals salts such as carbonates, silicates and phosphates of calcium, potassium and magnesium. Bark contains similar extractives, present at higher concentrations than in wood. These natural components, especially resin and fatty acids, contribute to up to 70% of effluent toxicity in pulp mills (Leach and Thakore, 1976; Werker et al. 1996).

While Table 4-1, Table 4-2, Table 4-3 and Table 4-4 present an overview of effluent streams across sections of a pulp and paper mill, the characteristics of the effluents are influenced by the type of wood or non-wood raw material, type and amount of chemicals used, and various process-specific conditions during the stages of pulp and papermaking. This means that a more detailed analysis is necessary.

4.3 A detailed analysis of pulp and paper wastewater streams based on literature

For wastewater biorefinery design, we require data on the volume, concentration and complexity of the streams (Section 4.5). Edwards and Meyer (2014b) present an in-depth analysis of the typical composition of common pulp and paper wastewater streams compiled from various literature sources with a focus on reporting the COD (g/L), organic matter composition (mg/L), the concentration of primary inhibitors (mg/L), and TSS (mg/L). This study offers a good starting point for understanding the nature of common wastewater streams in the industry; however, typical flows of these streams are missing. In the following sections, the main wastewater streams from pulp and paper processes are presented with the data compiled by Edwards and Meyer (2014b) supported with additional literature, when available, to explore the volume, concentration and complexity of the streams.

4.3.1 Debarking wastewater

Debarking is one of the first steps in pulp production and generates a large number of extractives such as tannins, resins and fatty acids in its effluent. The wastewater generated is usually clarified and circulated for reuse to minimise the use of fresh water in the debarking and washing of logs (Salmi, 2020). Debarking effluent flow estimates for Finnish mills are given in Table 4-5. The flow and pollution load of the debarking wastewater is dependent on the species of wood used, the sampling procedure and whether it is dry or wet debarking (Salmi, 2020). While the volumetric load of this effluent is generally small compared to the rest of the mill (Table 4-6), the pollution load makes its treatment and discharge an important step in the operation of the mill. A breakdown of the composition of organics in crushed spruce bark water, industrial debarking water, and bark press water is shown in Table 4-7.

Table 4-5 Typical debarking effluent flows and pollution load for different pulp and paper. Finnish mills in 1995 reported in Salmi (2020) from Franzén et al. (1997)

Plant type	Wood used	Effluent flow m^3/m^3 wood	COD kg/m^3 wood	BOD_7 kg/m^3 wood	TSS kg/m^3 wood	P g/m^3 wood
Paper	Spruce	0.4 – 0.6	2.5 – 4.0	-	-	-
Paper	Spruce	0.54 – 0.68	1.23 – 5.48	0.58 – 2.6	0.31 – 0.79	-
Pulp	Pine, Birch	0.5 – 0.8	0.5 – 0.6	-	-	3 – 5
Paper and pulp	Softwood, Birch	0.2 – 0.6	-	0.2 – 0.5	-	1

Table 4-6 Debarking wastewater percentage contribution to total wastewater flow and pollution load of pulp and paper mills reported in Salmi (2020) from Mattinen (1974)

Mill type	Wastewater (%)	BOD_7 (%)	N (%)	P (%)	COD (%)	SS (%)
Paper	5.5	25	23	18	32	28
Pulp	3.1	4.7	20	22	5	16

Table 4-7 Concentrations of components in water from crushed spruce bark, industrial spruce log debarking process and industrial bark press. Total calculated TOCs were 4200 mg/L for spruce bark water, 1930 mg/L for debarking water and 16 100 mg/L for bark press water, as reported by Salmi (2020) from Kylliäinen and Holmbom (2004)

	Spruce bark water		Debarking water		Bark press water	
	Amount (mg/L)	Calculated TOC (mg/L)	Amount (mg/L)	Calculated TOC (mg/L)	Amount (mg/L)	Calculated TOC (mg/L)
Fructose	504	200	255	100	1007	400
Glucose	623	270	189	85	1978	870
Sucrose	394	160	414	170	2250	990
Oligosaccharides	421	170	233	90	1349	540
Polysaccharides	280	110	-	-	-	-
Isoharpontin and Astringinglucoside	2140	1280	460	280	4405	2640
Catechin	42	26	7.2	5	74	45
Isorhapontingenin and Astringenin	11	8	11.8	5	56	20
Resin acids	1.7	1.3	10.6	8	52	40
Polyphenols	-	920	-	240	-	2470
Total		**3150**		**980**		**8020**

4.3.2 Chemical and semi-chemical pulping

4.3.2.1 Kraft pulping

The main wastewaters in a kraft pulp and paper mill are in the following areas:

- wood handling
- cooking
- pulp screening and washing
- bleaching

- pulp drying
- papermaking

Estimates of the major flow and characteristics of wastewater are presented in Table 4-8, Table 4-9 and Table 4-10. The highest flow of wastewater stems from the bleaching section, which also produces high COD and BOD values. One noticeable characteristic is the low concentration of nitrogen found in the effluents.

Depending on characteristics, Texas A&M (2003) highlight the potential use of some effluent streams in other sections of the plant in order to decrease the intake of fresh water. For example, the use of evaporator condensate is common in the woodyard for wood or chip washing, the recovery plant for weak white liquor, and for cooling purposes (Macdonald, 2004). This is a good example to highlight the value of the use of fit-for-purpose water streams.

Table 4-8 Overview of wastewater composition in chemical pulping effluents, adapted from Meyer and Edwards (Meyer and Edwards, 2014)

Type of wastewater	COD concentration (g/L)	Organic matter composition (mg/L)	Concentration of primary inhibitors (mg/L)	TSS concentration (mg/L)	References
Kraft digester condensates	13.3	Methanol: 250–12000 Ethanol: 20–3200 Phenols: 31–40 Terpenes: 0.1–25000	Sulphides: 1–270 Sulphite: 8	17	(Dufresne et al. 2001)
Kraft evaporator condensates	0.6–6.5	Methanol: 375–2500 Ethanol: 0–190 2-propano: 0–18 Acetone: 1.5–5 Phenols: 17–42 Terpenes: 0.1–660	Sulphides: 1–690 Sulphite: 3–10 Resin acids: 28–230	0.5–105	(Blackwell et al. 1979)(Qiu et al. 1988)(Cornacchio, 1989)(Driessen et al. 2000)(Dufresne et al. 2001)(Xie et al. 2010)
Kraft combined condensates	0.7–4.0	Methanol: 300	Sulphides: 210	12	(Cornacchio, 1989)(Dufresne et al. 2001)
Kraft mill streams: Woodroom effluent Contaminated hot water Brown stock decker filtrate	 2.1–4.0 3.9 0.7	n.a	n.a	n.a	(Cornacchio, 1989)

n.a: not available

Table 4-9 Overview of wastewater generation in a Kraft pulp mill (Cabrera, 2017)

Department	**Flow** m^3/ADT	**TSS** kg/ADT	**BOD** kg/ADT	**AOX** kg/ADT	**COD** kg/ADT	**P** g/ADT	**N** kg/ADT
Debarking	2.5	4	2	0	5	20	0.20
Washing and screening	0.5	3	1	0	2	1	0.015
Bleaching	31	2	10	1.2	35	47	0.08
Condensates	1	0	1	0	3	0	0.00
Others	3	4	4	0	10	7	0.002

ADT: air dry tonne (10% water and 90% oven-dry pulp)

Table 4-10 Overview of untreated wastewater loadings from a typical bleached kraft mill (Springer, 1986; US EPA, 1997)

Process	**Flow** m^3/ADT (%)	**TSS** kg/ADT (%)	**BOD$_5$**kg/ADT (%)
Woodyard	0.7 (4.8)	3.1 (6.2)	0.8 (2.3)
Pulping	21 (14.3)	4.9 (10.0)	9.4 (26.3)
Recovery	17 (11.9)	11.1 (22.5)	4.1 (11.4)
Bleaching	48 (33.3)	4.9 (10)	12.7 (35.4)
Paper manufacturing	52 (35.7)	25.3 (51.3)	8.9 (24.6)
Total	138.7 (100)	49.3 (100)	35.9 (100)

ADT: air dry tonne (10% water and 90% oven-dry pulp)

4.3.2.2 Sulphite pulping

Sulphite pulping has a similar number of wastewater streams as kraft pulping, however since sulphites or bisulphites (salts of sulphurous acids) are used for lignin extraction, the evaporator condensate is toxic and requires neutralisation (Rintala and Puhakka, 1994). This is reflected in a large number of by-products in a sulphite cook (Table 4-11). An overview of typical wastewater composition in a sulphite mill is shown in Table 4-12.

The yearly range of total phosphorus and nitrogen emissions from a group of European sulphite mills (excluding NSSC) was reported by Suhr et al. (Suhr et al. 2015) to be 0.011–0.25 kg/ADT for total phosphorus and 0.006–2.5 kg/ADT for total nitrogen.

Compound	**Origin**	**Quantity** kg/t pulp
Methanol	Methoxyl group of the glucuronoxylan	7–10
Acetic acid	Acetyl groups of the xylan	30–90
Formic acid	Bisulphite oxidation of formaldehyde	0.5–1
Formaldehyde	Hydroxymethyl groups of lignin	2–6
Methyl Glyoxal	Degradation of hexoses	5–6
Furfural	Degradation of pentoses	5–6
Sugar sulphonic and aldolic acids	Bisulphite substitution and oxidation of sugars	150–200
Sugars	Hemicellulose and cellulose	200–400
Cymene	Bisulphite oxidation of terpenes	0.3–1
Lignosulphonates	Lignin	600–800

Table 4-11 Overview of wastewater composition in sulphite pulping effluents, adapted from Meyer and Edwards (Meyer and Edwards, 2014)

Type of wastewater	**COD concentration** (g/L)	**Organic matter composition** (mg/L)	**Concentration of primary inhibitors** (mg/L)	**TSS concentration** (mg/L)	**References**
Sulphite evaporator condensate	3.0–2.7	Acetic acid: 2000 Methanol: 0–250 Furfural: 0 –250	Sulphite: 450–800 Resin acids: 3.2–9.3	n.a	(Frostell, 1984) (Salkinoja-Salonen et al. 1985) (Walters et al. 1988)(Cornacchio, 1989) (Driessen et al. 2000)
Spent sulphite liquor	40 - 115	n.a	RFA: 40 Sulphate: 5100 Sulphite: 4800	320	(Cornacchio, 1989) (Schnell et al. 1992) (Jantsch et al. 2002)
Sulphite pulping effluent	6.2 - 48	n.a	n.a	n.a	(Cornacchio, 1989)

n.a: not available

4.3.2.3 *Semi-chemical pulping*

Pulp yields are usually higher for semi-chemical pulping methods, such as NSSC, as less lignin is removed (Meyer and Edwards, 2014). NSSC is the dominant semi-chemical pulping process. Table 4-13 presents an overview of effluent characteristics for semi-chemical pulping processes (Stoklosa and Hodge, 2014).

Table 4-12 Overview of wastewater composition in semi-chemical pulping effluents, adapted from Meyer and Edwards (2014b)

Type of wastewater	COD concentration (g/L)	Organic matter composition (mg/L)	Concentration of primary inhibitors (mg/L)	TSS concentration (mg/L)	References
NSSC (neutral sulphite semi-chemical) composite effluents	1.8–19	Lignin: 500 Carbohydrates: 610 Acetic acid: 54 Methanol: 9	n.a	120–940	(Hall et al. 1986) (Lee Jr et al. 1989)(Cornacchio, 1989) (Smith et al. 1994) (Arshad and Hashim, 2012)
NSSC spent liquor	28–40	Carbohydrates: 210 Acetic acid: 3200 Methanol: 90 Ethanol: 5	n.a	250	(Hall et al. 1986), (Cornacchio, 1989)
APMP (Alkaline peroxide mechanical pulping) effluent	10–31	n.a	Resin acids: 8.5–220 LCFAs: 32–172 Peroxide: 800–1000 Sulphate: 80–220	n.a	(Schnell et al. 1993)

n. a: not available

4.3.2.4 *Dissolving pulp*

In the case of the dissolving pulp process, a pre-hydrolysis step to remove hemicellulose is present, leading to the production of pre-hydrolysis liquor (PHL), which contains relatively high concentrations of carbohydrates, acetic acids and furfural, as seen in Table 4-14 resulting in high COD. PHL is usually burned in the recovery boiler of the kraft process or sent to the effluent treatment (Figure 4-1), but owing to its high carbohydrate content, it can be a promising feedstock for producing value-added bioproducts. Chen et al. (2018) analysed the industrial PHL of a kraft dissolving pulp located in China, which uses eucalyptus wood chips and the chemical constituents of this stream are shown in Table 4-15. Z. Liu et al. (2011) also presented a breakdown (Table 4-16) of the chemical constituents in a PHL industrial sample from a kraft-based dissolving pulp mill located in Canada. Both studies indicate the presence of sugars in the PHL liquor. Where bleaching and washing are required, the dissolving pulp process will also contain additional effluents, as for the other chemical pulping processes.

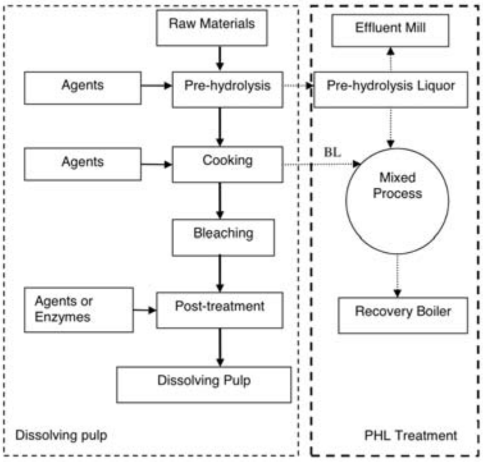


Figure 4-1 Fate of PHL and its traditional treatment lines (note BL: black liquor) (Wu, 2016a)

Table 4-13 Overview of wastewater composition for kraft pre-hydrolysis effluent, adapted from Meyer and Edwards (2014)

Type of wastewater	**COD concentration** (g/L)	**Organic matter composition** (mg/L)	**Concentration of primary inhibitors** (mg/L)	**TSS concentration** (mg/L)	**References**
Kraft dissolving pre-hydrolysis	70–120	Carbohydrates: 30000–54000 Lignin: 11000–25000 Furfural: 1140 Acetic acid: 2000	Sulphate: 200–450	1200–1300	(Debnath et al. 2013), (Kale and Singh 2013), (Bajpai, 2000)

Table 4-14 Breakdown of the chemical constituents in a pre-hydrolysis liquor stream generated in a kraft dissolving pulp mill processing eucalyptus wood chips (Chen et al. 2018)

Monomeric form	(g/l)	**Oligomeric form**	(g/l)	**Other products**	(g/l)
Xylose	12.3 ± 0.68	Xylose	23.3 ± 0.79	Soluble lignin	9.7 ± 0.49
Arabinose	0.2 ± 0.005	Arabinose	0.1 ±0.006	Acetic acid	6.2 ± 0.26
Galactose	0.4 ± 0.013	Galactose	1.4 ± 0.067	Furfural	1.9 ± 0.1
Glucose	0.4 ± 0.017	Glucose	1.2 ± 0.055	HMF	0.4 ± 0.032
Mannose	0.3 ± 0.006	Mannose	1.0 ± 0.03		
Total	**13.6 ± 0.721**	**Total**	**27.0 ± 0.948**	**Total**	**18.2 ± 0.453**

Table 4-15 Chemical constituents in a PHL industrial sample from a kraft-based dissolving pulp in Canada (Z. Liu et al. 2011; Wu, 2016b)

Ash content (%)		0.43
Lignin content (%)		0.76
Furfural (%)		0.17
Arabinose (%)	Monomeric	0.008
	Oligomeric	0.012
Galactose (%)	Monomeric	0.039
	Oligomeric	0.041
Glucose (%)	Monomeric	0.090
	Oligomeric	0.205
Xylose (%)	Monomeric	0.253
	Oligomeric	0.302
Mannose (%)	Monomeric	0.048
	Oligomeric	0.128
Total sugars (%) (Monomeric + Oligomeric)		**1.126**
Total sugars (%) (Oligomeric)		**0.688**

HMF: hydroxymethylfurfural

4.3.2.5 *Cooking liquors wastewater from chemical pulping*

The nature of pulp screening, washing and recovery cycles in chemical and semi-chemical pulping leads to losses of spent pulping liquors–black liquor (kraft and soda pulping), red liquor (sulphite pulping) and NSSC pulping liquor. These lead to an increase in the pollution load in the discharged wastewater streams (US EPA, 1997). Despite the benefit of the lack of sulphur compounds in the soda pulping liquor, soda pulping is less efficient than kraft pulping, forming more black liquor per ton of pulp; this results in larger recovery systems in the soda mills (US EPA, 1997).

Spilling of these liquors usually happens during pulping processes, and the spills are usually treated alongside other wastewater streams. The spillage is likely to be weak black liquor, which consists of around 15% dry solids. Weak black liquor can also be recovered from brownstock pulp washing, and this stream usually has a liquor solids content in the range of 15–20%, depending on the mill washing systems (Clay, 2007).

It is important that cooking liquors produced during chemical pulping are not waste streams per se but are currently used for energy generation; therefore, the question to consider is whether these liquors can be used in other valorisation routes. Bajpai (2018) reported an estimate of 7 tonnes of black liquor at 15% solids (about 10% organic chemicals and 5% inorganic chemicals) is produced per tonne of pulp. Black liquor can be roughly divided into organic and inorganic materials in a two-thirds to one-third ratio. There are smaller concentrations of other elements (below 1g/kg dry black liquor) such as magnesium, iron, manganese, phosphorus, silicon, aluminium and so on. Approximate concentrations of some common elements in black liquor are shown in Table 4-17. A further percentage solids breakdown is given in Table 4-18 for black liquors from pine and spruce. The components for the pine liquor are presented in percentage ranges since the data was collected from four different pine liquors.

Table 4-19 and Table 4-20 compare the pulping of red liquors across four sulphite pulping processes using different bases. Table 4-21 presents typical characteristics of NSSC pulping liquors.

While black liquor is mostly comprised of lignin and carbohydrate degradation products (e.g. hydrocarboxylic acids, acetic acid and formic acid) and small amounts of extractives (Ek et al. 2009; Pereira et al. 2013; Sjöström, 1993), hemicellulose and lignin are released in the sulphite cooking liquor, which can be used as raw materials for various products such as lignosulphonates, ethanol, fodder yeast, soda, vanillin, acetic acid and furfural. Spent sulphite liquors have also been identified as a potential feedstock for bioethanol production (Schroeder et al. 2017).

Table 4-16 Estimated component breakdown of black liquor (Bajpai, 2017; Theliander, 2009)

Element	Amount (%)	Organic material	Amount (wt%)
Oxygen	33–38	Hydroxy acid	29–45
Hydrogen	3–5	Lignin	25–35
Carbon	34–39	Extractives	~ 5
Sodium	17–25	Acetic acid	3–5
Potassium	0. 1–2	Formic acid	~3
Sulphur	3–7	Methanol	~1
Chlorine	0. 2–2		
Nitrogen	0. 05–0. 2		

Table 4-17 Percentage solids breakdown for black liquors from pine and spruce processing (Green and Hough, 1992; US EPA, 1997)

Component	Pine liquor (% w/w, dry solids)	Spruce liquor (% w/w, dry solids)
Lignin	28.9–31.1	41
Hemicellulose and sugars	0.11–1.3	
Extractives	2.53–6.69	3
Saccharinic acids	18.8	28
Acetic acid	2.08–5.2	5
Formic acid	2.7–4.48	3
Other organic acids	2.22–5.5	
Methanol		1
Unknown organic compounds	5.8–19	
Inorganic salts	18.5–25.6	
Organically combined sodium	8.7–10.3	
Unknown inorganic compounds	1.35–2.08	
Sulphur		3
Sodium		16

Table 4-19 Characteristics of calcium base and magnesium base sulphite pulping liquors (Ingruber et al. 1985; US EPA, 1997)

Characteristic	Calcium base	Magnesium base1
Pulp yield (%)	46	50
Liquor volume (m^3/ODT)[2]	9.28	6.08
pH	5.3	3.4
BOD (kg/ODT)	357	222
Dissolved organics (kg/ODT)	1533	975
Dissolved inorganics (kg/ODT)	1043	782
UV lignin (kg/ODT)	250	126
Total sugars (kg/ODT)	264	129
Reduced sugars (kg/ODT)	238	106
Toxicity emission factor (TEF)[3]	422	Not tested

[1] Average across two mills, data collected by Ingruber et al. (Ingruber et al. 1985)

[2] Estimated liquor volume just before "blow."

[3] TEF = (100%/96hr LC50,%) x Liquor volume (m^3/ODT pulp)

Table 4-18 Characteristics of ammonia base and sodium base sulphite pulping liquors (Ingruber et al. 1985; US EPA, 1997)

Characteristic	Ammonia base1	Sodium base2
Pulp yield (%)	42.5	62
Liquor volume (m^3/ODT)[3]	9.46	7.10
pH	2.4	3.5
BOD (kg/ODT)	413	235
Dissolved organics (kg/ODT)	1728	938
Dissolved inorganics (kg/ODT)	12.5	226
UV lignin (kg/ODT)	892	410
Total sugars (kg/ODT)	288	137
Reduced sugars (kg/ODT)	212	74
Toxicity emission factor (TEF)[4]	3663	714

[1] Average across four mills, data collected by Ingruber et al. (Ingruber et al. 1985)

[2] Average across 12 mills except for reduced sugars which were averaged across 11 mills

[3]Estimated liquor volume just before “blow.”
[4]TEF = (100%/96hr LC50,%) x Liquor volume (m^3/ODT pulp)

Table 4-19 Characteristics of typical spent NSSC pulping liquors (US EPA, 1997)

Characteristic	Typical values
pH	6.5–8.5
Total solids (%)	8–22
Volatile solids (% of total solids)	43–52
BOD (mg/l)	16000–50000
Acetate (mg/l)	12000–20000
Wood sugars (mg/l) (mostly pentoses)	5000–10000
Lignin (mg/l)	25000–85000

4.3.2.6 Condensate wastewater from chemical pulping

The COD of these condensates varies considerably across the literature, with reported concentrations of 0.7–13 g/L for kraft condensates and 3–27 g/L for sulphite condensates (Meyer and Edwards, 2014b). Table 4-22 shows the major components usually present in kraft condensates. In terms of flow, for chemical condensates, Bajpai (2010) reported 8–10 m^3/ADT of total condensates with a COD load of 20–30 kg/t and BOD_5 of 7–10 kg/t. The evaporator condensates for sulphite pulping have a higher COD load than for kraft mills due to the presence of acetic acid and furfural. Primary inhibitors in chemical pulping are sulphur components, in the range of 60–700 mg/L of sulphites in kraft condensates and 450–800 mg/L of sulphites in sulphite condensates.

COD is usually higher for hardwood pulp condensates when compared to softwood pulp. The strong condensates are usually stripped with a removal efficiency of over 90%, greatly influenced by pH. The COD can be reduced to 1–1.5 kg COD/m^3 of condensate, and an estimated 7–9 m^3 of weaker condensates are formed per the ADT of the pulp. Being free of metals, these weak condensates can be used in a number of places in the mill for washing in the bleach plant, as scrubbing liquor for the lime kilns and/or as white liquor make-up water. For condensate streams which are not reused or used in open parts of the mill, these streams are discharged directly as effluents (around 4–8 kg COD/ADT) and are usually easily biodegradable (Suhr et al. 2015).

Table 4-20 Typical major components found in kraft condensates (Blackwell et al. 1979; US EPA, 1997)

Concentration: ppm	Batch digester vent condensate	Batch digester blow condensate	Continuous digester flash–stream condensate	Evaporator combined condensate	Evaporator condenser condensate	Stripper feed
Hydrogen sulphite	30–270	1–230	210	1–90	1–240	5–660
Methyl mercaptan	20–5300	40–340	70	1–30	1–410	5–720
Dimethyl sulphide	15–7400	40–190		1–15	1–15	10–1000
Dimethyl disulphide	5–4100	2–210		1–50	1–50	10–150
Methanol	1800–12000	250–9100	570–8900	180–700	180–1200	
Ethanol	90–3200	20–900		1–190	1–130	140–10000
Acetone	8–420	5–95		1–15	1–16	20–1100
MEK	27			1–3	2	15–500
Terpenes	0.1–5500	720–9200	1950–8800	60–1100	450–2500	20–25
Phenolics	12				3	800–13000
Guaiacol				1–10		1–82
Resin acids				25–230		

4.3.2.7 Solid waste in chemical pulping processes

There is a considerable amount of solid waste generated during chemical pulping processes, and Table 4-23 gives an estimate of solid waste during kraft pulping. The wood waste comes from the residues generated during wood handling. The solids formed during the chemical recovery processes are inorganics waste in the form of dregs, green liquor sludge and lime mud. The wastewater sludge is a mixture of organic and inorganic waste. Wood waste which constitutes a significant amount of organics is usually burnt for energy recovery (Suhr et al. 2015).

Table 4-21 Solid waste generation during Kraft pulping (Suhr, 2015)

Type of waste	kg dry solids/ADT of pulp
Wastewater treatment sludge	10
Wood ash[2]	9[1]
Other ashes[3]	14[1]
Fibre	5
Wood waste[4]	6
Dregs, grits and green liquor sludge	10–20
Lime enriched with non-process elements	10–20
Hazardous waste	0.2
Total	**60–80**

[1] Values for ash/ADT are higher if additional biomass from external sources is used as complementary fuel.
[2] Wood ash is fly ash and dust from the incineration of wood material (e.g. from the bark boiler)
[3] Other ashes' are ashes from fuels used in energy generation other than wood and black liquor
[4] Wood waste' is bark, chips, sawdust, wood package

4.3.2.8 Natural by-products in chemical pulping processes

The nature of chemical pulping processes is primarily to promote organic separation. This leads to the production of natural by-products of value at different stages of the chemical pulping process. The main by-products for kraft pulping are tall oil soap (TOS)–originating from the extractives in the pulpwood, crude oil (CTO)–originating from the acidification of TOS, crude sulphite turpentine (CST)–originating from the volatile organic components in specific types of pulpwood, and lignosulphonates (Suhr et al. 2015). The tall crude oil is usually sold to the chemical industry, while some pulp mills burn the oil directly for bioenergy. The main by-products of sulphite pulping are lignosulphonates, acetic acid and furfural. Lignosulphonates are found in the spent sulphite liquor (SSL), which can make up to 70%. The most common use of lignosulphonates is as a binding agent in the construction industry. Acetic acid and furfural can also be extracted from the SSL.

4.3.3 Wastewater from mechanical pulping

For mechanical pulping, the water systems are typically closed to maintain the high process temperatures required. Fresh water is only used for cooling and sealing purposes (Suhr et al. 2015). Most mechanical pulping mills are integrated with paper manufacture, which usually means that water for pulping comes from the recycled water from the paper machine and the effluents produced are sent to the wastewater treatment facility where they are combined with the wastewater from the paper machine. However, for an integrated pulp and paper mechanical mill, GW and TMP water requirements are typically lower than for papermaking, leading to an excess of contaminated water from the pulping line to the sewer (Suhr et al. 2015).

The filtrates from the wash steps have a high COD and are usually discharged. Fibres can be recovered from these streams. The stability of the cellulose and lignin is not affected, but simple carbohydrates, hemicellulose, lignin derivatives, resins acids and fatty acids are dispersed in the process water. The organic load increases with a decreasing pulping yield and increasing temperature (Suhr et al. 2015). The resin acid concentration in mechanical pulp mills is higher compared to chemical pulp mills as the chemical mills have their chemical recovery process and, most of the time, collect the tall oil as well. Resins and fatty acids are usually removed during secondary wastewater treatment and sorption to biosolids (Liss et al. 1997; Williams et al. 1997). The streams having the highest resins and fatty acid concentrations are the pulp mill decker filtrate and bleach plants (Makris, 2003).

Table 4-24 and Table 4-25 represent a range of values characterising the general pollution load of the different types of mechanical pulping, demonstrating that TMP and CTMP have higher pollution loads. A yield of 86–97% can lead to 30–140 kg/tonne of wood being lost in the form of solid and dissolved substances during processing (Suhr et al. 2015). If bleaching is done on mechanical pulps, the release of pollutants will be higher – the upper values in Table 4-24 correspond to peroxide-bleached mechanical pulps. Due to the chemical chip treatment, CTMP effluent is more contaminated than the rest of the mechanical pulping processes. For an integrated CTMP mill, if bleaching is done, water is recycled using the bleaching filtrate, and excess contaminated water is sewered (Suhr et al. 2015).

Table 4-26 gives the collated data on additional effluent characteristics for mechanical pulping processes from Meyer and Edwards (2014b). In terms of flow estimates, it was much harder to get data for mechanical pulping processes. Konn et al. (2002) conducted a material balance in a CTMP mill to understand the fate of wood components throughout the various processing step - a schematic diagram and overall mass balance are depicted in Figure 4-2, highlighting the large volume of the effluent generated in the washing steps.

Table 4-22 General wastewater characteristics of different types of mechanical pulping (FAO, 1996)

Process parameter	Stone groundwood pulping (SGW)	Refiner mechanical pulping (RMP)	Thermo-mechanical pulping (TMP)
Dissolved organic substances (%)	1–2	2	2–5
BOD (kg/t)	10–22	12–25	10–30
COD (kg/t)	22–50	23–55	22–60
Suspended solids (kg/t)	10–50	10–50	10–50

Table 4-23 Typical characteristics of pollutant load in wastewater effluents from the mechanical pulping of Norway spruce before treatment (Suhr et al. 2015)

Pulping process	**Yield** (%)	**BOD5** (kg/t)	**COD** (kg/t)	**Nitrogen** (g/t)	**Phosphorus** (g/t)
Groundwood pulping (GW)	95–98.5	8.5–10	20–30	80–100	20–25
Pressurised groundwood pulping (PGW)	95–96	10–13	30–50	90–110	20–30
Refined mechanical pulping (RMP)	95–96	10–13	40–60	90–110	20–30
Thermochemical pulping (TMP)	93–97.5	10–15	50–80	100–130	30–40
CTMP	90–94	17–30	60–100	110–140	35–45
Bleached CTMP:					
Bleached softwood	91–93	25–50	80–130	130–400	50–60
Bleached hardwood	86–92	50–80	120–200	No data	No data

Table 4-24 Overview of wastewater composition in mechanical pumping effluents, adapted from Meyer and Edwards (2014)

Type of wastewater	**COD concentration** (g/L)	**Organic matter composition** (mg/L)	**Concentration of primary inhibitors** (mg/L)	**TSS concentration** (mg/L)	**References**
Thermochemical (TMP) composite	2.0–2.7	Carbohydrates: 1230–2700 Acetic acid: 235 Methanol: 25	Sulphate: 200–700 Peroxide: 0–100 Resin acids: 30–200	40–810	(Jurgensen *et al.* 1985), (Hall et al. 1986), (Cornacchio, 1989), Habets and de Vegt (1991), Hoel and Aarsand (1995)
TMP chip washing	5.6	n.a	n.a	n.a	(Cornacchio, 1989)
TMP whitewater	3.3–9.0	n.a	n.a	36–1400	Mehner *et al.* (1988)
Chemi-thermomechanical pulping (CTMP)	6.0–10.4	Acetic acid: 1500 Carbohydrates: 1000 Wood extractives: 1000	Sulphate: 50–200 Resin acids: 50–550 Peroxide: 0–500 DTPA: 100		Welande and Andersson (1985), (Habets and de Vegt, 1991), (Cornacchio, 1989)
Bleached chemi-thermomechanical pulping (BCTMP)	9.3	Acetic acid: 1360	Resin acids: 36–40	2450	Kennedy *et al.* (1992), Yang et al. (2010)

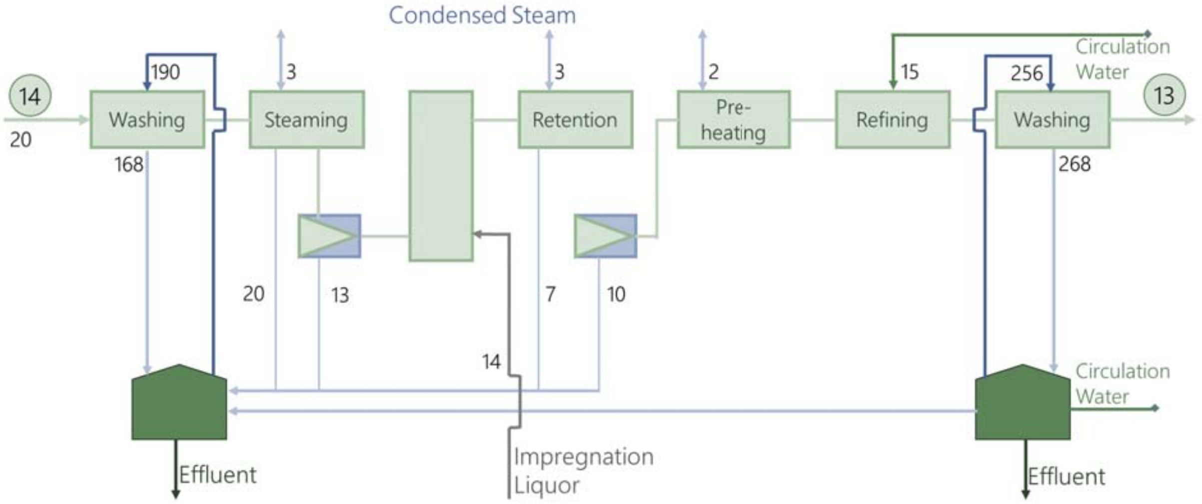


Figure 4-2 Mass balance in a CTMP process as reported by Konn et al. (2002). The water flows are given in t/h. The incoming chip flow and outgoing pulp flow are given in oven-dried t/h (circles)

4.3.4 Wastewater from bleaching

As seen in Table 4-1, the bleaching section tends to generate the highest volume of effluent - the wastewater characteristics are influenced by the degree of delignification of the unbleached pulp, the bleaching process, the washing loss, type of wood, final brightness desired, chemical and water consumption and the degree of closure (Cabrera, 2017; Suhr et al. 2015). An overview of the wastewater composition for the bleaching process is shown in Table 4-27. The maximum removal of lignin before the bleaching process will reduce the number of pollutants discharged from the bleaching section (Suhr et al. 2015). The bleach plants use a mixture of fresh and recycled water streams from the mill. The purpose of each stage is to brighten and clean the pulp. The more pulp goes through the process, the cleaner it gets; thus, the wastewater gets "cleaner" as well (Suhr et al. 2015).

Table 4-25 Overview of wastewater composition in bleaching effluents adapted from Meyer and Edwards (2014b)

Type of wastewater	**COD concentration** (g/L)	**Organic matter composition** (mg/L)	**Concentration of primary inhibitors** (mg/L)	**TSS concentration** (mg/L)	**References**
Kraft elemental chlorine-free bleaching effluents (Z, D, EOP, O_2) from two mills	1.1–2.4	n.a	Chloride: 417 ± 93 696 ± 57 AOX: 16 ± 5 22 ± 2 Phenols: 208 ± 17 635 ± 49 (N = 8)	n. a	Chaparro and Pires (2011),
Total chlorine-free bleaching agents	0.7–0.9	n.a	n.a	n. a	Vidal et al. (1997) 1997
Chlorine bleaching effluents	0.6–3.9	Methanol: 140 Acetate: < 40	AOX: 110–120	40–60	(Cornacchio, 1989), Yu and Welander (1994), Dorica and Elliott (1994), (Vidal et al. 1997)
Kraft alkaline bleaching effluent	0.3–4.3	Methanol: 40.0–75.6	AOX: 2.6–200 Chloride: 1200–1400 Sulphate: 170–250	7–2200	Qiu et al. (Qiu et al. 1988), Cornacchio (Cornacchio, 1989), Setiawan et al. (2008), Larsson et al. (2013)
TMP peroxide bleaching effluents	1.5–3.5	n.a	Sulphate: 600 Peroxide: < 100	< 100	Driessen and Wasenius (1994)

n.a. information not available; AOX - adsorbable organic halides

4.3.5 Wastewater from paper and recycling mills

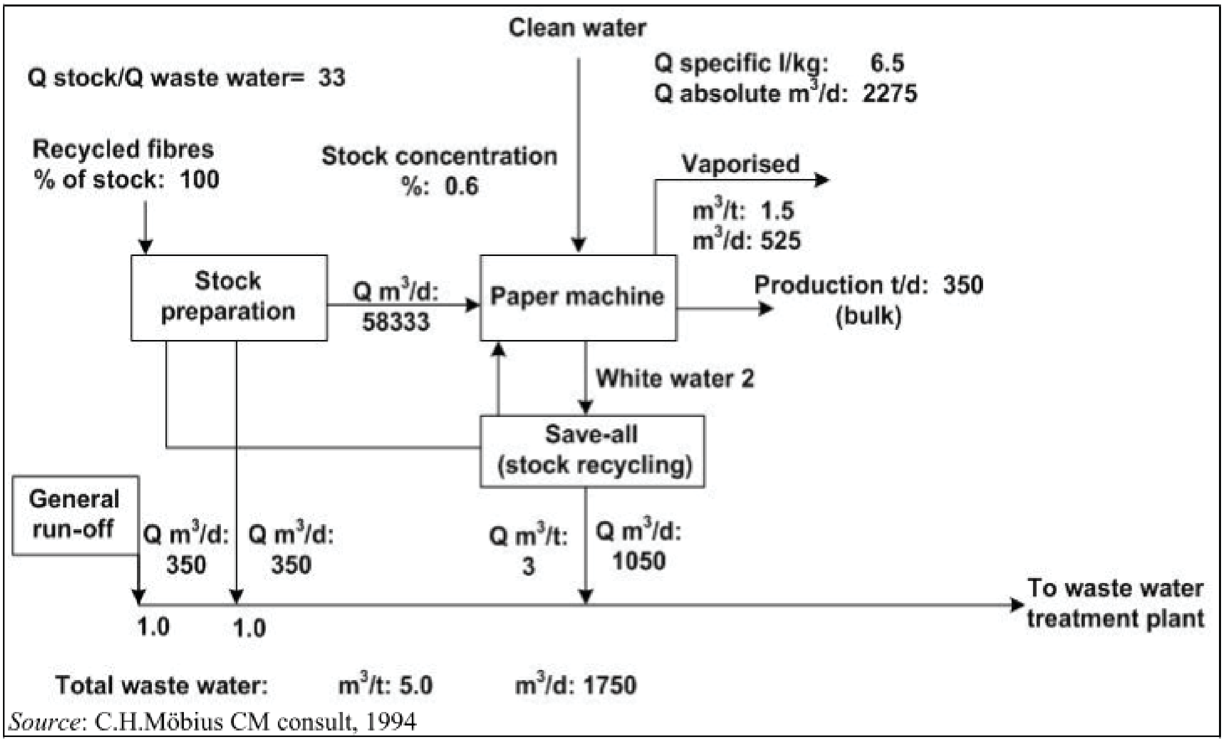
Table 4-28 gives a general overview of the typical characteristics of effluents in paper mills, demonstrating a high COD concentration. A high degree of closure in paper mills often leads to a high accumulation of dissolved matter in white water systems, up to 40 000 mg/L in some recycled fibre mills. In addition, the recovered fibres from recycled papers contain a variety of pollutants because of their different sources, paper types, and additives used for dispersing the fibres, removing the ink and bleaching (Muhamad et al. 2012). This results in high organic loading of the recycling wastewater. Effluents usually have low concentrations of nutrients (N and P) (Suhr et al. 2015). It is common practice to purge wastewater at the following sections, where it is mostly polluted (cleaning, de-inking and fibre recovery) as the rate of recycling is increased:

- Water from rejects separation by screens and centrifugal cleaners
- Filtrates from washers, thickeners and sludge handling
- Excess whitewater depending on the rate of water recycling

Table 4-26 Overview of wastewater composition in effluents from paper and board production, adapted from Meyer and Edwards (2014b)

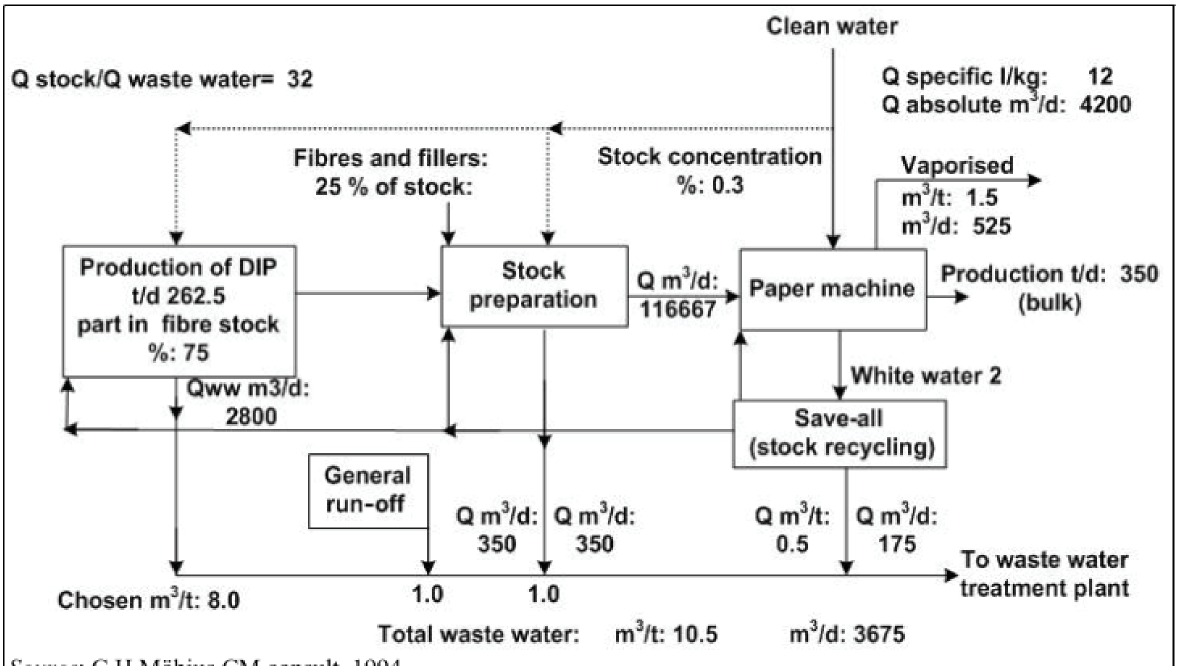
Type of wastewater	COD concentration (g/L)	Organic matter composition (mg/L)	Concentration of primary inhibitors (mg/L)	TSS concentration (mg/L)	References
Recycled paper mill effluent	0.6–15	n.a	n.a	300–800	Maat (1990), Paasschens et al.(1991), Mermillod et al. (1992), Driessen et al.(1999)
Recycled paper mill whitewater	32	n.a	Resin acids: 0.002–1.8 Fatty acids: 0.3–5.2	n.a	(Alexandersson and Malmqvist, 2005), (Latorre et al. 2007)

In terms of mass balance and flow, Suhr et al. (2015a) presented two schematic diagrams to demonstrate the difference in water circuits for a recycling mill processing corrugated medium without de-inking (Figure 4-3) and a mill producing de-inked pulp (Figure 4-4).



Source: C.H.Möbius CM consult, 1994

Figure 4-3 Water balance for an integrated RCF mill for a corrugated medium without de-inking (Suhr et al. 2015)



Source: C.H.Möbius CM consult, 1994

Figure 4-4 Water balance for the integrated production of de-inked pulp (Suhr et al. 2015)

4.3.6 Biosolids streams

An overview of the types of solid waste generated in the PULP AND PAPER industry is shown in Table 4-29. One of the largest waste streams is the sludge produced from the wastewater treatment section of the mills. This sludge is difficult to handle owing to its large volume and high moisture content, requiring, at times, conditioning treatment before it can be handled (Krigstin and Sain, 2006; Lynde-Mass et al. 1997).

Paper mill sludge is generally more fibrous in nature. Chemical pulp sludge contains more sulphurous compounds, originally from raw materials such as sodium sulphite (Na_2S), sulphurous acid (H_2SO_3) and bisulphite ion (HSO_3^-). Bleached pulp mill sludge generally contains high levels of chlorinated organic compounds coming from the bleaching agents, chlorine (Cl_2), chlorine dioxide (ClO_2) or sodium hypochlorite (NaOCl). De-inking sludge has a higher ash content due to the presence of inorganics in the recovered paper. Bark and other mill rejects are easy to dewater and have a high solids content, making them suitable to be used as fuels. De-inking sludge has a low moisture content. Primary wastewater sludge can be more easily dewatered than secondary sludge due to its lower biosolids content (Monte et al. 2009).

Current pulp and papermaking operations focus on separating the biosolids from the wastewater and concentrating them to increase their potential to be used as biosolids or decrease the tonnage of solid waste. The bark and wood residues from wood handling are usually incinerated, but drying must be properly done prior to this. While drying and burning biosolids streams for energy production are common waste management options, the value of these streams can be better exploited through alternate uses (Suhr et al. 2015).

Table 4-27 Overview of different types of solid waste generated in pulp and paper mills adapted from Monte et al. (2009)

From pulp mills	
Rejects	Rejects from virgin pulp consist of sand, bark and wood residues. They typically have low moisture content and high heating values and can be easily dewatered. They are thus generally burnt in the mill's bark boiler for energy recovery
Green liquor sludge, dregs and lime mud	Inorganic sludge was obtained from the chemical recovery section of the plant. They are usually dewatered and dried before being sent to a landfill
Wastewater treatment sludge	Usually comes from two sources: primary and secondary sludge. They are combined and dewatered to a 25–40% dry solid content. The solids can be combusted for energy recovery or sent to the landfill
Chemical flocculation sludge	Comes from water treatment and is usually disposed of in a landfill due to high inorganic content and water
From paper mills	
Rejects	Consists of impurities, fibres, metals and paper constituents such as fillers and sizing agents. Has a relatively low moisture content, high heating value and can be easily dewatered. Generally incinerated or disposed of in a landfill.
De-inking sludge	Contains mainly short fibres, coatings, fillers, ink particles, extractive substances and de-inking additives. It has a low heating value and is typically reused in other industries (e.g. cement, ceramics)
Primary sludge from wastewater treatment	Generated in primary clarification steps. It consists mainly of fines and fillers and is relatively easy to dewater. It is usually combined with de-inking or secondary sludge
Secondary sludge from wastewater treatment	Generated in the biological treatment units. It is usually thickened, dewatered and either incinerated or disposed of in a landfill

4.3.7 Component concentrations in the pulp and paper wastewater

4.3.7.1.1 Recalcitrant organic compounds in pulp and paper mill wastewater

There are recalcitrant organic compounds in PULP AND PAPER effluents that make waste treatment difficult. Some examples are lignosulphonic acids, chlorinated resin acids, chlorinated phenols, dioxins and chlorinated hydrocarbons (Kumara Swamy et al. 2012; Singh and Srivastava, 2014). While some of these compounds have low toxicity, they have high COD (1000–7000 mg/L), a significant concentration of suspended solids (500–2000 mg/L), a low biodegradability ratio (BOD/COD) in the range of 0.02–0.07 (De los Santos Ramos et al. 2009; Eskelinen et al. 2010). Additionally, compounds containing chlorine, which are usually characterised by the AOX parameter, are generally difficult to treat due to the strong carbon-chlorine bond (Jokela et al. 1993; Mounteer et al. 2007). High molecular weight organic matter (HMW > 1 kDa) is more difficult to treat than low molecular weight organic matter (LMW < 1 kDa) (Savant et al. 2006). The presence of dissolved lignin and its degradation products, hemicelluloses resin acids, fatty acids, diterpene alcohols, juvabione, tannins and phenols are responsible for the dark colour and toxicity of effluent (Chopra and Singh, 2012; Pokhrel and Viraraghavan, 2004).

4.3.7.1.2 Lignin and its derivatives

Lignin and its derivatives are the most difficult biomass components to undergo biological degradation (Kumar et al. 2010). During pulp and paper production, lignin is degraded to a mixture of high, medium and low molecular weight chlorinated and non-chlorinated fractions (McKague, 1981). The HMW lignin compounds are the least degraded in traditional effluent treatment and are eventually discharged into water bodies (Hyötyläinen and Knuutinen, 1993). During pulp bleaching, lignin, its derivatives and other organic matter present in the pulp react with chlorine leading to the formation of highly toxic and recalcitrant compounds such as chlorinated lignosulphonic acids, chlorinated resin acids, chlorinated phenols, guaiacols, catechols, benzaldehydes, vanillins, syringo-vanillins, and chloropropioguaiacols (Kringstad and Lindström, 1984; Thakur, 2004).

4.3.7.1.3 Chlorinated organic compounds

Suntio et al. (Suntio et al. 1988) and Freire et al. (Freire et al. 2003) reported that there are hundreds of chlorinated organic compounds in the PULP AND PAPER effluents and some examples are chlorinated hydrocarbons, phenols, catechols, guaiacol, furans, dioxins, syringyl lignin and vanillins amongst others. Chlorinated organic compounds are recalcitrant to biological processes mainly due to the number and position of their halogen substitutes resulting in a high pollution load when discharged to water bodies (Naumann, 1999). Over recent decades, there have been mitigation efforts aimed at decreasing the use of chlorine as a bleaching agent by replacing it with chlorine dioxide (Elementary Chlorine-Free, ECF), molecular oxygen, peroxide or ozone (Totally Chlorine-Free, TCF), resulting in a significant decrease in AOX, (Rantio, 1997; Shimp and Owens, 1993). Other strategies involve increasing delignification efficiency, modifying the cooking and oxygen stages, installing spill collection systems and introducing more efficient washing, stripping and reuse of condensates (Hubbe et al. 2016). External treatment plants can also be used to further reduce the emissions of AOX and unchlorinated toxic organic compounds to receiving water (Suhr et al. 2015).

4.3.7.1.4 Non-chlorinated recalcitrant compounds

Resin acids, fatty acids, sterols, diterpene alcohols and tannins are examples of wood extractives which are hydrophobic components soluble in neutral solvents (Lacorte et al. 2003). According to Johnsen et al. (1993), resin acids are normally released in large amounts during pulping and paper production. Dethlefs and Stan (1996) further reported that because of their stable tricyclic structure, they are very resistant to chemical degradation, contributing to the overall toxicity of the pulp mill effluents. Other non-chlorinated compounds are chelating agents such as DTPA and EDTA–large organic molecules used with peroxide and ozone bleaching of wood pulp, known to resist degradation or be prone to slow degradation (Hinck et al. 1997).

4.3.7.1.5 Challenges associated with inhibitors

The compounds mentioned so far can act as inhibitors in the conversion of the lignocellulosic biomass present in the pulp and paper industry into biofuel and bioproducts (Coz et al. 2016). In the case of biological transformation, detoxification and pre-treatment steps are usually required to access and process the lignocellulosic biomass. These steps will be covered in Chapter 9. To facilitate the selection of the appropriate detoxification steps, inhibitors can be broadly classified into five main groupings (Chandel et al. 2013, 2011; Coz et al. 2016; Mussatto and Roberto, 2004; Palmqvist and Hahn-Hägerdal, 2000):

- Group 1: Furan derivatives such as furfural and 5-hydroxymethylfurfural(HMF)
- Group 2: Phenolic compounds
- Group 3: Weak organic acids (levulinic, formic and acetic acids)
- Group 4: Raw material extractives (acidic resins, tannic acids and terpene acids)
- Group 5: Heavy metal ions (iron, nickel, aluminium, chromium)

4.3.8 Accumulation of non-process elements

A major issue with recycling water in the pulp and paper industry is the accumulation of non-process elements (NPEs) (Suhr et al. 2015). The most common NPEs, according to Jemaa et al. (1997), are K, Cl, Ca, Mg, Mn, Na, Fe, Si, Al, Cu, Ni, Cr and Zn, and they can cause problems such as corrosion and influencing the quality of the pulp produced. A list of common NPEs, with their sources, potential problems and usual purge points, is shown in Table 4-30. Some of the elements, like Mg, Al, and P, can form insoluble complexes and accumulate in the lime cycle, while others, like Cl, K, Si, and Al, can be highly soluble in liquors and can thus accumulate in the liquor cycle (Jemaa et al. 1997). NPEs usually leave the system in wastewater, sludge, electrostatic precipitator (ESP) and the final pulp.

Table 4-28 Overview of common non-process elements in the pulp and paper industry and the problems they may cause in the process plants (Suhr et al. 2015)

Elements	Main Sources	Potential problems	Main purge points
K	Chips (> 99%)	Boiler plugging decreases causticising efficiency, increases heat demand in the lower part of the recovery boiler, and affects black liquor density and viscosity	ESP catch
Cl	Chips (generally > 50%), chemicals	Boiler plugging acts as a dead load component and increases energy demands in the recovery boiler and in the lime kiln	ESP catch
Ca	Chips (> 80%)	Forms scales, competes with transition metals for chelants and affects oxygen delignification	Dregs, pulp
Mn	Chips (> 90%)	Forms scales and deposits, lowers product brightness	Dregs
Fe	Chips (> 50%), corrosion of equipment	Forms scales and deposits, lowers product brightness and hampers lime mud filtration	Dregs
Al	Chips (> 50%)	Forms scales and deposits and competes with transition metals for chelants	Removal of scales and deposits
Cu	Chips (> 90%)	Decomposes O2-based bleaching chemicals	Dregs
Co	Chips	Decomposes O2-based bleaching chemicals	Dregs
Cr	Chemicals	Increases the frequency of ClO_2 generator puffs and affects product brightness	Dregs
P	Chips (> 90%)	Decreases the available CaO	Grits
Si	Chips and lime (> 50%)	Forms scales and deposits and causes a decrease in lime porosity	Removal of scales and deposits
Mg	Chips (50%)	Disturbs the settling properties of the dregs	Pulps, dregs, grits
Ba	Chips	Forms scales and deposits	Removal of scales and deposits

4.4 Classification and identification of promising wastewater streams for a pulp and paper wastewater biorefinery

In the pulp and paper industry, the main resource present in wastewater streams before treatment is carbon in the form of lignocellulosic biomass or the hydrolysed hemicellulose, cellulose and lignin fractions or a combination. Lignocellulosic biomass is considered solid waste and is removed or reclaimed throughout the operations of a pulp and paper mill, while the hydrolysed components are lost to wastewater treatment.

In the wastewater biorefinery, resource efficiency is fundamental. Maintaining separation of the wastewater streams at the source may aid this. Cherubini and Strømman (2011) recommend that biomass-based feedstocks should be separated before biorefining into those preferred for the production of bioproducts and those for bioenergy purposes. Higher quality feedstocks are often required for bioproducts, while bioenergy processes may tolerate mixed, lower grade and more variable feedstocks. Wastewater streams with high volume, high concentration and low complexity are postulated to have the greatest potential as feedstocks for the wastewater biorefinery to produce value-added products (Harrison et al. 2017). Effluents which contain high pollutant quantities (VOCs, methanol, phenols and AOXs) should not be mixed with carbon-rich wastewater streams to ensure that pre-treatment costs are minimised. Remediation and bioenergy generation should be investigated for streams where high-value products are not feasible, as well as in the polishing of streams subsequent to their use for the production of value-added bioproducts.

To investigate the wastewater biorefinery concept, the wastewater streams are classified with regard to their volume, concentration and complexity (Section 4.5). Table 4-32 to Table 4-38 present an overview of wastewater streams in the pulp and paper industry to identify streams suited for valorisation, energy generation, remediation or a combination. Since data are reported in various forms and units, to facilitate comparison, the bases and assumptions summarised in 31 were used.

Table 4-29 Basis and assumptions used to classify pulp and paper effluents

Pulp produced per annum	100 000 air-dried tonnes (ADT) of pulp
Paper products produced per annum	100 000 tonnes
ADT pulp composition	90% pulp and 10% water
Oven-dried and bone-dry pulp	100% pulp
Number of days a plant runs	365 days
Density correlation for kraft black liquor [≤ 50% solids(S) and temperature (T) ≤ 100 °C] (Clay, 2007)	Density(g/cm^3) = 1.007 + 0.006S - 0.000495T
Density of condensates	1000 kg/m^3
Density of washing and screening wastewater	1000 kg/m^3
AOX compounds are present in pulp and paper effluents (Mandeep et al. 2019)	Methyl mercaptan, hydrogen sulphite, sulphur dioxide, sodium sulphite
Organic and inorganic pollutants in pulp and paper effluents (Mandeep et al. 2019)	Chlorophenols, benzoic acid and octacosane
Heavy metals present in pulp and paper effluents	Nickel, chromium, cadmium, arsenic, lead

4.4.1 Debarking and woodyard

For debarking and woodyard processes (Table 4-32), the stream volumes are small, and the concentration is low to medium, with medium complexity. While the medium concentration suggests potential resources (carbohydrates) contained within these wastewaters, the inhibitors present (raw material extractives) need to be investigated to ascertain whether valorisation, especially bio-valorisation, of these small-volume streams is worthwhile.

4.4.2 Kraft pulping

Multiple wastewater streams exist in the kraft pulping process with varying volumes, concentrations, and complexity. The largest volume is the bleaching effluent; this has medium concentration and high complexity. These streams are not carbohydrate-rich; thus, valorisation into bioproducts has low technical viability. However, due to the medium COD concentration, these streams can be considered for energy generation or remediation.

In terms of volume, the weak black liquor is next. It has a high concentration and medium complexity. This stream contains carbohydrates and some inhibitors and can thus be considered for product formation. However, typically the weak black liquor volume calculated is the total liquor produced, which, under normal operations, undergoes multiple-effect evaporation to increase its solids content. Thereafter, it can be used for energy generation. Owing to its carbohydrate content, this stream is included in the analysis to investigate the trade-off between traditional energy products and bioproducts.

The condensates and wash water effluents are smaller in volume and medium in concentration and complexity. The condensate streams do not contain significant carbohydrates but have significant COD concentration, thus suited for energy products and/or water remediation. Referring to traditional pulping operations covered earlier in the report, mills mostly focus on remediation for their condensate streams so that they can re-circulate the water to lower their freshwater intake.

The washing and filtrate reject effluents are also small in volume, and further information on their concentration and complexity is missing, hindering the assessment of their full potential.

4.4.3 Other pulping processes

For the sulphite pulping process (Table 4-34), the volume of the effluents is micro to small, but the concentration is high owing to the carbohydrate content for the SSL and washing streams. The complexity of these streams is low to medium, suggesting valorisation may be considered.

There was limited data for the semi-chemical pulping process (Table 4-35). From that available, the NSSC effluents have high concentration and small to medium volume, with medium complexity. The presence of carbohydrates in the stream suggests that the effluent streams in the NSSC process can be suitable for producing bioproducts. As was the case for the kraft pulping, the NSSC liquor is included in our table to evaluate the trade-off between using the carbohydrates present for energy products or for bioproducts. For the dissolving pulp process (Table 4-36), the medium volume, high stream concentration and presence of carbohydrates in the pre-hydrolysis liquor present an opportunity to investigate the formation of bioproducts.

In the mechanical and chemi-thermomechanical pulping processes (Table 4-37), individual effluent streams are dominated by the presence of raw material extractives, which act as significant inhibitors in the biological processes and would therefore be suited for remediation purposes. Combined streams appear to have some carbohydrates; therefore, energy bioproducts can be investigated for these streams.

For the paper and recycling process (Table 4-38), the potential lies in the combined streams, which have medium volume, high concentration and low complexity.

Table 4-30 Investigating the volume, concentration and complexity of debarking and woodyard effluents

Debarking and woodyard processes												
Wastewater streams	**Flow** (m^3/ADT) (m^3/ODT)	**Flow** (m^3/annum)	**Flow** (m^3/day)	**Flow** (ML/day)	**Volume**	**COD** (g/l)	**COD** (kg/ADT)	**COD** (kg/annum)	**Concentration**	**Components present**	**Complexity**	**References**
Debarking	2.51	2500002	6852	0.6852	Small	22	51	5000002	Medium	Fatty acids, resin acids, sterols, triglycerides, phenols, tannins, carbohydrates	Medium	Cabrera (2017), Salmi (2020)
Wet debarking	2–251	200000–25000002	548–68492	0.548–6.852	Small–medium	0.8–12	5–201	500000–20000002	Low-medium			Rintala and Puhakka (1994), Salmi (2020)
Woodyard	0.71	700002	1922	0.1922	Micro	n.a	n.a	n.a	–			US EPA (1997)

[1] Raw data in black

[2] Calculated using raw data and data from Table 6–33

n.a: not available

Table 4-31 Investigating the volume, concentration and complexity of Kraft pulping effluents

Kraft pulping processes													
Wastewater streams	**Flow** (m^3/ADT) (m^3/ODT)	**Flow** (m^3/annum)	**Flow** (tonnes/ODT)	**Flow** (m^3/day)	**Flow** (ML/day)	**Volume**	**COD** (g/l)	**COD** (kg/ADT)	**COD** (kg/annum)	**Concentration**	**Components present**	**Complexity**	**References**
Pulping	21[1]	2100000[2]		5753[2]	5.753[2]	Medium	n.a	n.a	n.a	-	Bark particles, soluble wood materials, resin acids, fatty acids, AOX, VOCs, dissolved organics	Medium	US EPA (1995), US EPA (1997); Pokhrel and Viraraghavan (2004)
Recovery	17[1]	1700000[2]		4658[2]	4.66[2]	Medium	n.a	n.a	n.a	-	n.a	-	US EPA (1997)
Weak black liquor[4]				2772[2]	2.77[2]	Medium	184[2,5]			High	Carbohydrates, extractives, acetic acid, formic acid, methanol, lignin, sulphur, sodium	Medium	US EPA (1997), Arosenius (2007), Ragsdale (2011)
Condensate	1[1]	100000[2]		274[2]	0.274[2]	Micro	3; 2–8[2]	3; 2–8[1]	300000; 200000–800000[2]	Medium	Hydrogen sulphite, methyl mercaptan, dimethyl sulphite, dimethyl disulphite, methanol, ethanol, acetone, terpenes, phenolics, resin acids	Medium	Cabrera (2017), Suhr et al. (2015)
Kraft digester condensate	n.a						13.3[1]			High	Methanol, phenols, ethanol terpenes, sulphides), sulphites	Medium	Meyer and Edwards (2014)
Kraft evaporator condensate	5.934[2,3]	534060[2]	5.934[2]	1463[2]	1.463[2]	Small	0.6–6.5[1]			Medium	Methanol, phenols, ethanol, propanol, acetone, terpenes, sulphides, sulphites, resin acids	Medium	Meyer and Edwards (2014); (A&M Texas, 2003); (El-Halwagi, 2012)

Kraft pulping processes

Wastewater streams	**Flow** (m^3/ADT) (m^3/ODT)	**Flow** (m^3/annum)	**Flow** (tonnes/ODT)	**Flow** (m^3/day)	**Flow** (ML/day)	**Volume**	**COD** (g/l)	**COD** (kg/ADT)	**COD** (kg/annum)	**Concentration**	**Components present**	**Complexity**	**References**
Kraft concentrator condensate	0. 682[2,3]	248. 93[2]	0. 683[2]	0. 682[2]	0. 001[2]	Micro	n. a			-	n. a	-	(A&M Texas, 2003); (El-Halwagi, 2012)
Kraft combined condensate	n. a	n. a	7 –8	n. a	n. a	n. a	0. 7 –4[1]			Medium	Methanol, sulphides	-	Meyer and Edwards (2014)
Washing and screening	0. 5[1]	50000[2]		137[2]	0. 137[2]	Micro	4[2]	2[1]	200000[2]	Medium	n. a	-	Cabrera (2017)
Screening WW	0. 967[2,3]	87000[2]	0. 967[2]	238[2]	0. 238[2]	Micro	n. a	n. a	n. a	-	n. a	-	(A&M Texas, 2003); (El-Halwagi, 2012)
Filter rejects WW	0. 003[2,3]	240[2]	0. 003[2]	0. 658[2]	0. 001[2]	Micro	n. a	n. a	n. a	-	n. a	-	(A&M Texas, 2003); (El-Halwagi, 2012)
Bleaching	31[1]	3100000[2]		8493[2]	8. 49[2]	Medium	1. 13[2]	35[1]	3500000[2]	Medium	Dissolved lignin, colour, carbohydrate, inorganic chlorines, AOX, EOX, VOCs, chlorophenols and halogenated hydrocarbons	High	US EPA (1995), Cabrera (2017)
Bleaching	48[1]	4800000[2]		13151[2]	13. 2[2]	Large	0. 313 –1. 35[2]	15 –65[1]	1500000 – 6500000[2]	Medium	Dissolved lignin, colour, COD, carbohydrate, inorganic chlorines, AOX, EOX, VOCs, chlorophenols and halogenated hydrocarbons	High	US EPA (1995), US EPA (1997), To check NATSURV or BAT
Kraft elemental chlorine-free bleaching	20. 7[2,3]	1863000[2]	20. 7[2]	5104[2]	5.10[2]	Medium	1. 1 –2. 4[1]			Medium	Dissolved lignin, colour, carbohydrate, inorganic chlorines, AOX, EOX, VOCs, chlorophenols and halogenated hydrocarbons	Medium-high	(A&M Texas, 2003); (El-Halwagi, 2012), Table 6. 3
Kraft alkaline bleaching	n. a	n. a	n. a	n. a	n. a	-	0. 3 –4. 3[1]			Medium	Colour, bark particles, soluble wood materials, resin acids, fatty acids, AOX, VOCs, dissolved organics, methanol, sulphate, chloride	High	Table 6. 3
Kraft – unbleached effluent	40 –60[1]	4000000 – 6000000[2]		10959 – 16438[2]	10. 9–16. 4[2]	Large	0. 667 –1[2]	40 –60[1]		Low –medium	Colour, bark particles, soluble wood materials, resin acids, fatty acids, AOX, VOCs, dissolved organics	Medium-high	Rintala and Puhakka (1994), Salmi (2020), Table 6. 3
Kraft– bleached effluent	60 –90[1]	6000000 – 9000000[2]		16438 – 24658[2]	16. 4–24. 7[2]	Large	1. 11–2. 33[2]	100 –140[1]		Medium	Dissolved lignin, colour, bark particles, carbohydrate, inorganic chlorines, AOX, EOX, VOCs, chlorophenols and halogenated hydrocarbons	High	Rintala and Puhakka (1994), Salmi (2020), Table 6. 3

Kraft pulping processes													
Wastewater streams	**Flow** (m^3/ADT) (m^3/ODT)	**Flow** (m^3/annum)	**Flow** (tonnes/ODT)	**Flow** (m^3/day)	**Flow** (ML/day)	**Volume**	**COD** (g/l)	**COD** (kg/ADT)	**COD** (kg/annum)	**Concentration**	**Components present**	**Complexity**	**References**

[1] Raw data
[2] Calculated using raw data and data from Table 6-33
[3] Values are in m^3/ODT
[4] Weak black liquor from washes: 15–20% solids, 80–85% water; black liquor to recovery boiler: 65–85% solids, 15–25% water (Clay, 2007)
[5] Average COD calculated for weak black liquor samples collected from four bleached kraft mills (Ragsdale, 2011)
n. a: not available

Table 4-32 Investigating the volume, concentration and complexity of sulphite pulping effluents

Sulphite pulping processes													
Wastewater streams	**Flow** (m^3/ADT) (m^3/ODT)	**Flow** (m^3/annum)	**Flow** (tonnes/ODT)	**Flow** (m^3/day)	**Flow** (ML/day)	**Volume**	**COD** (g/l)	**COD** (kg/ADT)	**COD** (kg/annum)	**Concentration**	**Components present**	**Complexity**	**References**
Sulphite evaporator condensate	n.a	n.a	n.a	n.a	n.a	–	3–2.7[1] (?)			Medium	Acetic acid, methanol, furfural, sulphites, resin acids	Medium	Meyer and Edwards (2014)
Spent sulphite liquor (SSL)	Calcium base: 9.28[1,3]; Magnesium base: 6.08[1,3]; Ammonia base: 9.46[1,3]; Sodium base: 7.10[1,3]; From paper (5.67[1,3,4])	510300–851400[2]		1398–2333[2]	1.40–2.33[2]	Small–medium	40–115[1]			High	lignin, sulphites, sulphate	Medium	US EPA (1997), Llano et al. (2015); Meyer and Edwards (2014)
Washing WW	1.22[2,3,4]	109907[2]		301[2]	0.301[2]	Micro	6.2–48[1]			High	Methanol, acetic acid, formic acid, formaldehyde, carbohydrates, lignosulphonates	Medium	Meyer and Edwards (2014); Llano et al. (2015); Rydholm (1965)

[1] Raw data
[2] Calculated using raw data and data from Table 6-33
[3] Values are in m^3/ODT
[4] Assuming two cooks per day using data and process description from Llano et al. (2015)
n.a: not available

Table 4-33 Investigating the volume, concentration and complexity of semi-chemical pulping effluents

Semi-chemical pulping processes												
Wastewater streams	**Flow** (m^3/ADT) (m^3/ODT)	**Flow** (m^3/annum)	**Flow** (m^3/day)	**Flow** (ML/day)	**Volume**	**COD** (g/l)	**COD** (kg/ADT)	**COD** (kg/annum)	**Concentration**	**Components present**	**Complexity**	**References**
Neutral sulphite semi-chemical (NSSC) composite	n.a	n.a	n.a	n.a	n.a	1.8–1.9[1]			Medium	Carbohydrates, acetic acid, methanol, lignin	Medium	Meyer and Edwards (2014)
NSSC condensate	n.a	n.a	n.a	n.a	n.a	7[1]			–	Sulphur, ammonia	–	Rintala and Puhakka (1994)
NSSC spent (black) liquor–not waste	2.6[1,3]	260000[2]	712[2]	0.712[2]	Small	28–40; 39.8[1]			High	Carbohydrates, acetic acid, methanol, ethanol, lignin	Medium	Meyer and Edwards (2014), US EPA (1997), Bajpai (2000), Mokebe (2007)
Alkaline peroxide mechanical pulping (APMP)	n.a	n.a	n.a	n.a	n.a	10–31[1]			High	Sulphate, peroxide, resin acids, LCFAs	Medium	Meyer and Edwards (2014)
NSSC effluent	20–80[1,3]	2000000–8000000[2]	5479–21918[2]	5.48–21.9[2]	Medium–large	0.38–6[2]	30–120[1]	3000000–12000000[2]	Medium	Carbohydrates, acetic acid, methanol, lignin	Medium	Rintala and Puhakka (1994), Meyer and Edwards (2014)

[1] Raw data

[2] Calculated using raw data and data from Table 6-33

[3] Values are in m^3/ODT

n.a: not available

Table 4-34 Investigating the volume, concentration and complexity of dissolving pulp effluents

Dissolving pulping processes													
Wastewater streams	**Flow** (m^3/ADT) (m^3/ODT)	**Flow** (m^3/annum)	**Flow** (tonnes/ODT)	**Flow** (m^3/day)	**Flow** (ML/day)	**Volume**	**COD** (g/l)	**COD** (kg/ADT)	**COD** (kg/annum)	**Concentration**	**Components present**	**Complexity**	**References**
Kraft dissolving pulp pre-hydrolysis	17.0[2,3]	1704231[2]		4669[2]	4.67[2]	Medium	70– 120[1]			High	Carbohydrates, acetic acid, lignin, furfural, sulphates sulphites, ash, HMF	Medium	Meyer and Edwards (2014), Wu (2016), Chen et al.(2018), Kärkkäinen (2021)
Dissolving pulp effluent	25[1]	2500000[2]		6849[2]	6.85[2]	Medium	1.22	30[1]	3000000[2]	Low-medium	Dissolved lignin, colour, COD, carbohydrate, inorganic chlorines, AOX, EOX, VOCs, chlorophenols and halogenated hydrocarbons	High	US EPA (1995), Cabrera (2017), Kärkkäinen (2021)

[1] Raw data

[2] Calculated using raw data and data from Table 6-33

[3] Volume was calculated for a weak liquor containing 13.8% solids (Kärkkäinen, 2021), and density was calculated using (Clay, 2007) formula in Table 6-33, with S = 13.8 and T =100

Table 4-35 Investigating the volume, concentration and complexity of mechanical and chemi-thermochemical pulping effluents

Mechanical and chemi-thermochemical pulping processes													
Wastewater streams	**Flow** (m^3/ADT) (m^3/ODT)	**Flow** (m^3/annum)	**Flow** (tonnes/ODT)	**Flow** (m^3/day)	**Flow** (ML/day)	**Volume**	**COD** (g/l)	**COD** (kg/ADT)	**COD** (kg/annum)	**Concentration**	**Components present and**	**Complexity**	**References**
TMP composite	n.a	n.a	n.a	n.a	n.a	n.a	2–2.7[1]			Medium	Carbohydrates, acetic acid, methanol, sulphate, peroxide, resin acids	Medium	Meyer and Edwards (2014)
TMP chip washing	n.a	n.a	n.a	n.a	n.a		5.6[1]			Medium	n.a	-	Meyer and Edwards (2014)
TMP whitewater	n.a	n.a	n.a	n.a	n.a	n.a	3.3–9[1]			Medium	n.a	-	Meyer and Edwards (2014)
TMP effluent	9.4–20[1]	940000–2000000[2]		2575–5480[2]	2.58–5.48[2]	Medium	n.a			-	Carbohydrates, acetic acid, methanol, sulphate, peroxide, resin acids	Medium	Meyer and Edwards (2014) et al.(2015)
TMP–unbleached effluent	10–30[1]	1000000–3000000[2]		2740–8220[2]	2.74–8.22[2]	Medium	2–6[2]	40–60[1]		Medium	Carbohydrates, acetic acid, methanol, sulphate, peroxide, resin acids	Medium	Meyer and Edwards (2014), Rintala and Puhakka (1994)
TMP–bleached effluent	10–30[1]	1000000–3000000[2]		2740–8220[2]	2740–8220[2]	Medium	1.67–1[2]	50–120[1]		Medium-high	Carbohydrates, acetic acid, methanol, sulphate, peroxide, resin acids, inorganic chlorines, AOX, EOX, VOCs, chlorophenols and halogenated hydrocarbons	-	Rintala and Puhakka (1994)
CTMP chip washing	12.9[2,3]	1163077[2]	12.9[2]	3187[2]	3.19[2]	Medium	n.a	n.a	n.a	-	n.a	-	Konn and Holmbom (2002)
CTMP pulp washing	20.6[2,3]	1855385[2]	20.6[2]	5083[2]	5.08[2]	Medium	n.a	n.a	n.a	-	n.a	-	Konn and Holmbom (2002)
CTMP chip impregnation	n.a	n.a	3.85[2]	n.a	n.a	-	n.a	n.a	n.a	-	n.a	-	Konn and Holmbom (2002)
CTMP effluent	9–27.2[1]	900000–2720000[2]		2466–7452[2]	2.47–7.45[2]	Medium	6–10.4[1]			Medium	Carbohydrates, acetic acid, wood extractives, sulphate, resin acids, peroxide, DTPA, organic acids, lignin	Medium-high	Meyer and Edwards (2014); Suhr et al.(2015)
CTMP–unbleached effluent	10–15[1]	1000000–1500000[2]		2740–4110[2]	2.74–4.11[2]	Medium	7–12[2]	70–120[1]		Medium-high	Carbohydrates, acetic acid, wood extractives, sulphate, resin acids, DTPA, organic acids, lignin	Medium-high	Rintala and Puhakka (1994)
CTMP–bleached effluent	10–15[1]	1000000–1500000[2]		2740–4110[2]	2.74–4.11[2]	Medium	10–18[2]	100–180[1]		High	Carbohydrates, acetic acid, wood extractives, sulphate, resin acids, DTPA, organic acids, lignin, AOXs, chlorophenols and halogenated hydrocarbons	Medium-high	Rintala and Puhakka (1994)

BCTMP	n.a	n.a	n.a	n.a	n.a	n.a	9.3[1]			Medium	n.a	-	Meyer and Edwards (2014)
TMP peroxide bleaching effluent	n.a	n.a	n.a	n.a	n.a	n.a	1.5–3.5[1]			Medium	n.a	-	Meyer and Edwards (2014)

[1] Raw data

[2] Calculated using raw data and data from Table 6-33

[3] Values are in m^3/ODT

n.a: not available

Table 4-36 Investigating the volume, concentration and complexity of papermaking and recycling effluents

Papermaking and recycling processes													
Wastewater streams	**Flow** (m^3/ADT) (m^3/ODT)	**Flow** (m^3/annum)	**Flow** (tonnes/ODT)	**Flow** (m^3/day)	**Flow** (ML/day)	**Volume**	**COD** (g/l)	**COD** (kg/ADT)	**COD** (kg/annum)	**Concentration**	**Components present**	**Complexity**	**References**
Recycled paper mill effluent				1750–3675[1]	1.75–3.68[2]	Medium	0.6–5[1]			Medium	Particulates, biosludge, heavy metals, organic and inorganic pollutants, resin acids, inorganic dyes	Medium	Meyer and Edwards (2014); Suhr et al.(2015), (SUEZ, n.d.)
Recycled paper mill whitewater	n.a	n.a	n.a	n.a	n.a	-	32[1]			High	Resin acids, fatty acids, sedimented fibre	Medium	Meyer and Edwards (2014)
Integrated RCF, de-inked corrugated medium without de-inking	5[2]	500000[2]		1370[1]	1.37[2]	Medium	n.a			-	Particulates, biosludge, heavy metals, organic and inorganic pollutants, resin acids, inorganic dyes	Medium	Suhr et al.(2015)
Papermaking	10–52[1]	1000000–5200000[2]		2740–14247[2]	2.74–14.2[2]	Medium–large				Medium	Particulates, biosludge, heavy metals, organic and inorganic pollutants, resin acids, inorganic dyes	Medium	Rintala and Puhakka (1994), Table 6.5, US EPA (1997), Durairaj and Nouri (2015)

[1] Raw data

[2] Calculated using raw data and data from Table 6-33

4.5 Categorising wastewater streams for a wastewater biorefinery

4.5.1 Categorising wastewater streams

As detailed by Harrison et al. (2017), the wastewater biorefinery requires an overall characterisation of the wastewater streams to extract the maximum available information on the carbon, nitrogen and phosphorus nutrients, potential for energy, and toxic compounds. The proposed approach relies on three main categories: volume, concentration and complexity (DWA SA, 2009; van den Berg, 2009). The volume classification follows the wastewater capacity of wastewater treatment plants according to Table 4-39. A high concentration is classified as above 10 g/L COD, and a low concentration by less than 1 g/L COD (Table 4-40). The complexity is classified according to Table 4-41. The volume and concentration classifications are presented as a matrix in Figure 4-5, showcasing several major wastewater groupings.

Table 4-37 Volume classification of wastewater processing plants (Harrison et al. 2017b)

Size	Volume of wastewater
Micro	< 0.5 ML/day
Small	0.5–2 ML/day
Medium	2–10 ML/day
Large	10–25 ML/day
Macro	> 25 ML/day

Table 4-38 Concentration classification of wastewater streams (Harrison et al. 2017b)

Concentration	COD
Low	< 1 g/L
Medium	1–10 g/L
High	>10 g/L

Table 4-39 Complexity classification of wastewater streams (Harrison et al. 2017b)

Complexity	Change in composition	Number of components
Low	composition does not change much	< 5 main components
Medium	composition changes in a predictable manner	5–15 main components
High	composition changes often / unpredictably	> 15 main components

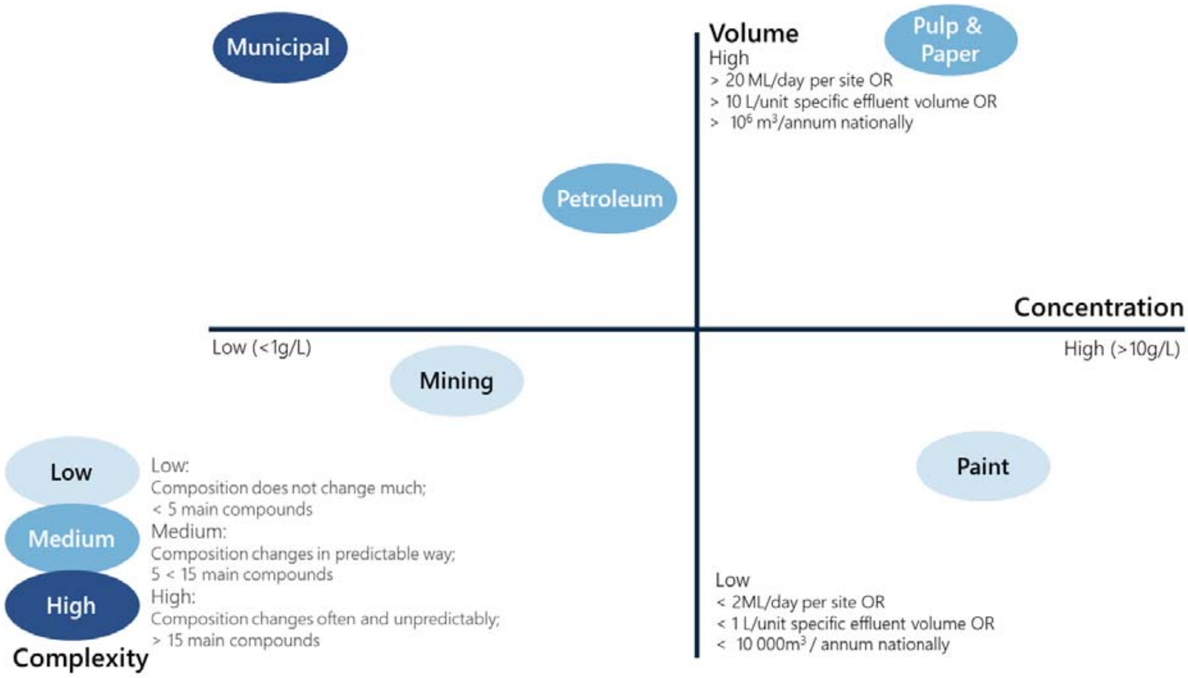


Figure 4-5 Matrix representing the wastewater biorefinery potential of feedstock qualities with respect to volume, concentration and complexity adapted from Harrison et al. (2017)

4.5.2 Developing a scoring system for the potential of wastewater for valorisation

A simple scoring system (Table 4-42) allows for a cumulative evaluation of the overall characteristics of each waste stream. The lowest score of one is given for the most desirable values of each category (macro volume, high concentration, low complexity) and the highest score of three for the least desirable values (micro-volume, low concentration, high complexity). Each of the three categories is given equal weight. The cumulative score ranges from nine for the waste streams least suitable for valorisation in the biorefinery to three for those most suitable.

Table 4-40 Scoring matrix to evaluate the potential of wastewater streams for valorisation in a wastewater biorefinery

Volume	Score	Concentration	Score	Complexity	Score
Macro: >25 ML/day	1	High: >10 g/L COD	1	Low: <5 components	1
Large: 10< ML/day <25	1. 5				
Medium: 2< ML/day <10	2	Medium: 1 g/l < COD < 10g/L	2	Medium: 5< components < 15	2
Small: 0. 5< ML/day <2	2. 5				
Micro: <0. 5 ML/day	3	Low: <1 g/L COD	3	High: >15 components	3
Lowest score	Macro, high, low		3		
Highest score	Micro, low, high		9		

4.5.3 Scoring pulp and paper wastewater streams

Using Table 4-32 to Table 4-38, streams for which information on the three wastewater biorefinery evaluation categories (volume, concentration and complexity) were available were scored using the template (Table 4-42). The results of this scoring exercise are shown in Table 4-43. The lowest scores for the individual streams were for the pulping liquors, namely, the weak black liquor, spent sulphite liquor, NSSC spent liquor and the PHL liquor, demonstrating their high potential to be considered in a pulp and paper wastewater biorefinery for value-added products. These streams have been shown to be rich in carbohydrates in the form of lignocellulosic biomass or the hydrolysed hemicellulose, cellulose and lignin fractions or a combination, as highlighted in Section 4. 3. This challenges the status quo of using liquor streams for energy generation purposes only as they demonstrate higher resource potential. The washwater effluent in the sulphite pulping process can also be considered for valuable product formation and, ideally, should not be mixed with other effluents in order to preserve its resource potential. For the combined streams, the NSSC effluent and papermaking effluent has the lowest score, followed by the recycling paper effluent, demonstrating that for some processes, the combined streams have more potential than individual streams.

The highest scores obtained were for the individual condensates and combined dissolving effluent streams, suggesting that valorisation in a wastewater biorefinery would be technically challenging, and thus the focus should be on remediation for “fit-for-purpose” water. As mentioned in Section 4. 3. 1. 6, the current best practices techniques for condensates in the industry are indeed for recycling purposes. The rest of the streams in 43 falls within the 6–6. 75 scores (5.00–6. 8 when normalised), and these streams can be potentially considered for energy products as they demonstrate a high enough COD concentration but limited accessible carbohydrates when compared to the liquor streams.

However, a look at the complexity data suggests that most of the wastewater streams in the pulp and paper industry tend to fall between medium and high complexity. Therefore, it is important to investigate the potential of each stream on a case-by-case basis, as the resources and inhibitors they contain will greatly influence viable product formation.

Table 4-41 Evaluation of individual and combined wastewater streams in the pulp and paper industry according to the matrix of potential. (Score: 3 = best, 9 = worst. Normalised score 1 = best, 10 = worst)

Stream	**Process**	**Individual or combined streams**	**Volume**	**Concentration**	**Complexity**	**Score**	**Normalise. score**
Debarking	Pulping	Individual	2. 5	2	2	6. 5	6. 25
Wet debarking	Pulping	Individual	2. 25	2. 5	2	6. 75	6. 62
Condensates	Kraft pulping	Individual	3	2	2	7	7. 00
Weak black liquor	Kraft pulping	Individual	2	1	2	5	4. 00
Bleaching	Pulping	Individual	1. 75	2	3	6. 75	6. 62
Kraft - unbleached effluent	Kraft pulping	Combined	1. 5	2. 5	2. 5	6. 5	6. 25
Kraft-bleached effluent	Kraft pulping	Combined	1. 5	2	3	6. 5	6. 25
Spent sulphite liquor (SSL)	Sulphite pulping	Individual	2. 25	1	2	5.25	4. 38
Washing WW	Sulphite pulping	Individual	3	1	2	6	5.50
NSSC spent (black) liquor - not waste	Semi-chemical pulping	Individual	2. 5	1	2	5.5	4. 75
NSSC effluent	Semi-chemical pulping	Combined	1. 75	2	2	5.75	5.12
Kraft dissolving pulp pre-hydrolysis	Dissolving pulp	Individual	2	1	2	5	4. 00
Dissolving pulp effluent	Dissolving pulp	Combined	2	2. 5	3	7. 5	7. 75
TMP - unbleached effluent	Mechanical pulping	Combined	2	2	2	6	5.50
TMP - bleached effluent	Mechanical pulping	Combined	2	1. 5	2. 5	6	5.50
CTMP - unbleached effluent	Mechanical pulping	Combined	2	2	2	6	5.50
CTMP - bleached effluent	Mechanical pulping	Combined	2	1	3	6	5.50
Recycled paper mill effluent	Papermaking	Combined	2	2	2	6	5.50
Papermaking	papermaking	Combined	1. 75	2	2	5.75	5.12

N.B: For categories which were listed as intermediaries, an average score was used. For example, if the concentration was marked low-medium, an average score value of 2.5 was used.

4.6 Concluding remarks

This chapter investigated the detailed characteristics of individual and combined wastewater streams in the PPI. The scoring exercise enabled us to identify promising streams for establishing **a pulp and paper wastewater biorefinery (P&P WWBR)**. It further highlighted the need to investigate different valorisation routes for different processes and streams of different concentration, volume and complexity. For example, where liquors are produced, it is beneficial to consider them as potential feedstocks for the production of higher value-added products rather than only energy products. Additionally, owing to the high complexity of the bleaching effluents, they should be handled separately as much as possible.

Contrary to combined pulping wastewater, the combined wastewater streams for papermaking and recycling processes demonstrate higher potential for a value-added bioproduct formation in the P&P WWBR over energy products. There are also some streams, such as the condensate stream in chemical pulping processes, which seem best suited for remediation purposes only. It is expected that the scoring exercise for local mills in South Africa will yield similar information to that presented in Table 4-42, as pulp and papermaking processes are generally well-established globally. This will guide the selection of streams and processes for the integrated treatment of the wastewater streams for value creation, energy production and generation of fit-for-purpose water for recycling, reuse or release.

To evaluate the full potential of promising streams, they need to be matched with the appropriate valorisation route and products (high-value bioproducts, energy products and/or remediated water). In Chapter 5, potential products of value for consideration are discussed. In Chapter 6, production platforms for lignocellulosic-rich feedstocks are investigated with a focus on the potential product spectrum as well as the detoxification and pre-treatment steps required. In Chapter 7, we propose a framework to identify the appropriate bioproducts for the **pulp and paper wastewater biorefinery,** while in Chapter 9, we explore **pulp and paper wastewater biorefinery process flowsheets** across an expanded spectrum of wastewater streams.

5 Towards Successful Product Selection for A Pulp and Paper Wastewater Biorefinery

5.1 Characteristics of the wastewater biorefinery product portfolio

The differentiating attribute of a wastewater biorefinery is that it uses the contaminants in wastewater as a substrate for the generation of value-added products. This aims to enhance resource efficiency and minimise the waste burden. Primary and secondary products must be selected, taking into consideration a variety of factors, including the nature and composition of the waste streams, the available conversion technologies and their associated products, and the requirement for fit-for-purpose water. The decision-making process is non-linear and iterative. It requires focus on the following foundational traits of the wastewater biorefinery to ensure techno-economic and environmental feasibility (Harrison et al. 2017):

- prioritisation of processes and products that generate clean water or fit-for-purpose water as the non-negotiable product
- design at least one primary product for maximum economic benefit
- inclusion of secondary products to ensure resource efficiency and minimum environmental burden
- a multi-unit process to enable the optimisation of both product of value and water quality
- minimisation of process complexity to avoid over-extending the capacity of the main production facility

The successful implementation of a new facility, such as pulp and paper wastewater biorefinery, is dependent on the selection of a strong product portfolio which is informed by these design and process constraints. Pertinent product selection methods, as presented in Section 5.3, are required in order to develop an integrated decision-making approach tailored for the pulp and paper wastewater biorefinery presented in Section 5.4.

5.2 Background to a successful product portfolio for a wastewater biorefinery

Product selection for a wastewater biorefinery needs to overcome the following challenges (Harrison et al. 2017):

- the predefined feedstock
- the dual intention of nutrient removal and product formation
- the non-negotiable final product of fit-for-purpose water

5.2.1 The influence of wastewater as feedstock

A number of constraints are presented by wastewater as raw material. The typical process selection based on the selection of a product first, leading to the choice of process and raw material, is inverted. Here, the characteristics of the wastewater are fundamental to the possible products to be selected. The fixed ratios of C:N:P in the wastewater and its typically dilute nature (Verster et al. 2014; Harrison et al. 2017) are key. Where the wastewater contains toxins or inhibitors, bioprocesses need to be robust, or a physicochemical process may be needed as a precursor to the biological processes. Products for use in the food or health industries can only be selected when the wastewater contains no harmful substances. Microbial cultures must exhibit resilience if the wastewater is variable in composition.

Because the feedstock is typically dilute, a product which separates into a non-aqueous phase and a bioprocess in which the biomass phase can be enriched by natural selection are both advantageous.

5.2.2 Cascading product processing

Harrison et al. (2017) presented a list of potential products classifying them into four levels, as shown in Table 5-1, representing a progression of economic value, with first-level products typically having the highest value and the most demanding bioprocesses. These first-level products can also be divided into levels, from high-value-low-volume products to lower-value-high-volume products. Fit-for-purpose water is the fourth level category owing to its current economic value and the fact that it is the final product; however, it is the single imperative product with high environmental value. This is especially true in a water-stressed context such as South Africa, where the economic value is likely to rise as well.

Table 5-1 Overview of potential products for a wastewater biorefinery(Harrison et al. 2016; Harrison et al. 2017)

Levels of products	Description	Examples
1st level	bioproducts derived from microbial bioreactors	*fine bioproducts*: pigments, flavour and fragrance molecules, bioactives, agarose, nutraceuticals, pharmaceuticals *platform chemicals*: organic acids, volatile fatty acids, alcohols, lipids *function-based bioproducts*: bioflocculants, biosurfactants, biosolvents, biolubricants, soil conditioners, pre-conditioning enzymes, industrial enzymes *commodity bioproducts*: alginates, polyglutamic acid, polyhydroxyalkanoates, polylactic acid, polyethylene terephthalate
second level	biofuels and bioenergy	biogas, ethanol, algal lipids for biodiesel, biodiesel, biobutanol biomass for combustion/gasification/pyrolysis
third level	processed biomass	construction materials, composite materials, packaging materials, compost, animal feed
4th level	acceptable quality water	fit-for-purpose water for recycling, cooling, irrigation, potable water, and water released into the environment

A first-level product is characteristically the anchor product, ensuring the economic feasibility of the wastewater biorefinery. The choice of the first-level product, its microbial bioreactor, and the quality necessary in the fit-for-purpose water influence other product and bioreactor selections. The second and third-level products are typically selected to combine extended resource efficiency as well as compliance with respect to water quality by removal of contaminants. It is preferable that one or more products are of use in the parent production site or in the wastewater biorefinery itself. This reduces the complexity of concomitant marketing and decreases dependence on external market forces.

5.2.3 The non-negotiable water product

The ideal in the wastewater biorefinery is that, as far as possible, every process produces a product. Harrison et al. (2017) indicate a preference for products produced by microorganisms that scavenge the organics to low concentrations such that clean, or fit-for-purpose, water, the final product of the wastewater biorefinery, is obtained with minimal polishing requirements.

After selecting the most suitable value-added products and selecting suitable steps for the production of the fit-for-purpose water, the likely quality of the water remaining in the biorefinery must be evaluated. Comparing this with the quality needed for different possible purposes (reuse in the parent process, irrigation, release to the environment, or potable water) allows for the selection of the most suitable purpose for the water produced from the wastewater biorefinery. Once the quality which is required is defined, the final processes required to produce the fit-for-purpose water can be selected.

The preferred route for polishing the water product in a wastewater biorefinery is using an engineered wetland approach. This may be coupled with a macrophyte product or replaced or proceeded by an algal reactor to yield an additional algal product. For certain applications, some form of filtration may be necessary, such as microfiltration, reverse osmosis or nanofiltration.

5.3 Overview of methods and criteria used for product selection

There are many proposed methods for identifying appropriate bioproducts of interest. Batsy et al. (2013)describe two fundamental orientations (Figure 5-1):

- A process-centric design approach can be used in which the use of innovative technology delivers or 'pushes' products
- A product-centric approach can be taken to select products with a known market 'pull'.

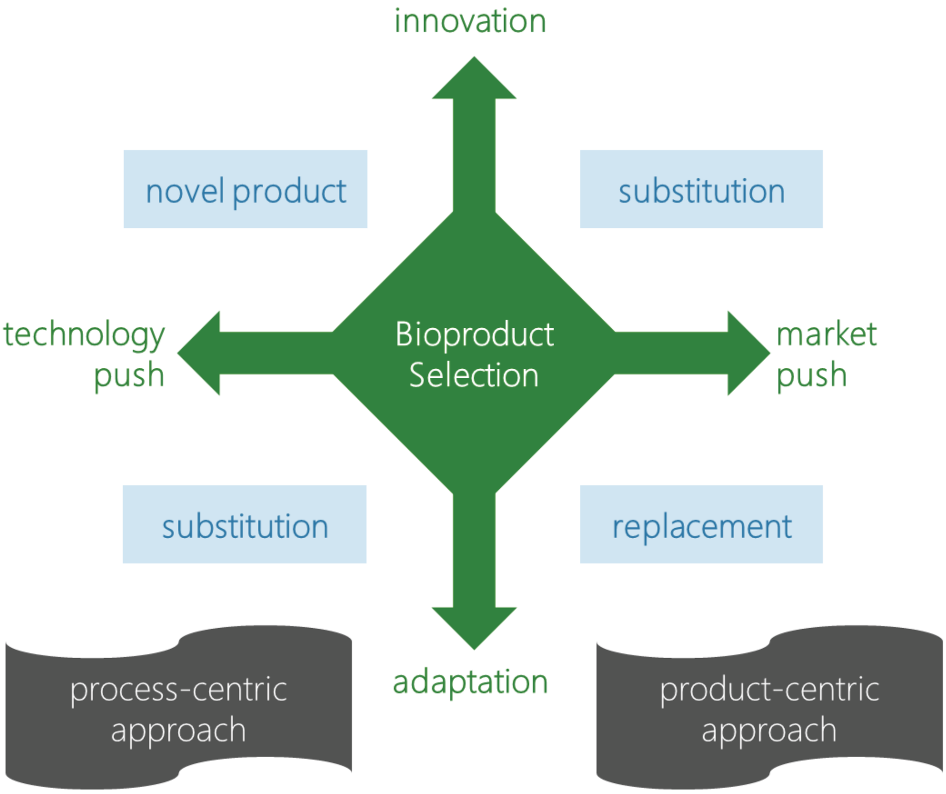


Figure 5-1 Process-centric and product-centric approaches for the selection of products adapted from Batsy et al. (2013) and Chambost et al. (2008)

This project uses a combination of both approaches to identify products for the wastewater biorefinery, as advised by Chambost et al. (2008). This dual approach asks the two questions, "What can we make?" and "What can we sell?" It has also been outlined through the previous work of the CeBER research group (Verster et al. 2014; Harrison et al. 2016; Harrison et al. 2017). The suitability of the feedstock for conversion, the market pull of the product, the positioning of the company implementing the biorefinery, and the technical readiness of the process are considered in concert.

In the wastewater biorefinery, feedstock suitability is the essential criterion on which the design is built (Harrison et al. 2017). Both the feedstock and the requirements of the wastewater biorefinery for feasible operation may impose constraints on product selection. Harrison et al. (2017) propose a decision-making matrix (Figure 5-2) for the selection of suitable bioreactors for the wastewater biorefinery; this can then inform the product selection process. This is important to integrate the essential features of bioreactors designed for wastewater treatment with those of conventional bioreactors designed for product formation. Traditional wastewater treatment bioreactors are mostly suited for nutrient removal and not designed for product formation. Conversely, bioreactors used for intensive bioproduct formation are not typically designed to handle dilute or complex feedstocks. Through the selection of appropriate bioreactors, according to Figure 5-2, the suitability of these reactors for selection of academic guidance on product selection can be ensured.

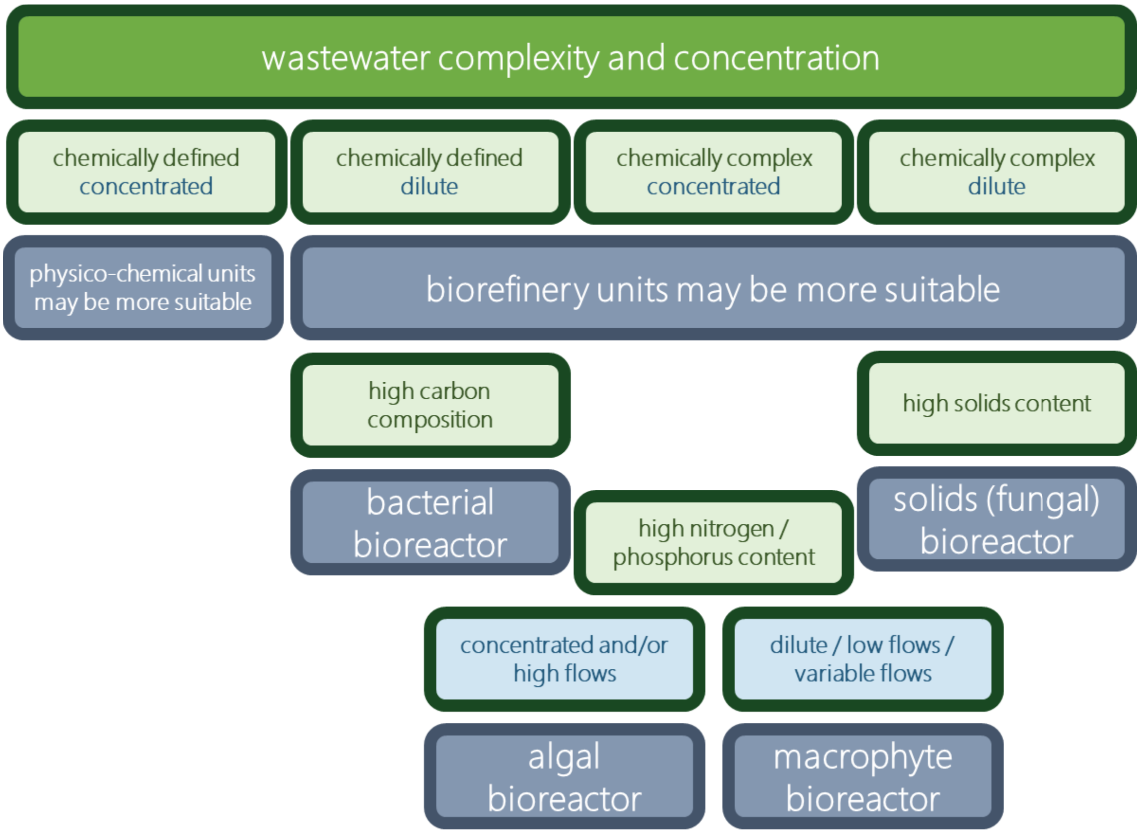


Figure 5-2 Decision-making matrix to guide the selection of priority bioreactors for the wastewater biorefinery (Harrison et al. 2017)

Methods for bioproduct selection have been proposed by various researchers, including Landucci et al. (1994), Moncada et al. (2013), Ng et al. (2009), Pham and El-Halwagi (2012), Harrison et al. (2016) and Zondervan et al. (2011). For the purposes of this project, we discuss the following methods in detail: the National Renewable Energy Laboratory (NREL) method (Werpy and Petersen, 2004a; Holladay et al. 2007), the Landucci method (Landucci et al. 1994), the multi-criteria decision making (MCDM) method; Harrison et al. 2016).

5.3.1 National Renewable Energy Laboratory method–U. S centric

A common methodology used is the process-driven selection developed by Werpy and Petersen (2004a) at the National Renewable Energy Laboratory (NREL) to identify the top value-added chemicals produced from biomass using biological or chemical conversion routes. In this method, the following information is assessed when screening for products:

i. Preliminary economic and technical criteria
ii. Chemical functionality and technical screening
iii. Technical barriers based on the best available technical pathways
iv. Potential for each building block chemical to produce a range of derivatives

The NREL method focused on identifying 12 top products with clear market potential for the building blocks and their derivatives, as well as the technical complexity of their synthesis pathways. The authors started with a list of over 300 products and used a biorefinery fit criteria (Table 5-2) as an initial screening to narrow down to 50 products, which was further organised using their carbon number (C1–C6). Each candidate was once more evaluated using the biorefinery strategic fit criteria for chemical functionality and potential use, with chemical functionality being based on the number of potential derivatives that can be synthesised in chemical and biological transformations (Werpy and Petersen, 2004b). Each product was then screened on two more criteria–(i) their ability to serve as a simple intermediate in traditional chemical processing, as a reagent molecule for additional functionality to hydrocarbons, or as by-products from petrochemical syntheses (ii) their potential status as a super commodity chemical, which is derived from building block chemicals or are co-products in petrochemical refining. While biomass can be used as a source for these super commodity chemicals, the economic challenges of large capital investments and the low market price of their non-biomass competitors would be difficult to overcome (Werpy and Petersen, 2004b).

Thus, the list of 50 products was reduced to 30 products which 1) exhibited multiple functionalities suitable for further conversion as derivatives or molecular families, 2) could be produced from both lignocellulosics and starch, 3) were C1–C6 monomers, 4) were not aromatics derived from lignin, and 5) were not already super commodity chemicals (Werpy and Petersen, 2004b). A second round of selection was then performed to further narrow down the list of 30 to 12 sugar-derived building blocks.

Table 5-2 Biorefinery strategy fit criteria adapted from Werpy and Petersen (2004b)

	Direct product replacement	Novel products	Building block intermediates
Characteristics	Competes directly against existing products and chemicals derived from petroleum	Possesses new and improved properties for replacement of existing functionality or new applications	Provide a basis for a diverse portfolio of products from a single intermediate
Examples	Acrylic acid obtained from either propylene or lactic acid	Polylactic acid (glucose via lactic acid is the sole viable source)	Succinic, levulinic, glutamic acids, glycerol, syngas
Upside	- Markets already exist - Cost structures and growth potential are well understood	- Novel products with unique properties - No competitive petroleum routes - Differentiation is usually based on the desired performance - New market opportunities - Most effective use of properties inherent in biomass	- Product swing strategies can be employed to reduce market risks - Market potential is expanded - Capital investments can be spread across wider unit operations - Incorporates advantages of both replacement and novel products
Downside	- Strictly competing on cost - Competing against depreciated capital - Limited green label; “market differentiation” for bio-based vs petrochemical based sources	- Market not clearly defined - Capital risk is high - Time to commercialisation is an issue	- Identifying where to focus R&D

The NREL method was further adapted by the Pacific Northwest National Laboratory (PNNL) to identify the potential of lignin by-products (Holladay et al. 2007). Biddy et al. (2016a) extended this by publishing a report on the market assessment of bioproducts with high potential for commercialisation via biochemical, thermochemical and algal processing routes by focusing on 12 chemicals. The criteria by which the products were assessed are shown in Table 5-2. While this list was built up on the previous studies of Holladay et al. (2007) and Werpy and Petersen (2004), some criteria were added by Biddy et al. (2016a). These include the possible integration in hydrocarbon pathways and the inclusion of funding opportunities that can drive market penetration using the factors shown in Table 5-3.

Table 5-3 List of factors considered by Biddy et al. (2016a) to investigate the market potential and successful near-deployment of bioproducts

1) Sufficiently high market volume and value (greater than fuel). Both domestic and global market share and growth potential were evaluated for each bioproduct
2) A well-established and mature market to facilitate near-term deployment. Platform chemicals were considered advantageous as there was potential for a greater market development
3) Feedstock flexibility
4) Potential to be integrated with representative hydrocarbon conversion pathways supported by the U. S Department of Energy (DOE) Bioenergy Technologies Office (BETO) program
5) Ongoing or prior support for research and development of each of the products from the DOE, which was considered favourable since many of these projects focused on lignocellulosic feedstocks
6) Avoidance of products that would be in competition with natural gas-derived petrochemicals. Inexpensive natural gas in the United States has changed the chemicals market, as it has greatly reduced the cost and increased the production of a number of petrochemicals. Any bioproduct that directly competes with natural gas-derived chemicals would be disadvantaged
7) Chemicals that could be made at a lower cost from biomass versus petroleum were deemed to have a favourable bioprocess advantage

5.3.2 Landucci method

Landucci et al. (1994) put together an iterative screening method to select promising products which can be produced biologically. In this, they compare the biological and conventional processing routes of the given products. It is noted that their methodology did not stem from a biorefinery constraint in which the feedstock is specified. Further, their work precedes the prioritisation of bio-based products for the green economy. They described their screening as a forecasting methodology since they explore the products' market potential for near-term (0–5 years), mid-term (5–10 years) or long-term (10 + years). This methodology comprises five stages:

Phase 1: Portfolio selection
Phase 2: Initial economic screening
Phase 3: Comparative analysis
Phase 4: Qualitative analysis
Phase 5: Detailed economic analysis

Phase one, centred on product selection, allows for the selection of products which demonstrate high theoretical yields from available substrates and have a market interest. Phase one targets products that can be produced in high volumes with non-food uses and are preferably produced from the common sugars derived from biomass. Phase two ranks the products on economic criteria. Landucci et al. (1994) used the Fraction of Revenue for Feedstock (FRF), which is the ratio of the cost of the feedstock to the value of the derived products. Phase three compares the petroleum processing route to the bioprocessing route based on a raw material cost ratio (RMCR). Equations for the FRF and RMCR can be found in the Landucci et al. (1994) study. The rationale behind comparing raw materials is that 50% to 90% of production costs for commodity chemicals and bioenergy products are typically attributed to raw material costs (Landucci et al. 1994). The risk factor is added to address possible barriers or hindrances for the emerging bioprocessing routes compared to the established and optimised petrochemical routes. Qualitative analysis is performed in phase four (Landucci et al. 1994) when expert opinions are sought and weighed, investigating the products in three categories–energy impacts, environmental quality and economic competitiveness. The final phase, phase five, comprises a detailed techno-economic analysis of the products, which the preceding four phases reveal as having the greatest potential (Landucci et al. 1994).

It should be noted that the phases introduced by Landucci et al. (1994) do not take into account the value and associated niche of the novel product category. Harding and Harrison (2016a, 2016b) developed an early design stage framework, the CeBER Bioprocess Modeller, for developing process material and energy inventories early in their design from which both techno-economic analysis (de Beer, 2010) and environmental analyses (Harding et al. 2007, 2008, 2018) can be performed. The CeBER Bioprocess Modeller has the potential to provide value in the product identification phase of the wastewater biorefinery.

5.3.3 Multi-criteria decision-making method

Janssen and Stuart (2010) suggest the use of multi-criteria decision making (MCDM) to examine different sets of biorefinery configurations and select the most sustainable in terms of products and technology. An example of how MCDM can be helpful in selecting promising options for waste management in the pulp and paper industry can be seen in the work of Eikelboomet al. (2018) and Azagele (2018). Eikelboomet al. (2018) proposed a multi-criteria decision analysis to identify the most appropriate management alternatives for the anaerobically digested kraft pulp mill sludge. The rationale behind this investigation was the comparison of different recycling options for the digested sludge and to assess each option in three main categories: environmental, economic and technical. These categories were further broken down into several decision criteria each (Eikelboom et al. 2018):

- *Environmental*–CO_2 emission, exposure to pathogens, risk of pollution, material and energy recovery
- *Economic*–overall costs, the value of products
- *Technical*–maintenance and operation, the feasibility of implementation

While not considered by Eikelboom et al., a '*societal'* category is important, especially in developing countries such as South Africa. Each criterion was then given a different weighting factor to differentiate the levels of importance in the final decision making. It must be noted that the relevant weightings of these criteria are likely to vary across the category of application. For example, the feasibility of implementation was given the highest weighting since it represents the ease with which an alternate process option for the digested sludge can be integrated into current industry practices. The total weighted value for each alternative was then computed, with the highest sum giving the best alternative.

A similar approach has been used in the Centre for Bioprocess Engineering Research in evaluating the valorisation of pyrite-containing mine wastes (Stander et al. in prep). Following a brainstorming of possible products and their feed requirements, the flowsheets were generated for promising products. These were then evaluated against a matrix of criteria located in the four categories environmental, technical, economic and societal. This rating was further informed through a ranking exercise with industry experts. The joint analysis of the outcomes led to the detailed investigation of the three most promising products for final selection.

This approach can be used as an additional decision-making criterion for the selection of products for the pulp and paper wastewater biorefinery after the initial product screening. It enables the comparison of traditional wastewater treatment with chosen value-added process alternatives for the pulp and paper wastewater biorefinery.

5.3.4 Contextualising for South Africa: Harrison et al. (2016)

Harrison et al. (2016) extended their list of candidate products to include platform chemicals, fine chemicals, biopolymers, biosurfactants, biolubricants, biofuels, nutraceuticals, pigments, enzymes, animal feeds and fertiliser and added some criteria not emphasised in the selection processes presented so far - South African market demands and expert opinion, main constraints and challenges preventing the valorisation of biomass. This enabled the prioritisation of the most promising 20 and 20 bioproducts in this context for South Africa. Three flagship projects were proposed for prioritisation in

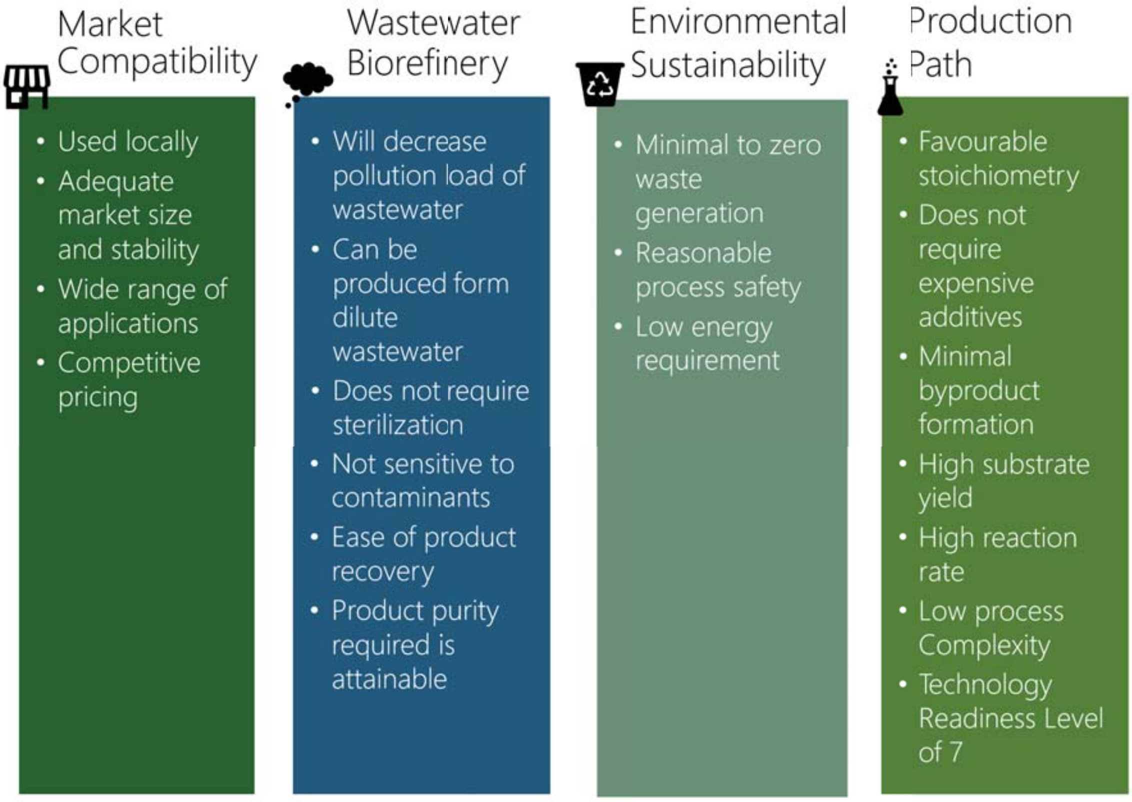
South Africa in a phased approach to operating across different scales, levels of technology and geographical locations with a focus on generating substantial job opportunities in the country:

1) Flagship 1: Biofuel, biopolymers and next-generation bio-based chemicals from biomass in South Africa
2) Flagship 2: Establishment of the algal product pipeline and biorefinery
3) Flagship 3: Novel bioactives from South Africa's biodiversity

A phased and incremental approach for each flagship project was detailed by Harrison et al. (2016) to ensure their successful uptake by the South African economy, together with possible funding possibilities. The need to upgrade South African skills in bioprocess engineering, industrial microbiology and bioentrepreneurship was emphasised.

5.4 Conceptualising a product selection guide for the pulp and paper wastewater biorefinery

By combining the requirements for these methods with those for the wastewater biorefinery set out in the 2017 report on the WRC project K5/2380 (Harrison et al. 2017), the selection method shown in Figure 5-3 has been developed. It can be applied to any wastewater stream to be valorised. It is important to mention here that this procedure is intended for the selection of the primary bioproduct to be produced in the wastewater biorefinery. Secondary products are chosen during the flowsheet development phase, where the choice of bioproduct is influenced by both the wastewater characterisation, particularly its nitrogen and phosphorus content, and the type of bioreactor selected to address the further treatment of the wastewater and to support the primary bioreactor. As an example, in the case of a pulp and paper wastewater biorefinery in which the lignocellulosic-containing wastewater stream is an important stream, a key focus in selecting the primary bioreactor and associated product is on removing the bulk of the lignocellulose contained in the wastewater. The lignocellulosic component has a high carbon content compared to the other main nutrients, nitrogen and phosphorous, and therefore a bacterial reactor, as defined in the WRC 2380 report conceptualising the wastewater biorefinery (Harrison et al. 2017), forms the primary reactor and only products that can be made from lignocellulose are considered at this stage. The selection method is qualitative and consists of four main hurdles that the product being considered needs to "jump" before being subjected to quantitative analyses. These four hurdles are market compatibility, wastewater biorefinery requirements, environmental sustainability and production path. There is no prescribed order for the evaluation, and it is at the discretion of the user.



Market Compatibility

- Used locally
- Adequate market size and stability
- Wide range of applications
- Competitive pricing

Wastewater Biorefinery

- Will decrease pollution load of wastewater
- Can be produced form dilute wastewater
- Does not require sterilization
- Not sensitive to contaminants
- Ease of product recovery
- Product purity required is attainable

Environmental Sustainability

- Minimal to zero waste generation
- Reasonable process safety
- Low energy requirement

Production Path

- Favourable stoichiometry
- Does not require expensive additives
- Minimal byproduct formation
- High substrate yield
- High reaction rate
- Low process Complexity
- Technology Readiness Level of 7

Figure 5-3 Product selection guide for a PULP AND PAPER WASTEWATER BIOREFINERY

5.4.1 Market compatibility factors

5.4.1.1 Market demand

Ideal products have a market demand within the industrial sector, preferably at the site from which the wastewater comes (Verster et al. 2013). The global market demand for a product needs to be considered, but the local market is of greater importance. To ensure that there will be a continuous demand to meet the supply, a product that has a wide application portfolio is preferred. An example of this would be to choose a platform chemical which can be used as a feedstock to produce other chemicals rather than a speciality chemical with a very specific market. The more markets into which the product can feed, the better in terms of profit stability.

5.4.1.2 Market price

For a specific product, the market trend and not just the market value must be considered since choosing a product for which the market is volatile or not well established incurs a larger risk for the project. The market price of a product will always be linked to non-process factors, including the price of competing products and the price of the traditional raw material feedstock. An example of this is the selling price of ethanol which is influenced by the oil price and the price of corn and sugar. Lactic acid is another example, where the price is closely related to the price of sugar (Biddy et al. 2016), which is used as the substrate during its fermentative production.

Product prices might also be sensitive to other variables, for example, the impact weather has on the ethanol price since its volatile and corrosive nature necessitates transport in tanks instead of pipelines (futuresknowledge.com, 2015). One would prefer a product that has a more stable market and price structure; however, should this prove to be a problem, it may be overcome by learning about what affects the market and then adjusting for it in the feasibility study.

5.4.2 Wastewater biorefinery factors

The defining characteristic of a wastewater biorefinery is that it has the dual objective of the production of fit-for-purpose water *and* the bioproduction of other valuable products (Harrison et al. 2017).

Secondly, in the wastewater biorefinery, wastewater is the feedstock with concomitant restrictions in terms of composition, including variability and concentration (Johnstone-Robertson, 2016). A wastewater biorefinery is designed to operate using a particular waste feedstock, and the nature of this waste stream is a crucial factor in bioproduct selection. This runs counter to the first phase proposed by Landucci et al. (1994) for general biorefineries, which focuses on theoretical yield and market interest.

Wastewater as feedstock is of special interest for products for which the feedstock contributes substantially to the operating costs.

However, it must be possible to maintain productivity under the constraints associated with wastewater feed. Therefore, a consideration in product choice is the preference for a process that does not require sterilisation of the feed since this is impractical and costly with the typically large flow rates. The dilute nature of the feedstock makes energy-intensive production processes uneconomical. The purity required of the product should be attainable with minimal downstream processing suggesting ready phase separation with a minimum of additives. Product purity requirements cannot be stringent due to wastewater potentially including contaminants, which suggests that bioproducts used for human consumption be avoided or, at least, considered with due care.

To lessen the economic stress of diversifying the product portfolio of the plant, it is suggested that products for use on-site be given preference in the selection step. By using a product made by the wastewater biorefinery within the wastewater biorefinery or associated plant, a cost-saving is achieved from not having to purchase the compound without adding marketing and product management requirements to the business.

5.4.3 Environmental sustainability factors

In product selection, all aspects of the environmental impact of the wastewater biorefinery process must be addressed since they challenge the foundational rationale for the implementation of a wastewater biorefinery (Bardhan et al. 2015). The aim of a wastewater biorefinery is to improve the environmental sustainability of the parent facility; therefore, keeping the environmental impact of the processes to a minimum is critical. The primary product is responsible for the removal of the major contaminant in the wastewater; what should be kept in mind is that the contaminant is the substrate for the primary product, and therefore there is still a process to arrive at the final primary product to be marketed.

Products where the waste generated in production, including emissions to the atmosphere, additional contamination of effluent, and solid waste, is a minimum should be given preference in the selection procedure. Solid waste can be generated as a by-product of the reaction chemistry (such as salts) or can form a component removed during the separation and purification (such as bacterial biomass). There will be cases where the chosen product will meet all the requirements discussed earlier but fail at this stage. If so, before discarding the potential product, the choice of reactors and downstream processing trains can be re-evaluated against alternatives that generate less waste for the same product. Alternatively, the waste can be repurposed by using it as a feedstock to a secondary reactor within the wastewater biorefinery for the delivery of a second product. This will inform the development of the flowsheet for an integrated wastewater biorefinery.

In some cases, a product may require process steps that carry a high risk to the safety of the persons in and around the facility. These risks require careful consideration since the implementation of the correct safety measures can incur extra costs both during the construction and operation of the plant. Using dangerous chemicals and operating at high temperatures and pressures should be avoided as far as possible. Substituting one technology for a safer technology may be the best option, even if it means the process cannot achieve the same product yield or production rate. In this regard, bioprocessing holds an advantage over processes such as pyrolysis and gasification in that the operating temperature and pressure of the bioreactors are much lower. Some physiochemical processes, such as acid hydrolysis, make use of strong acids, whereas enzymatic hydrolysis operates at a milder pH and temperature.

5.4.4 Production path factors

The production path has two aspects. At the core is process chemistry, which in turn defines the second aspect, namely, technology for the conversion of the feedstock to the desired product.

Process chemistry includes the reaction stoichiometry and rate, which determines the product yield, productivity and substrate conversion. This plays an important role in the decision-making process because if the reaction for the conversion of the substrate into a product diverts a part of the substrate to other by-products such as CO_2, it has far-reaching implications such as the generation of a waste stream and a decrease in product volumes, which affect the sustainability of the biorefinery. The reaction rate plays a significant role in the sizing of equipment in continuous production and the duration of a production cycle in batch processes. These design aspects determine the economic viability of the biorefinery. It can therefore be concluded that when a short list of products has been generated, the option with the highest reaction rate and most favourable reaction stoichiometry should be given preference to minimise the capital and operating expenditure of the biorefinery as well as to limit the generation of side streams that need further processing.

Two other considerations related to the process chemistry are any additives required and contaminants present, which may negatively influence the reaction rate and product yield. Additives, such as medium components or catalysts, can increase the operational costs quite substantially. A way in which this issue can be addressed is by careful consideration of which microorganism to use for the conversion of the substrate to the product. As an example, Table 5-4 compares *Bacillus* and *Lactobacillus*, two bacterial species, with *Rhizopus,* a type of fungus for the production of lactic acid. *Lactobacillus* has the advantage of being able to operate at a lower pH than *Bacillus*, but *Bacillus* can ferment the sugars at a higher temperature than *Lactobacillus* and *Rhizopus,* which can eliminate the need for sterile operation. *Rhizopus* holds the key benefit of not requiring complex media, which has an impact on the economics of the process. From this quick comparison, it can be seen that it is unlikely that one microorganism will be the better option in all aspects but that a compromise will have to be made. To assess the different organisms and associated processes, a more quantitative approach must be applied.

Table 5-4 A comparison of *Bacillus, Lactobacillus* and *Rhizopus* species for the production of lactic acid, adapted from Poudel et al. 2016)

• Bacillus	• Lactobacillus	• Rhizopus sp.
• Can grow in simple mineral salt media and a small amount of a complex nitrogen source such as yeast extract	• LAB require organic nitrogen sources that include amino acids, vitamins etc.	• Can grow in minimal salt media
• Optimum temperature for the production of lactic acid varies between 45-60 °C	• Most LAB have optimum lactic acid production between 30-43 °C	• Optimum temperature for lactic acid production is between 25 and 37 °C
• pH optimum between 5-9	• pH optimum between 4-7	• pH optimum at 5-6; some strains can go as low as 3. 5
• Facultatively anaerobes	• Facultatively anaerobes	• Obligatory aerobes
• Can ferment both hexoses and pentoses homofermentatively	• Can ferment both hexoses and pentoses, but not all strains do so homofermentatively	• Ferments hexoses and pentoses heterofermentatively

The second aspect relating to the production path is the choice of technology for the production of the potential product. The nature of the technology influences several factors in determining whether the product is suitable for a wastewater biorefinery. Examples include the ability to retain the microorganisms in the reactor handling large volumes of a diluted substrate as well as the need to minimise expensive separations from these large volumes. The stage of development of the technology is also a key consideration in technology selection and is considered in terms of technology readiness levels.

Technology Readiness Levels (TRL), a term that refers to the maturity of the technology, was originally developed by NASA and is now being used in decision-making processes within several industries related to science and engineering. Table 5-5 shows the definitions of the different levels of science and engineering as defined by the Research Contracts and Innovation department at the University of Cape Town.

Table 5-5 Technology readiness levels (TRL) definitions (http://www.rci.uct.ac.za/technology-readiness-levels)

TRL 1	**TRL 2**	**TRL 3**	**TRL 4**	**TRL 5**	**TRL 6**	**TRL 7**	**TRL 8**	**TRL 9**
Basic idea	Concept developed	Experimental proof of concept	Lab demonstration	Lab scale validation	Prototype demonstration	Pilot scale	Commercial design	Ready for full deployment

A high TRL, preferably of seven or above (Harrison et al. 2016), is desirable for implementation into the wastewater biorefinery. The main reason for this is that a product with a TRL of seven has been researched to a point where profitable operation is likely to be possible. Should one choose a product at lower TRL, significant development must be factored in with associated R&D costs and potential delay of the implementation of the wastewater biorefinery. In addition, some R&D work will be required to ‘prove’ the technology for use with the specific waste stream to optimise the process flowsheet and its profitability. It must be kept in mind that some products may have been proven economically feasible at a commercial scale when produced from a pure substrate, but that does not automatically qualify its production from waste material due to the unique challenges associated with the preparation of waste. These issues are what lies at the core of making the wastewater biorefinery a success, both in terms of treatment of wastewater and bioproduction.

Finally, a key consideration for choosing a product is the complexity of the production process associated with it. It should be kept in mind that the wastewater biorefinery is often an addition to an already operational facility and is, therefore, not the primary focus of the company. Incorporating complex technologies that require continuous monitoring and control may expose the company to more risks. As a result, it is important for the wastewater biorefinery to provide distinct benefits as an alternative to current wastewater disposal methods in order to motivate its implementation.

5.5 The foundational wastewater biorefinery product portfolio

The motivation behind the qualitative screening method, presented in Figure 5-3, is to enable the investigator to consider an overview of the multiple parts involved in making a wastewater biorefinery work for the parent facility. The interactions between the different considerations are represented in Figure 5-4, showing the interdependence of key factors. Factors that play a large role in the optimisation of the WWBR include the dilute nature of the wastewater, the downstream processing and by-product generation. When working through the suggested criteria, the amount of information that needs to be gathered to inform the decision can become substantive. It is suggested that experts in the field of the different chemical groupings be involved to speed up the process, and seminal review articles may prove useful for comparing different products that are closely related.

Figure 5-4 Chord diagram showing the interdependent nature of the considerations that form part of the decision-making process

Discernment should be exercised when eliminating contenders from the final shortlist of potential primary products; in the face of uncertainty, it can be advisable to retain a potential product for further investigation rather than excluding it too early.

Once the short list of potential primary products has been compiled, the next phase of the decision-making process explores the options from a more quantitative approach and includes the development of flowsheets using simulation software such as Superpro Designer and Aspen Plus. The level of detail on these flowsheets depends on the number of product options and the time available for this part of the selection process. Technical, economic, societal and environmental indicators need to be considered to assess and compare the sustainability attributes of the emerging flowsheets.

Part 2

Evaluating the potential for the valorisation of lignocellulosic-rich wastewater streams in wastewater biorefineries towards resource efficiency

6 Exploring Different Production Platforms To Establish Pulp And Paper Wastewater Biorefinery

6.1 Introduction to product platforms for a pulp and paper wastewater biorefinery, processing lignocellulosic-rich wastewaters

Pulp and paper wastewater effluent streams, suited for valorisation as identified in Chapter 4, contain a significant quantity of organic matter in the form of lignocellulosic material, which can be processed into value-added products. Lignocellulosic biomass can either be processed directly to biofuels and biochemicals or converted to intermediary compounds before being further processed into a range of bioproducts.

6.2 Processing lignocellulosic biomass directly

6.2.1 Thermochemical processes

Lignocellulosic biomass can be directly converted to heat, power and liquid fuels by various thermochemical processes, namely pyrolysis, liquefaction, co-firing, carbonisation and combustion (Patel et al. 2016). Pyrolysis decomposes lignocellulosic biomass at 300–800 °C in the absence of, or in the presence of very low, oxygen concentration. The main product of this reaction, bio-oil, can be upgraded into drop-in fuels like gasoline and diesel (Liu et al. 2020; Wang et al. 2020). Liquefaction, also termed hydrothermal liquefaction, uses water as a reactant and catalyst at high temperatures (250–374 °C) and pressures (4–22 MPa) to chemically convert lignocellulosic biomass into an oil product, which can also be used as fuel (Elliott et al. 2015; Patel et al. 2016). Co-firing of biomass is a low-cost technology where a primary fuel, such as coal, is partially substituted with a biomass source like lignocellulosic biomass in a high-efficiency boiler to produce electricity (Agbor et al. 2014; Patel et al. 2016). Carbonisation is an extension of the pyrolysis process, where biochar, a carbon-rich solid residue, is the main product (Strezov et al. 2007). It is important to note that biochar is also formed during pyrolysis and liquefaction (Liu and Yu, 2021). Biochar is commonly used as a soil conditioner, as insulation or as a catalyst (activated carbon) (Patel et al. 2016). Combustion is the simplest thermochemical process and takes place in the presence of air to convert lignocellulosic biomass into heat and power. Due to the emissions of NO_x, CO_2, particulate matter, and ash pose environmental concerns (Kumar et al. 2003).

6.2.2 Biological processes

Without decomposition, the structural composition of the biomass is not broken, and biological processes such as solid-sate and submerged fermentation can be used to yield products such as single-cell protein, enzymes and organic acids (Kumar et al. 2016).

Single-cell protein

The dried cells of microorganisms referred to as single-cell proteins (SCPs) are a natural source of proteins suited for food and feed purposes (Kurbanoglu and Algur, 2002). SCPs can come from various microorganisms such as algae, fungi, yeast and bacteria, with the yeast *Candida sp*. being one of the most widely used microorganisms (Adoki, 2002).

As reviewed by Suman et al.(2015), microbial production of SCPs has the added advantage of not being dependent on climatic conditions as compared to the production of animal and plant proteins. SCPs also have additional benefits, such as a wide amino acid spectrum, low-fat content, and good protein-carbohydrate ratio. A wide variety of waste substrates have been tested for SCP production, such as starch, molasses, vegetable wastes, petroleum by-products, ethanol, methanol and lignocellulosic biomass. The main characteristic of these substrates is the presence of mono and disaccharides since they can be digested by most microorganisms (Richmond, 2004).

SCPs may also be produced via solid-state fermentation, where the substrates are agitated with the microorganisms in the absence of water (Prabhakar et al. 2005; Yadav et al. 2014). Lignocellulosic biomass is a suitable substrate for SCP protein due to its cellulosic fraction, which the microorganism can use for growth (Yunus et al. 2015). Suman et al. (2015) listed sulphite waste liquor as another potential substrate to consider for SCP production.

Lignocellulolytic enzymes

Lignocellulolytic enzymes have applications in various industries (textile, food, animal feed, paper, biofuel, pharmaceutical) due to the ability to actively degrade lignocellulosic substrates, and are expected to have an estimated market of $ 7. 0 billion by 2023 (Toushik et al. 2017; Saldarriaga-Hernández et al. 2020). Using lignocellulosic wastes as substrates can effectively lower the cost of production of lignocellulolytic enzymes by replacing pure and expensive raw materials (Klein-Marcuschamer et al. 2012).

The enzymes can be extracted by in situ recovery of aqueous solutions in SSF bioreactors and through a series of downstream processing units, including filtration to remove the fermented solid, ultrafiltration to remove the microorganisms and a concentration step to obtain the enzyme as a dry solid. Common enzymes which are produced via SSF using fungi or bacteria are xylanases, cellulases, laccases and lignin peroxidases (Catalán and Sánchez, 2020). Interestingly, in **the pulp and paper industry**, a mixture of lignocellulolytic enzymes can be used in the biopulping of lignocellulosic material to produce paper (Singh et al. 2013)

Organic acids

Volatile fatty acids (VFAs) such as acetic acid, propionic acid and butyric acid are used as building blocks to manufacture a variety of chemicals with various industrial applications (Baumann and Westermann, 2016). VFAs are natural intermediates of major metabolic pathways of microorganisms, and while they have been produced commercially by chemical synthesis and biological fermentation, their production via SSF has been investigated and demonstrated in recent years due to the possibility of obtaining high VFA concentrations using low-cost substrates such as lignocellulosic biomass (Sauer et al. 2008; Yazid et al. 2017).

6.3 Processing lignocellulosic biomass through intermediary compounds

There are two fundamental ways in which lignocellulosic biomass can be decomposed, as seen in Figure 6-1. (i) It can be completely decomposed to synthesis gas (syngas) by high temperatures through gasification processes (a thermochemical process) and subsequently converted into fuels and chemicals (Dahmen et al. 2017). (ii) It can be separated into cellulose, hemicellulose and lignin, which can be further converted to biofuels, bio-based chemicals and bio-based materials (Harmsen and Hackmann, 2013; Brodin et al. 2017; Lask et al. 2019). The different characteristics of the two processing routes are highlighted in Table 6-1. The list of products which can be synthesised from both processing routes is explored in subsequent sections.

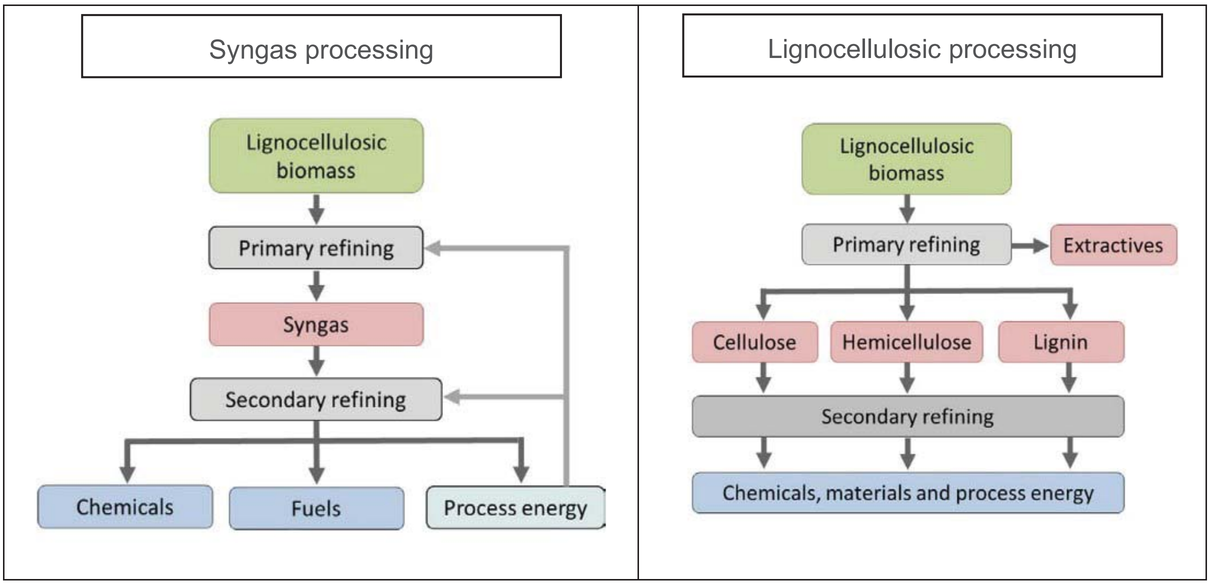


Figure 6-1 Processing routes for lignocellulosic biomass adapted from Dahmen et al. (2018)

Table 6-1 Characteristics of syngas and lignocellulosic processing compiled by Dahmen et al. (2018)

• **Syngas processing**	• **Lignocellulosic processing**
• Complete decomposition of biomass into C1 units (CO) and hydrogen • High conversion temperatures • High feedstock flexibility • A single, defined intermediate after gas cleaning • Products are hydrogen, hydrocarbon fuels and methanol and its derivatives. Heat and electricity are desired, unavoidable products • Complex high-temperature technology requiring large-scale operation for economic application • Requires infrastructure for long-distance biomass logistics • Process energy is an inevitable by-product of heat recovery from the high-temperature gasification process •	• Decomposition into natural intermediate units, for example, carbohydrates and aromatics • Lower conversion temperatures • Lower feedstock flexibility, parameters need to be adapted to the feedstock • A number of intermediates at the same time • Products are platform molecules (C2-C4) from the microbial and enzymatic conversion of sugars, monomeric, oligomeric and polymeric bio-aromatic fractions (>C6) • Multistage process, parallel processing of biomass components • Can be built in modular form and close to the biomass source.

6.3.1 Syngas processing

Gasification takes place inside a reactor, commonly called a gasifier, which operates at high temperatures (800–1500°C). Oxygen is supplied in low concentrations by a gasifying agent, such as air, pure oxygen, water steam or a mixture thereof, to partially oxidise the feedstock. Unlike biological or chemical hydrolysis employed in lignocellulosic processing, gasification can convert the entire carbon content in the lignocellulosic biomass into gaseous compounds (Kennes et al. 2016; Ciliberti et al. 2020).

The resulting syngas can be used directly as a combustion fuel in power plants for heat and power production. However, syngas can also be used as a platform chemical to produce a range of gaseous and liquid fuels, as well as chemicals. Common examples of syngas-derived products are methanol, ethanol, dimethyl ethylene, propylene, ammonia, hydrogen, gasoline, liquefied petroleum gas (LPG), diesel, bio oil, diesel, electricity, and naphtha (Patel et al. 2016). Methanol and ethanol can be used as platform chemicals for the production of additional higher value-added products.

6.3.2 Lignocellulosic processing (with a focus on holocellulose)

Lignocellulosic material can be converted to a greater variety of products if adequate production pathways are identified to facilitate the integral use of the lignocellulosic components to obtain energy, chemicals and products (Moreno and Olsson, 2017). Chakraborty et al. (2019) estimate that only between 30 - 50% of organic matter contributing to COD in pulp and paper effluent streams is considered easily biodegradable. To ensure that the value of this organic matter is fully utilised and, consequently, the downstream conversion into biochemicals made feasible, more organic material must be made available for conversion. This necessitates the implementation of pre-treatment methods to decompose the lignocellulosic biomass.

Factors affecting the recalcitrant nature of lignocellulose are either direct (accessible surface area) or indirect. Pre-treatment is aimed at reducing the effect of indirect factors on the enzymatic digestibility of lignocellulose. These indirect factors include (Zhao et al. 2012):

- Biomass structure factors (pore size and volume, particle size, specific surface area)
- Chemical composition (lignin, hemicelluloses, acetyl groups)
- Cellulose structure factors (crystallinity and degree of polymerisation)

Zhao et al. (2012) report that the overall aims of pre-treatment can be summarised as follows:

- Facilitate the removal and separation of hemicellulose from cellulose
- Disrupt the lignin components in the cell wall to remove the barrier to cellulose
- Remove acetyl groups to minimise interference with enzyme performance
- Reduce the crystallinity and degree of polymerisation of cellulose
- Ensure that the specific surface area of substrates is increased (decrease particle size/ increase porosity) for facilitating action by hydrolysing agents

Kucharska et al. (2018), Chakraborty et al. (2019) and Clarkson (2018) all note that pre-treatment methods can be classified into four groups, namely: physical, chemical, physicochemical and biological methods. Combinations of multiple pre-treatment methods may be applied, and pre-treatment methods may vary depending on the effluent stream characteristics (Chakraborty et al. 2019). However, costs associated with pre-treatment are high, amounting to approximately 40% of the total cost of biomass processing (Kucharska et al. 2018). Summarised in Table 6-2 are various pre-treatment methods discussed in Kucharska et al. (2018), Chakraborty et al. (2019) and Clarkson (2018) and Zhao et al. (2012).

Physical pre-treatment methods involve the reduction in particle size, which consequently decreases cellulose crystallinity and increases surface area. Zhao et al. (2012) note that physicochemical pre-treatment methods, which combine physical and chemical methods, are some of the most promising pre-treatments to be employed. Furthermore, a steam explosion which increases cellulose digestibility has the ability to hydrolyse more than 90% of hemicellulose and redistribute lignin (Zhao et al. 2012). In contrast to this, Clarkson (2018) argues that organic solvents and ionic liquids are favourable pre-treatment methods given the ease with which the solvents can be recovered, the ability to separate high-quality lignin, and the low generation of inhibitory compounds. The major drawback of implementation is that they are expensive (Clarkson, 2018).

In reviewing the challenges with chemical pre-treatment, Clarkson (2018) found that while previous studies show acidic and alkaline treatments to be effective in the delignification and recovery of hemicellulose and cellulose, both treatments are disadvantaged by the destruction of lignin. Acidic treatments are less effective than alkali treatments and result in the generation of refractory organic compounds. Alkali treatments suffer from an accumulation of salts and an increase in digestate pH, while acidic treatments are characterised by low substrate pH. these characteristics are considered detrimental to biological processes (Clarkson, 2018).

Microorganisms suitable to be used for biological pre-treatment of organic matter must be able to produce lignocellulosic compound-degrading enzymes. Chakraborty et al. (2019) also suggest laccase enzyme producers, currently used for biobleaching, could be considered as they are able to remove toxic substances. Microbial pre-treatments tend to be very slow owing to the high tensile strength of intermolecular bonds within cellulose. To increase the efficiency of microbial pre-treatments, Chakraborty et al. (2019) suggest that prior enzyme treatments using xylanases, laccases, or cellulases may be advantageous.

Another challenge which arises during pre-treatment processes is the formation of lignocellulosic biomass-derived compounds, which tend to have an inhibitory effect on enzymes and microorganisms, affecting the sugar yield during the subsequent hydrolysis of hemicellulose and cellulose after the pre-treatment step (Branco et al. 2019). These inhibitors are similar to the compounds mentioned in Section 0 and include the following:

- Furans such as furfural and HMF (5-hydroxymethyl-2-furaldehyde) from the degradation of hexoses and pentoses, which can be further degraded to formic and levulinic acid
- Acetic acid originating from hemicelluloses
- Phenolic compounds from lignin degradation

There are several detoxification technologies which have been studied to remove these inhibitors, but they represent an additional cost to the pre-treatment step. Table 6-3 presents some of the common detoxification methods employed with their target inhibitors, advantages and disadvantages. If detoxification steps are not used, alternate strategies must be used to reduce or at least mitigate the effects of inhibitory compounds. One possibility is to use a lignocellulosic feed which is lower in lignin content. Alternatively, a careful selection of microorganisms which are resistant to inhibitors can be used. Genetic and metabolic engineering is another avenue which can be investigated (Jönsson and Martín, 2016; Kim, 2018)

Table 6-2 Summary of pre-treatment methods for lignocellulosic biomass

Method	Type of Pre-treatment	Mechanism of Action	References
Physical	Fragmentation	Breaks lignocellulose into smaller parts	[2]
		↑Accessibility of COD for biodegradation	[2]
	Sedimentation	Remove suspended solids	[6]
		Up to 80% SS removal	[5]
		No BOD removal	[5]
	Microwave radiation	Reduces crystallinity of cellulose	[1]
	Sonication and Electrohydrolysis	Hydrogen bonds in complex lignocellulose structures are broken	[1]
		↓Cellulose crystallinity and ↓degree of polymerisation	[2]
	Pyrolysis	Results in the carbonisation of cellulose. (T>300^{o}C)	[1]
	Ultrafiltration	Removes suspended solids, bacteria and pathogens	[4]
	Thermal treatments	Solubilisation of biomass sludge	[2]
Chemical	Acidic	Delignification and recovery of cellulose and hemicellulose	[3]
	Alkaline	Delignification; Recovery of cellulose and hemicellulose	[3]
	Oxidation	Dissolution of lignin and hemicellulose	[1]
		Advanced Oxidation Processes (AOPS): ↑biodegradability and decomposing bio-refractory compounds	
	Ozonation	Dissolution of lignin and hemicellulose	
	Ionic Liquids	Separates cellulose from lignocellulose	[1]
		↓crystallinity; ↓lignin content; ↑ surface area	[3]
	Solvents	Dissolution of lignin, breaking of hemicellulose bonds	[1]
Physicochemical	Steam and Carbon dioxide Explosion	Steam: dissolution of hemicellulose (150^{o}C) and lignin (>180^{o}C)	[1]
		Carbon dioxide: decomposition of lignin and hemicellulose	[1]
	Ammonia Fibre Expansion (AFEX)	Destruction of lignin and partially hemicellulose	[1]
Biological	Fungi (White, Brown and Soft rot)	Decomposition of hemicellulose and lignin	[1]
	Enzymatic	Faster than microbial; Decomposition of hemicellulose and lignin	[1], [2]

[1]:(Kucharska et al. 2018); [2]: (Chakraborty et al. 2019); [3]:(Clarkson, 2018); [4]:(Oliveira et al. 2007); [5]: (Samer, 2015); [6]: (Ashra et al. 2015)

Table 6-3 Common physico-chemical detoxification methods for lignocellulosic-derived materials (Coz et al. 2016)

Method	Characteristics	Inhibitors	Advantages	Disadvantages
Vacuum evaporation	• Reduce volatile compounds • No previous over-liming or neutralisation is recommended • Optimisation for pentoses in relation to hexoses, depending on the lignocellulosic material, is needed	Acids and furans	• Lower losses of sugars	• Not good for phenolics
Liming and over-liming	• Precipitate toxic compounds with alkali treatment • The use of $Ca(OH)_2$ is recommended • Optimisation of time and pH to compromise inhibitors • Removal and losses of sugars needed	Levulinic acids, furans	• Some phenolics can also be removed • Cheapest option • No high temperature is necessary	• Not good for acetic acid, depending on the material • Sometimes, high losses of sugars
Adsorption	• Separation of substances with an adsorbent • Activated charcoal is the most common sorbent; however, to reduce the losses of sugars, other sorbents can be used • Optimisation of the initial pH is necessary	Levulinic acids, furans, phenolics	• No high temperature • Ease of regeneration and valorisation options	• High losses of sugars in some cases • Costs of resins
Ion exchange resins	• Separation of substances by ion exchange • Both anionic and cationic are recommended to remove all of the inhibitors • Optimisation of the initial pH in the case of acids • And furans	Acids, furans, phenolics, heavy metals	• Removal of all of the inhibitors • Ease of regeneration and valorisation options	• High losses of sugars in some cases • Costs of the resins
Liquid-liquid extraction	• Ethyl acetate and trialkyl amine for furans and phenolics • Trialkyl amine and trichloroethylene for acids • Cloud point extraction in the case of phenolics	Levulinic acids, furans, phenolics	• Ease of regeneration and valorisation options	• Organic solvent management
Filtration by membrane operations	• Microfiltration, nanofiltration, and ultrafiltration • Previous pre-treatment to reduce the fouling	Lignin compounds	• Easy separation and valorisation options	• Fouling problems • Optimisation of the sugar losses is needed

Once the lignocellulosic biomass is pre-treated and detoxified, with most of the lignin and extractive compounds removed, the next step is to convert the cellulose and hemicelluloses to their monomers, C5 and C6 fermentable sugars, which can be done either biologically (enzymatic hydrolysis) or chemically (acidic hydrolysis) (Haldar et al. 2016; Kuila et al. 2016).

Table 6-4 lists the different techniques commonly used for hydrolysis. One major challenge lies in the efficient and low-energy production of these sugars (Isikgor and Becer, 2015). According to Zviely (2013), hydrolysis by HCl is the most industrially-proven process for conversion of lignocellulose to C5 and C6 sugars, but recovery of the acid still remains a challenge, together with low sugar yields. While enzymatic hydrolysis happens under milder conditions, the reaction is slower, and the costs of the enzymes are high (Branco et al. 2019).

During hydrolysis, cellulose can be degraded to glucose (C6), while hemicellulose can be broken down into both C6 sugars (glucose, mannose, galactose, rhamnose) and C5 sugars (xylose, arabinose). Once the lignocellulosic biomass has been hydrolysed, a wide range of products can be synthesised by the hydrolysed components, as depicted in Figure 6-2.

Table 6-4 Overview of different hydrolysis pathways with their advantages and disadvantages (Branco et al. 2019)

Hydrolysis	**Concentrated acid**	**Diluted acid**	**Enzymatic**
Hydrolysis agent	30–70% H_2SO_4/HCL	2–5% H_2SO_4/HCL	Cellulases and hemicellulases
Advantages	Low temperature High sugar yield	Low acid consumption	Mild conditions No inhibitors High sugar yield
Disadvantages	Large amounts of acids Equipment corrosion Environmental and cost issues	High temperatures Formation of inhibitors Low sugar yield	High cost Slow reactions

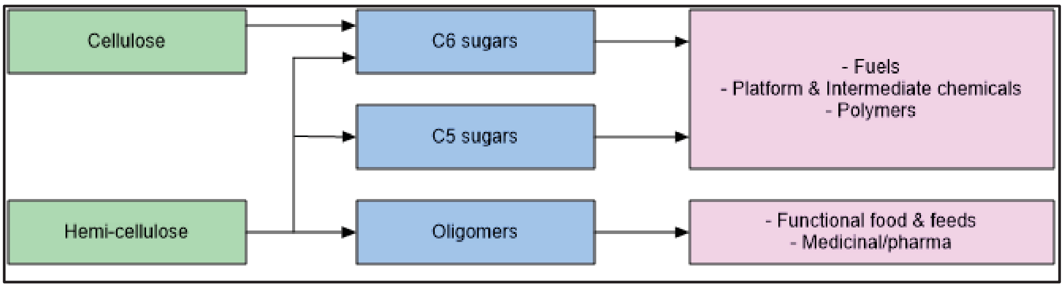


Figure 6-2 Overview of products derived from the components of lignocellulosic biomass adapted from Bevan (Bevan, 2013)

6.3.2.1 C5 and C6 Sugar platform

Cellulose and hemicellulose from lignocellulosic biomass can be used to produce a wide range of chemicals via the sugar production platform (Kobayashi and Fukuoka, 2013). Figure 6-3 illustrates the possible product pathways using the C5 and C6 platforms. Some of the first-level products can be categorised as platform chemicals and chemical building blocks, which can be further processed to give a wider range of value-added commodity products, highlighted by the ‘other chemicals’ in the second-level products block.

Table 6-5 highlights some promising chemicals which can be produced from lignocellulosic biomass via the C5 and C6 platforms. It is important to note that this list of chemicals is not exhaustive; rather, the studies short-listed promising candidates depending on their research focus and specific criteria selection. The extensive list of platform chemicals which can be synthesised via the C5/C6 sugars accentuates the resource potential of lignocellulosic biomass when it is pre-treated and hydrolysed. However, since the lignocellulosic biomass in the PPI is essentially a waste substrate, there are various technical, economic and environmental limitations which will dictate the feasibility of producing some of these platform chemicals in a pulp and paper wastewater biorefinery. Selected methods from Table 6-5 will be discussed in more detail in Chapter 7 as a basis for devising a methodology for selecting adequate products for a WWBR.

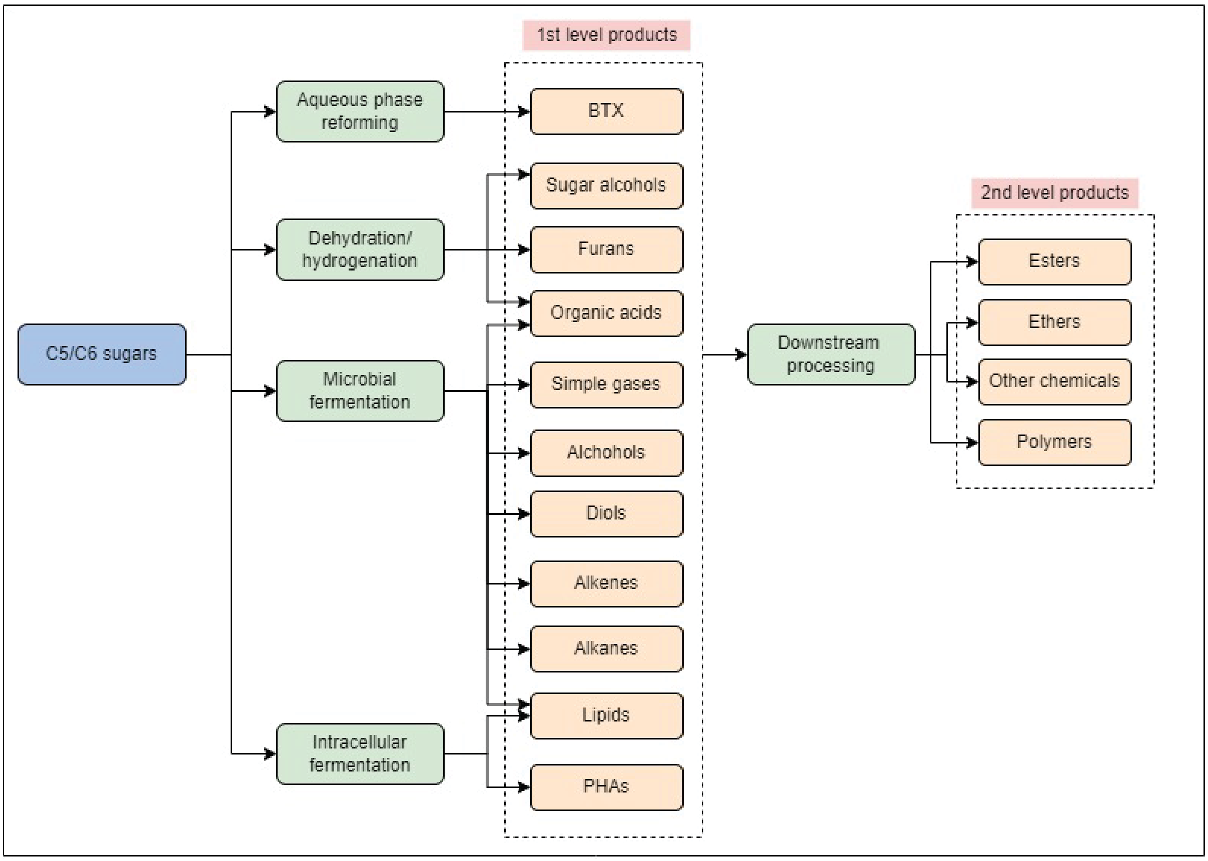


Figure 6-3 Product formation pathways from C5 and C6 sugar platforms adapted from Taylor et al. (Taylor et al. 2015), PHAs: polyhydroxyalkanoates

Table 6-5 List of studies that investigated promising chemicals which can be produced from lignocellulosic biomass

Study Title, Author, Year	Chemicals Listed	Notes
A review of commercial-scale high-value products that can be produced alongside cellulosic ethanol (Rosales-Calderon and Arantes, 2019)	1,2-butanediol, 1,3-propanediol, 1,4-butanediol, 2, 3-butanediol, acetone-butanol-ethanol, furfural, furfuryl alcohol, glutamic acid, isobutanol, itaconic acid, lactic acid, lactide, lysine, polylactic acid, polytrimethylene terephthalate, propylene glycol, sorbitol squalene, succinic acid, terpenes, xylitol and microfibrillated cellulose	The authors investigated an integrated cellulosic ethanol biorefinery with the production of high-value chemicals to improve the economics of cellulosic ethanol production. Their products of choice were presented as a list of chemicals and materials with a minimum technology readiness level (TRL) 8, thus having already attained commercial-scale production
An overview of biorefinery-derived platform chemicals from a cellulose and hemicellulose biorefinery (Takkellapati et al. 2018)	Ethanol, furfural, hydroxymethylfurfural (HMF), 2,5-furandicarboxylic acid (FDCA) glycerol, succinic acid, lactic acid, levulinic acid, 3-hydroxypropionic acid (3-HPA) sorbitol, xylitol, Isoprene	The chemicals discussed in this study are all platform chemicals.
Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential (Biddy et al. 2016)	1,3-Butadiene, 1,4-butanediol, ethyl lactate, fatty alcohols, furfural, glycerine, isoprene, lactic acid, 1,3-propanediol, propylene glycol, succinic acid, para-xylene	The chemicals that were focused on in this study show near-term deployment potential when considering their market and current state of development.
(Susan T. L. Harrison et al. 2016)	Top 20 chemicals for South Africa: Citric acid, lactic acid, iso-butanol, n-butanol, ethanol, isoprene, glutamic acid, acetic acid, algal lipids, ethylene, furfural, adipic acid, polylactic acid, succinic acid, lactate esters, farnesene, levunilic acid, polyhydroxyalkanoates, malic acid	This feasibility study ranked product potential (not limited to lignocellulosic biomass feedstock) in South Africa based on market demand in South Africa and globally, current use and future applications, the complexity of production routes, technology readiness, and barriers to market. A combination of technology review, market literature, import-export data, application analysis, and expert opinion was used.
Lignocellulosic biomass: A sustainable platform for the production of bio-based chemicals and polymers (Isikor and Bercer2015)	Undertook detailed product mapping for 15 C5/C6 derived platform chemicals: 1,4-diacid, 5-HMF and FDCA, 3-HPA, aspartic acid, glutamic acid, glucaric acid, itaconic acid, glycerol, sorbitol, levulinic acid, 3-HBL, lactic acid, xylose-furfural-arabinitol, acetone-butanol-ethanol (ABE)	This study reviewed over 200 value-added chemicals which can be produced from lignocellulosic biomass. The authors further conducted detailed mapping for specific chemicals and their associated polymers
From the Sugar Platform to biofuels and biochemicals (Taylor et al. 2015)	Acrylic acid (lactic acid), adipic acid (glucaric acid), 1,4-butanediol (acetylene, butadiene, succinic acid), farnesene, FDCA (HMF), isobutene (isobutanol), polyhydroxyalkanoates (PHAs), polyethylene (ethanol), polylactic acid (lactic acid), succinic acid	The chemicals in their shortlist are all final materials; the chemical in brackets next to some of them is the platform chemical it is derived from in the case where it is not directly produced from sugar. All these chemicals have a TRL of five and up, as well as an active market.
Chemicals from lignocellulosic biomass: opportunities, perspectives, and potential of biorefinery systems (Cherubini and Strømman 2011)	Promising building blocks were identified based on their number of carbon atoms: C2: ethanol C3: acetone, lactic acid, 3-hydroxypropionic acid (HPA) C4: organic acid (succinic acid, fumaric acid etc.) C5: furfural, itaconic acid, xylitol, levulinic acid C6: sorbitol, HMF, FDCA, gluconic acid	The main aim of the study was to investigate the potential replacement of fossil resources with lignocellulosic biomass in the production of platform chemicals
Technology development for the production of bio-based products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited (Bozell and Petersen, 2010)	Ethanol, furfural, HMF, FDCA, glycerol, lactic acid, succinic acid, hydroxypropionic acid/aldehyde, levulinic acid, sorbitol, xylitol	Nine different criteria were used to evaluate bio-based products from carbohydrates; they were: attention in the literature, broad technology with multiple products, direct substitute for petrochemicals, technology is applicable to high volume products, exhibits strong platform potential, scale-up is underway, existing commercial product, may serve as a primary

Study Title, Author, Year	Chemicals Listed	Notes
		building block in biorefinery, commercial production from renewable carbon is well established. Not all the chemicals listed adhere to all nine criteria.
Top value-added chemicals from biomass: Volume I– Results of screening for potential candidates from sugars and syngas (Werpy and Petersen, 2004)	1,4 diacids (succinic, fumaric, malic), 2,5 furandicarboxylic acid, 3, hydroxy propionic acid, aspartic acid, glutamic acid, itaconic acid, 3-hydroxy butyrolactone, glycerol, sorbitol, xylitol/arabinitol	12 building block chemicals which can be produced from sugars via biological or chemical conversions were identified based on their market potential and the technical complexities of their production pathways. It was noted that biological transformations are important pathways from plant feedstocks to building blocks, but chemical transformations are more predominant in the conversion of building blocks to molecular derivatives and intermediates

6.3.2.2 *Lignin platform*

Following the separation of the lignin from other components, this stream is available for further processing and valorisation. Lignin is an established by-product of the pulping industry and is traditionally burnt on-site for combined heat and power (Cline and Smith, 2017). The pulping industry, which is responsible for the majority of lignin produced, has previously not focused on the beneficiation of lignin to yield value-added lignin products (Cline and Smith, 2017). According to Beckham et al. (2016), lignin valorisation is essential to the pulp and paper biorefinery, based on its techno-economics. An increasing number of publications on lignin valorisation cover the whole process from its separation and recovery through its characterisation, depolymerisation techniques and upgrading to chemicals (Abejón et al. 2018).

The main routes for the valorisation of lignin into chemicals and materials are shown in Figure 6-4. In each process block, multiple process options are available to carry out the desired reaction, discussed further in the rest of this section.

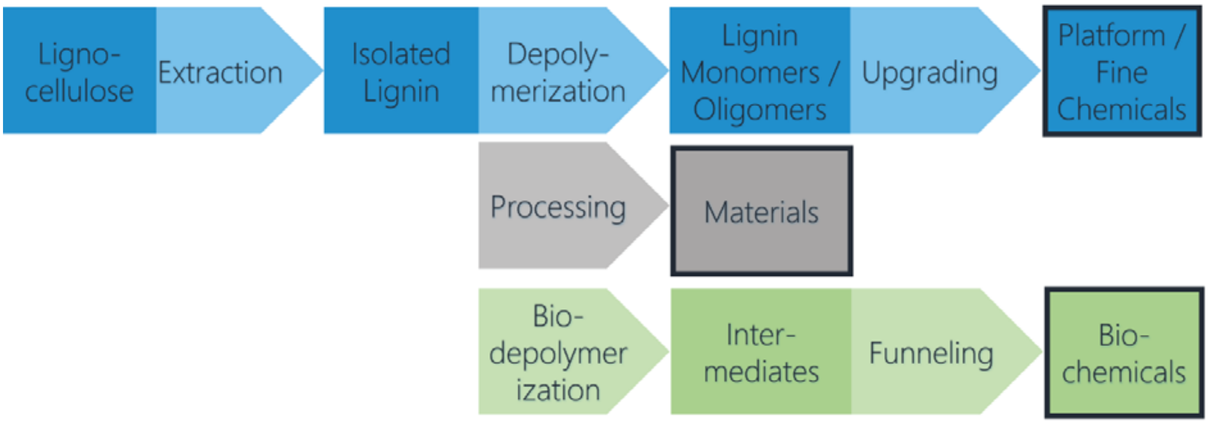


Figure 6-4 Main routes for valorisation of lignin

6.3.2.2.1 *Lignin extraction methods*

The pulping step at the pulp and paper mills serves to separate the lignocellulose into lignin and holocellulose, the latter being the polysaccharide fraction consisting of hemicellulose and cellulose. In the mills, the lignin stream is typically treated as waste and burnt for energy. The nature of the chemicals used influences the crosslinked structure of the lignin and its molecular weight distribution (Xu and Ferdosian, 2017). The four main technologies currently in use are the kraft, Sulphite, Soda and Organosolv processes.

In the kraft process, a portion of the lignin is dissolved in the solvent to form black liquor (Xu and Ferdosian, 2017). The chemicals used can be recovered from the black liquor to form white liquor for reuse in the mill. The residual solid lignin is burned in recovery boilers to generate steam. In the sulphite process, the lignin remains in the form of soluble lignosulphonates (Strassberger et al. 2014). Soda lignin is the product of a process similar to the kraft process but sulphur free, using only sodium hydroxide (Abejón et al. 2018). Since the process is sulphur free, the chemical composition of the lignin is closer to that of natural lignin than found with the Kraft and sulphite processes (Vishtal and Kraslawski, 2011). The Organosolv process uses a mixture of water and organic solvents, including acetic acid, ethanol and formic acid (Vishtal and Kraslawski, 2011), to solubilise the lignin, resulting in more homogenous lignin than that of Kraft lignin or lignosulphonates (Lora et al. 1993). While these four processes account for most commercial pulping, they are not the only extraction processes. Enzymatic and acid hydrolysis has been shown to be effective at an industrial scale, while other technologies, like ionic liquids, are still in the development phase (Ragauskas et al. 2005).

Following extraction of lignin from the lignocellulose, it must be upgraded for further processing. The method used depends on the extraction method used, with potential separation methods listed in Table 6-6. Some are proprietary, such as the Lignoboost™ process discussed in Chapter 4, and used to isolate the kraft lignin from the black liquor (Tomani, 2010). Kraft lignin and lignosulphonates have a higher ash and sulphur content and higher molecular weight than Soda and organosolv lignin (Vishtal and Kraslawski, 2011). Before lignin can be used for chemical synthesis or in biochemical conversion processes, it must be purified by removing other components still present in the lignin stream. These components include carbohydrates, ash and extractives; if these are not removed, they can affect the product yield negatively and form undesirable by-products which affect the properties of the desired final product (Vishtal and Kraslawski, 2011).

After the lignin is isolated, the rest of the processing is determined by the end application. For application in materials, the lignin is maintained in its polymeric form, while for chemicals and fuels, it is depolymerised and then modified.

Table 6-6 Separation methods for lignin (adapted from Vishtal and Kraslawski, 2011)

Process	Lignin separation method	Status
Kraft	Precipitation through the change in pH	Industrial
	Ultrafiltration	Industrial
Soda	Precipitation through a pH change	Laboratory/Pilot
	Ultrafiltration	Laboratory
Lignosulphonates	Ultrafiltration	Industrial
Organosolv	Dissolved air flotation	Laboratory
	Precipitation by the addition of non-solvent	Laboratory/Pilot

6.3.2.2.2 *Lignin for materials*

Unmodified lignin can be incorporated into materials as a way of enhancing properties. It has been used to offer protection against ultraviolet rays, as a flame retardant, and as a reinforcement filler, but due to its immiscibility with plastics, it can only be added to plastics in small amounts (Kai et al. 2016). However, lignin can be added to a range of polymers like polyethylene, polypropylene, polystyrene and natural rubbers to improve its biodegradability, mechanical performance, thermal stability and antioxidant properties (Xu and Ferdosian, 2017). A more recent development in this field is the incorporation of lignin into biopolymers like polylactide and polyhydroxybutyrate to improve their mechanical and thermal properties (Abejón et al. 2018). To increase the range of applications, lignin can be chemically modified while maintaining its polyol structure, using reactions that introduce new reactive sites or reactions that functionalised the hydroxyl groups (Kai et al. 2016).

Significant research has gone into the development of lignin-based carbon fibres, activated carbon and other carbonaceous materials (Chatterjee and Saito, 2015). The first step in producing carbon fibres is melt-spinning at high rates, resulting in high-purity lignin, free from water, salts and polysaccharides (Strassberger et al. 2014). Powdered activated carbon is a lignin-derived product that finds application in the removal of mercury from the flue gas of power plants (Cline and Smith, 2017). Preparation of activated carbon starts with the thermal treatment of lignin-rich streams; pyrolysis and hydrothermal carbonisation are two of the thermal treatment methods used. Thereafter the materials must be activated, which means the porosity and internal surface area have to be increased via physical and chemical methods (Abejón et al. 2018).

6.3.2.2.3 *Lignin for chemicals*

Depolymerisation and Upgrading

Lignin is a highly functionalised heteropolymer and, therefore, ideal for the production of chemicals in preference to low-grade fuels, which require it to be converted back into simple hydrocarbons (Strassberger et al. 2014). For the production of chemicals and deoxygenated hydrocarbon fuels, the lignin is depolymerised into oligomers and smaller molecules. The predominant lignin monomers are p-Coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, shown in Figure 6-5 (Linger et al. 2014). The main depolymerisation technologies are shown in Figure 6-6.

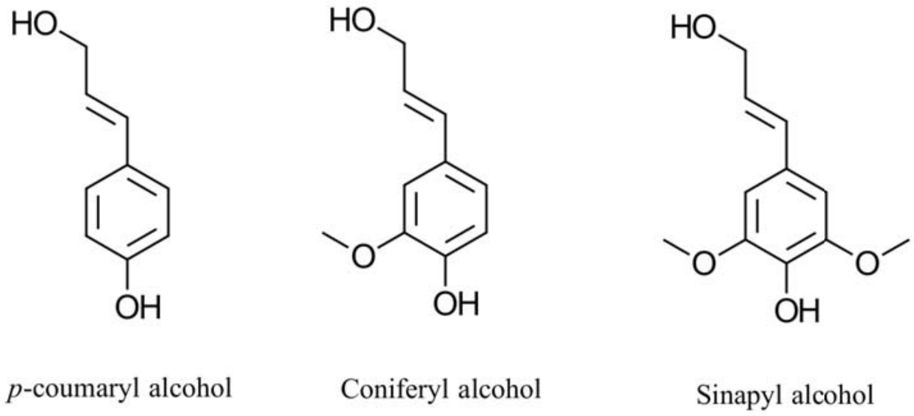
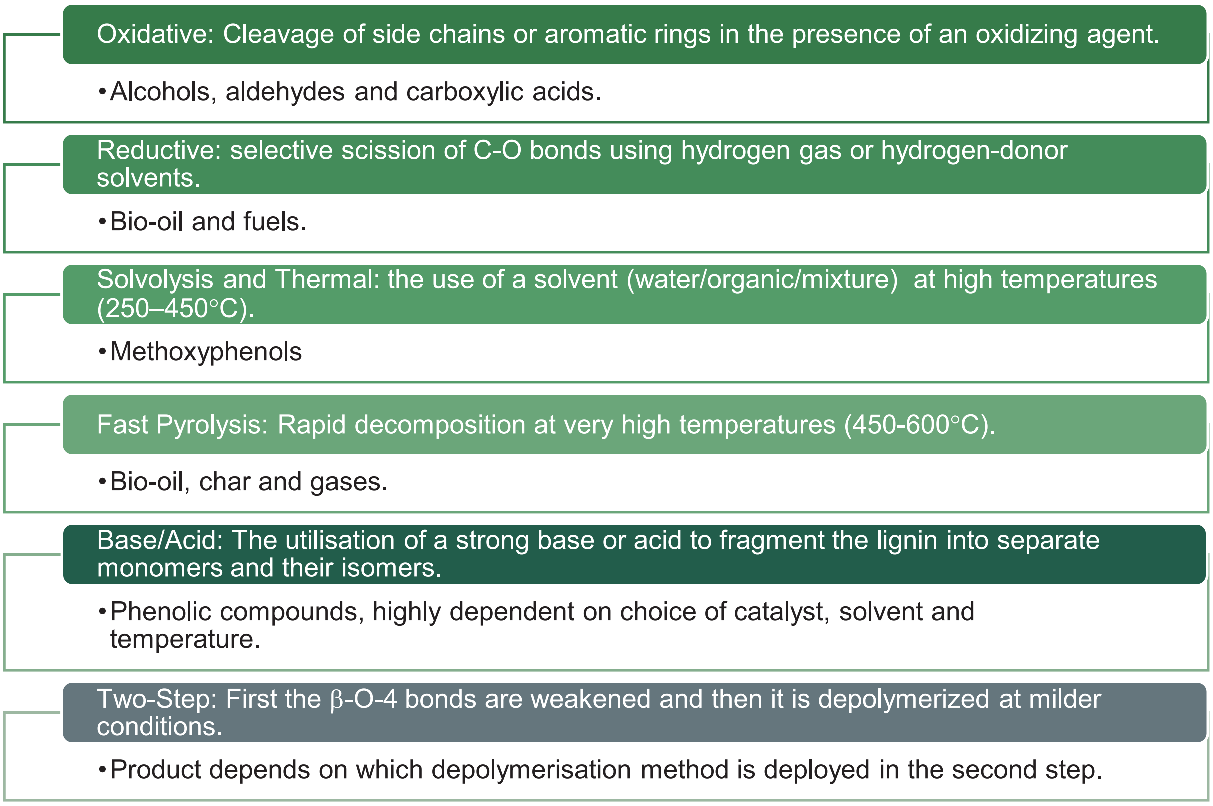


Figure 6-5 Monomers predominant in lignin structures



Oxidative: Cleavage of side chains or aromatic rings in the presence of an oxidizing agent.

- Alcohols, aldehydes and carboxylic acids.

Reductive: selective scission of C-O bonds using hydrogen gas or hydrogen-donor solvents.

- Bio-oil and fuels.

Solvolysis and Thermal: the use of a solvent (water/organic/mixture) at high temperatures (250–450°C).

- Methoxyphenols

Fast Pyrolysis: Rapid decomposition at very high temperatures (450-600°C).

- Bio-oil, char and gases.

Base/Acid: The utilisation of a strong base or acid to fragment the lignin into separate monomers and their isomers.

- Phenolic compounds, highly dependent on choice of catalyst, solvent and temperature.

Two-Step: First the β-O-4 bonds are weakened and then it is depolymerized at milder conditions.

- Product depends on which depolymerisation method is deployed in the second step.

Figure 6-6 Technologies for depolymerisation of lignin (Xu et al. 2014; Beckham et al. 2016; Rodriguez et al. 2017; Xu and Ferdosian, 2017; Abejón et al. 2018; Schutyser et al. 2018; Sun et al. 2018)

Subsequent to depolymerisation, the aromatic compounds can be transformed through either defunctionalisation for platform chemicals and fuels or functionalisation for fine chemicals and materials (Sun et al. 2018). Defunctionalisation refers to a process where the monomer complexity is lowered to produce bulk chemicals. Lignin monomers resemble their parent monolignol structure and are made up of a phenolic ring with one or two *o*-substituted methoxy groups and a *p*-sidechain (Schutyser et al. 2018). Defunctionalisation reactions can either act on the phenolic core and its level of substitution (hydrodeoxygenation) or on the side chain. Catalytic hydrodeoxygenation of lignin monomers to alkanes and aromatics for liquid fuels and petrochemical feedstock application is receiving increasing attention (Sun et al. 2018). Another defunctionalisation strategy is the selective hydrogenation of aromatic rings to produce the starting materials for polymers, dyes, resins and fine chemicals (Cui et al. 2016). Other defunctionalisation strategies include hydrogenation, demethylation, demethoxylation and total C-O cleavage (Sun et al. 2018).

In contrast, functionalisation increases the complexity of the monomeric units to produce value-added molecules or pharmaceutical intermediates and polymer building blocks (Sun et al. 2018). Two approaches to functionalisation are used: primary and secondary core transformations produce caprolactam, for example; side chain transformations such as isomerisation produce isoeugenol from eugenol as an example (Schutyser et al. 2018).

Biological conversion

Two main functions of lignin within woody biomass are to provide strength to the plant and to act as a barrier protecting the plant from microbial attack, explaining its recalcitrant nature. However, the cyclical processes within the natural environment mean that just as there are functions for the polymerisation of lignin during plant growth, there are counterparts able to break down the lignin at the end of a plant's life. Fungi have been the primary object of study for the degrading of lignin, but there are also bacteria able to degrade lignin, although they are less well studied (Brown and Chang, 2014).

Biological lignin valorisation occurs in three phases, as shown in Figure 6-7. The first phase is concerned with the initial attack on lignin. White-rot fungi are the main organisms that can mineralise lignin by employing three different class II peroxidases (Ayuso-Fernández et al. 2018). These extracellular ligninolytic enzymes are able to turn lignin oligomers into low molecular weight compounds (Beckham et al. 2016). The second phase catabolises the resultant aromatics to central intermediates such as catechol; thereafter, in the third phase, the aromatic rings are cleaved into ring-opened species, which can then be used in the cells' central carbon metabolism (Abejón et al. 2018). These two phases are referred to as the upper and lower pathways, respectively and collectively as biological funnelling.

Figure 6-7 Phases of biological lignin valorisation

Research into these natural mechanisms for the production of valuable chemicals is still in its infancy (Schutyser et al. 2018). Microbial decomposition has opened the door for innovative biotechnologies, especially with the discovery of enzymes in white-rot fungi which has led to emerging technologies for delignification in pulp bleaching and the treatment of environmental pollutants (Wertz et al. 2018).

6.3.2.2.4 *Promising lignin-derived products*

When looking at the current market, lignin-based phenol and carbon fibre seem poised to capture the largest market, although production costs and viable chemical pathways to products limit commercial feasibility (Cline and Smith, 2017). The aromatic chemicals shown in Figure 6-8 retain their lignin monomeric structure (Abejón et al. 2018). When it comes to the production of chemicals from lignin, Xu et al. (Xu et al. 2014) concluded their review on lignin depolymerisation strategies by stating that lignin recovery and valorisation may only reach the market if (1) a cheap, efficient and green protocol is developed for the depolymerisation step, (2) a cost competitive method for the separation, purification and isolation of the chemicals is brought forward, (3) the reaction conditions used are mild and (4) the process is scalable, continuous and able to diversify into more than one product.

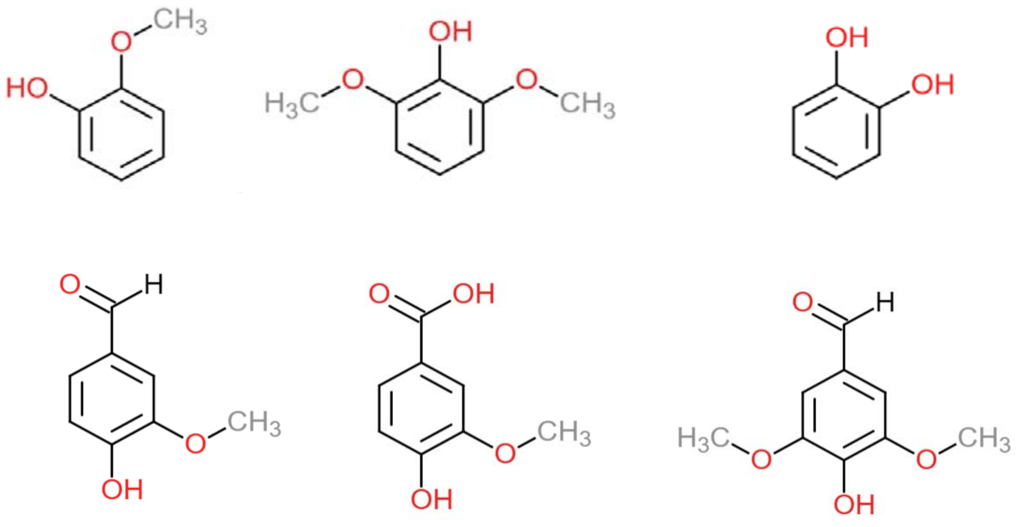


Figure 6-8 Aromatic chemicals with potential for production from lignin.
Guaiacol, Syringol, Catechol, (top, left to right)Vanillin, Vanillic acid, Syringaldehyde (bottom, left to right)

The consensus in literature is that lignin holds particular promise for the fabrication of chemicals that contain aromatic structures and that the current process of burning it for energy under-values its potential. The publications cited agree that, although further research is required to reach the feasibility stage for these upgrading technologies, lignin has the potential to solve the dependence on fossil-based hydrocarbons for the production of aromatic chemicals. While these are under development, there are product options in materials from lignin, such as powdered activated carbon, that do not require complex or under-developed processing methods.

6.4 Establishing a framework for a pulp and paper wastewater biorefinery focused on lignocellulose-containing wastewaters

For the pulp and paper industry, the main resource present in wastewater streams before treatment is carbon in the form of lignocellulosic biomass. Lignocellulosic biomass can be processed using thermochemical or biological processes. When converted to intermediary compounds, lignocellulosic biomass can yield a wide range of biofuels, biochemicals and bioproducts. Of interest are the platform chemicals which can feed into various product value chains and thus add economic complexity to a biorefinery. While thermochemical processes are highly efficient, they require high temperatures and pressures compared to biological processes, requiring stream concentration prior to application. One of the main challenges for the biological processes lies in the separation and, at times, detoxification processes required when lignocellulosic biomass is separated into cellulose, hemicellulose and lignin. Lignin is currently an under-utilised resource, but it is a promising feedstock which can enhance the flexibility of the product portfolio of a lignocellulose-centred biorefinery.

Since the major contaminant of water in a lignocellulosic wastewater stream from the PPI is carbon, the focus on the primary bioreactor in the wastewater biorefinery is to harness most of the carbon towards a valuable by-product. Depending on the residual resources contained within the water after this bioreactor, typically a bacterial bioreactor, an informed decision can be made on the unit operations to further clean the water, and the potential for additional products can be investigated to build an integrated process. Chapter 7 focuses on proposing a framework to select the appropriate mix of products for a pulp and paper wastewater biorefinery.

7 Potential flowsheet and product portfolio for lignocellulosic wastewater stream

7.1 Evaluating the lignocellulosic wastewater stream

For our major study, the wastewater stream chosen is the combined lignocellulosic wastewater stream exiting a paper recycling mill and the associated primary sludge that leaves the primary clarifier. As seen in Chapter 4, it has high volume, high-concentration and medium complexity. It is thus postulated as a good candidate for valorisation.

7.1.1 Composition of lignocellulosic wastewater streams

When comparing pulp and paper primary sludge with municipal biosludge, the nitrogen content or carbon-to-nitrogen ratios differ substantially. Meyer and Edwards (2014) report that municipal biosludge contains 2.4 to 5.0% nitrogen (% TS), whereas the pulp and paper primary sludge only has 0.1 to 0.5% nitrogen (% TS). In contrast, the pulp and paper sludge contains 36 to 45% (% TS) cellulose, whereas municipal biosludge contains less than 0.1%. From this and multiple published analyses (Table 7-1), the primary sludge originating from a paper recycling mill contains mostly ash and cellulose (glucan) with some hemicellulose (xylan) and small amounts of lignin. The high moisture content and dilute nature influence the technology choice to produce the primary product. Conversion of this cellulose and hemicellulose into a desirable product would serve well as a tool to lower the pollution load significantly.

Table 7-7 Composition of lignocellulose-rich waste sludge streams

Description	Moisture	Ash	Cellulose	Hemicellulose	Lignin	Reference
Paper recycling mill wastewater sludge	NR	29.3% (OD)	34.1% (OD)	7.9% Xylan (OD)	20.4% (OD)	(Marques et al. 2017)
Sludge from paper companies (wet cake)	60.60%	62.7% of TS (FS)	30.6% (TS)	ND	8.0% (TS)	(Lee et al. 2004)
	59.50%	44.3% of TS (FS)	33.5% (TS)	ND	11.8% (TS)	
	67.90%	51.8% of TS (FS)	30.3% (TS)	ND	12.7% (TS)	
	70%	28.5% of TS (FS)	28.9% (TS)	3.5% (TS)	16.2% (TS)	
	75.60%	51.9% of TS (FS)	28.3% (TS)	NM	5.6% (TS)	
Paper mill sludge	NR	38.3%	43.7% glucan	10.5% xylan	3.9%	(Acharjee, 2017)
Paper mill clarifier sludge	90% (before dewatering)	46.5%	21.1%	4.1%	13.9%	(Mukhopadhyay, 2009)
Recycled paper mill sludge (Kraft)	NR	34.5%	47.6% glucan	7.5% xylan	6.6%	Shi et al.(Shi et al. 2015)
Primary clarifier sludge (Kraft)	70.3%	34.4%	45%	12.5%	6.7%	(Budhavaram and Fan, 2009)
Primary clarifier sludge (Kraft)	79.8%	10% (AI) 26% (AS)	44.5% glucan	9.9% xylan	8.1%	(Kang et al. 2011)
Primary sludge (Kraft)	NR	26.2%	50.6% glucan	9.0% xylan	10.3%	(Chen et al. 2014b)
Primary sludge (Kraft)		50.8%	35.6% glucan	6.6% xylan	3.96%	
Recycled deinking mill primary sludge		54.4%	27.4% glucan	6% xylan	6. 72%	
Recycled deinking mill primary sludge		56.1%	25.5% glucan	4.7% xylan	6.74%	

Description	Moisture	Ash	Cellulose	Hemicellulose	Lignin	Reference
Recycled paper sludge	66.3%	57.7% (dry basis) with 45.9% AS and 11.8% AI	27.8%	5.7%	7.8% (acid soluble and acid insoluble)	(Schroeder et al. 2017)
Primary pulp and paper sludge	1.5-6.5%	20-49% of TS	36-45% of TS		20-24% of TS	(Meyer and Edwards, 2014)

NR: not reported; OD: Oven dried; ND: not detected; TS: total solids; FS: fixed solid; AS: acid soluble; AI: acid insoluble

7.1.2 Potential technologies for primary valorisation of lignocellulose

A way of improving the wastewater biorefinery's flexibility is to choose a processing route that can be used for a range of chemicals so that should the market demand for the chosen product drop below the selling price needed to maintain profitable operation, the wastewater biorefinery can be switched to another product making use of the same reactors, raw materials and downstream processing units. For this reason, fermentation was selected for implementation in the wastewater biorefinery. By changing the microorganism used together with other small changes to the operation, the product obtained can change; for example, in the case of anaerobic fermentation, by changing the bacterial strain used from Lactobacillus rhamnosus to *Zymomonas mobilis,* the same reactor can switch from producing lactic acid to produce ethanol.

The list of chemicals that can be produced from the C5/C6 platform through fermentation is long. As discussed in Section 6.2, the main product groups under fermentation are organic acids, simple gases, alcohols, diols alkenes, alkanes, lipids and polyhydroxyalkanoates. To narrow down the list, it was decided that the primary product should be a platform chemical rather than a fine chemical. Platform chemicals refer to a group of chemicals that are in themselves already products but can also act as a substrate for the production of multiple higher value-added chemicals (Takkellapati et al. 2018). One example of a platform chemical is succinic acid which is a fermentation product from glucose that can be further processed to form succinimide, 1,4-butanediol, tetrahydrofuran, fumaric acid and maleic acid (Takkellapati et al. 2018). By choosing to produce a platform chemical, some of the concerns related to market compatibility are addressed. A platform chemical is used by several industries, whereas a fine chemical usually only has a few applications within certain industries, making it more susceptible to price changes due to fluctuations within the related industry. Another market-related concern that is addressed by choosing a platform chemical is that because the product feeds into several markets, the volumes produced by the wastewater biorefinery are not limited by the demand of one industry only but by feeding into multiple industries if one should require less, the excess product can be absorbed by the other industries that use it for other purposes. Appropriate platform chemicals for production in South Africa have been rigorously reviewed by Harrison et al. (2016) and discussed in the WRC report 2380 introducing the wastewater biorefinery concept (Harrison et al. 2017). Table 7-2 gives a summary of the chemicals highlighted by different authors for application in a biorefinery, and Table 7-3 indicates which of these chemicals were eliminated at the start and the reason for their elimination.

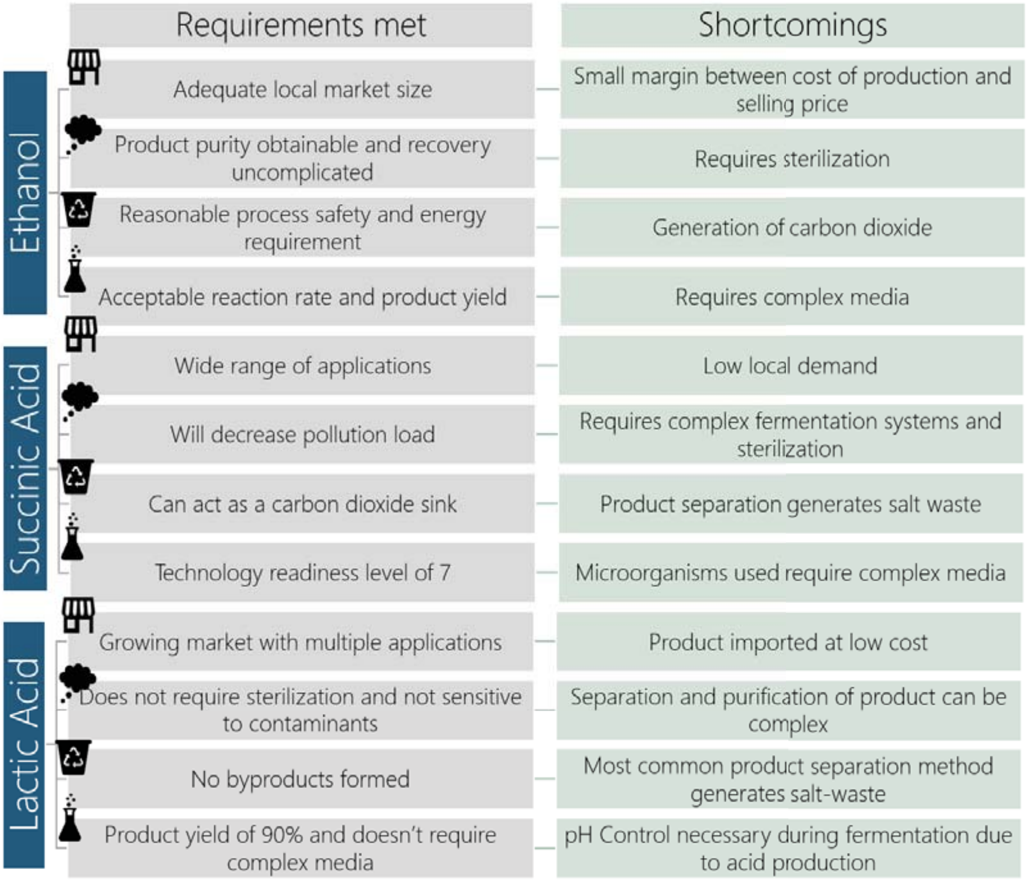
Table 7-8 List of studies investigating different chemicals which can be produced via bioprocessing routes

Study Title, Author, Year	Chemicals Listed	Notes
Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential (Biddy et al. 2016)	1,3-Butadiene, 1,4-butanediol, ethyl lactate, fatty alcohols, furfural, glycerine, isoprene, lactic acid, 1,3-propanediol, propylene glycol, succinic acid, para-xylene	The chemicals that were focused on in this study show near-term deployment potential when considering their market and current state of development.
An overview of biorefinery-derived platform chemicals from a cellulose and hemicellulose biorefinery (Takkellapati et al. 2018)	Ethanol, furfural, hydroxymethylfurfural (HMF), 2,5-furandicarboxylic acid (FDCA) glycerol, succinic acid, lactic acid, levulinic acid, 3-hydroxypropionic acid (3-HPA) sorbitol, xylitol, Isoprene	The chemicals discussed in this study are all platform chemicals.
From the Sugar Platform to biofuels and biochemicals (Taylor et al. 2015)	Acrylic acid (lactic acid), adipic acid (glucaric acid), 1,4-butanediol (acetylene, butadiene, succinic acid), farnesene, FDCA (HMF), isobutene (isobutanol), polyhydroxyalkanoates (PHAs), polyethylene (ethanol), polylactic acid (lactic acid), succinic acid	The chemicals in their shortlist are all final materials; the chemical in brackets next to some of them is the platform chemical it is derived from in the case where it is not directly produced from sugar. All these chemicals have a TRL of five and up, as well as an active market.
Technology development for the production of bio-based products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited (Bozell and Petersen, 2010)	Ethanol, furfural, HMF, FDCA, glycerol, lactic acid, succinic acid, hydroxypropionic acid/aldehyde, levulinic acid, sorbitol, xylitol	Nine different criteria were used to evaluate bio-based products from carbohydrates; they were: attention in literature, broad technology with multiple products, direct substitute for petrochemicals, technology is applicable to high-volume products, exhibits strong platform potential, scale up is underway, existing commercial product, may serve as a primary building block in biorefinery, commercial production from renewable carbon is well established. Not all the chemicals listed adhere to all nine criteria.

Table 7-9 Bioproducts eliminated early on with the reason for elimination

Chemical	Reason for Elimination
1,3 butadiene	Direct production via fermentation is not yet feasible due to high capital and operating costs and low overall yields.
ethyl lactate	Produced by the esterification of ethanol and lactic acid and cannot be produced directly by fermentation.
fatty alcohols, glycerine, propylene glycol, glycerol	Not produced from C5/C6 platform
furfural	Produced from C5 sugars only, need a product that can be made from both C5 and C6 sugars Commercial process operated by the sugar industry in South Africa
isoprene, farnesene,	An engineered strain is used to produce these biohydrocarbons
1, 3 propanediol	Not shown to be produced from C5 sugars, mainly produced from glycerol
para-xylene	Not directly produced via fermentation
HMF	Produced from fructose, which is not present in the lignocellulosic fraction of pulp and paper wastewater
FDCA	Starting block is HMF, which has been eliminated
levulinic acid, 3-HPA	Does not have the required technology readiness level.
sorbitol	When using glucose, it is not produced via fermentation but by chemical reduction
xylitol	Produced from C5 and not C6, also not a high-volume product, and industrial scale-up is lacking

The platform chemicals that were further evaluated for production from the recycled paper mill primary sludge hydrolysate are ethanol, lactic acid and succinic acid. The highlights of the product selection procedure are shown in Figure 7-1. This analysis highlighted the major findings from literature that prevent ethanol and succinic acid from being chosen as the primary product for a wastewater biorefinery built around valorising a paper recycling mill's primary sludge stream. The shortcomings listed for lactic acid can be addressed by the design and technology selection, whereas the same is less readily achieved for the other two products. The decision to move forward with lactic acid was settled by the unbeaten carbon utilisation of lactic acid production.



	Requirements met	Shortcomings
Ethanol	Adequate local market size	Small margin between cost of production and selling price
	Product purity obtainable and recovery uncomplicated	Requires sterilization
	Reasonable process safety and energy requirement	Generation of carbon dioxide
	Acceptable reaction rate and product yield	Requires complex media
Succinic Acid	Wide range of applications	Low local demand
	Will decrease pollution load	Requires complex fermentation systems and sterilization
	Can act as a carbon dioxide sink	Product separation generates salt waste
	Technology readiness level of 7	Microorganisms used require complex media
Lactic Acid	Growing market with multiple applications	Product imported at low cost
	Does not require sterilization and not sensitive to contaminants	Separation and purification of product can be complex
	No byproducts formed	Most common product separation method generates salt-waste
	Product yield of 90% and doesn't require complex media	pH Control necessary during fermentation due to acid production

Figure 7-9 Highlights from literature review of ethanol, succinic acid and lactic acid.

7.2 Development of pulp and paper wastewater biorefinery flowsheet around the production of lactic acid

Before developing the lactic acid production train in more detail, the inflow-outflow diagram shown in Figure 7-2 was drawn and used in the conceptualisation of the rest of the wastewater biorefinery. The two most important functions of the support processes are to facilitate the further treatment of the wastewater feedstock so that it can be repurposed either in the process or elsewhere and to turn the remaining constituents in the wastewater as well as those exiting the lactic acid production unit into saleable outputs.

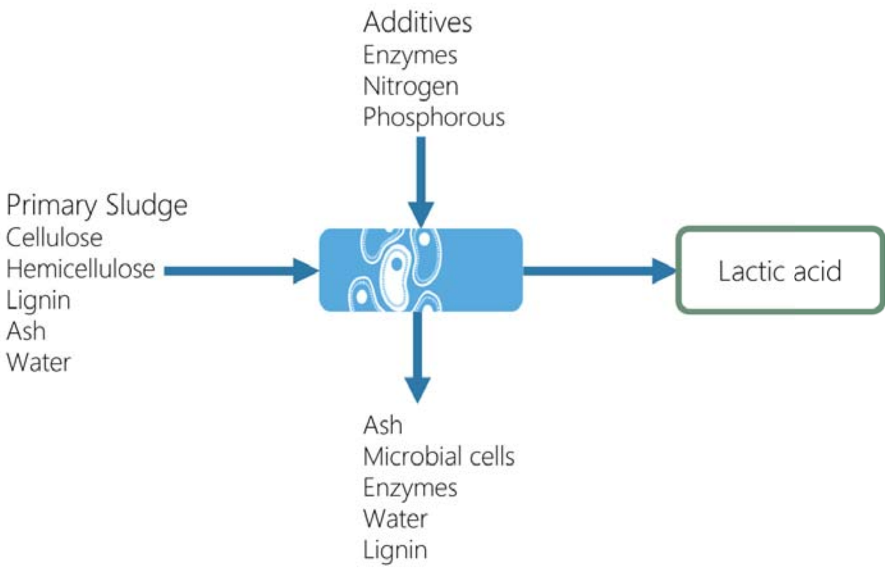


Figure 7-10 Components entering and exiting lactic acid bioproduction unit

Each of the three streams associated with the production of the selected primary product of lactic acid suggests one or more auxiliary support processes to create the biorefinery. A summary of the wastewater components which need to be addressed is shown in Figure 7-3, together with a product and process proposed to meet these. Figure 7-4 provides a framework for the associated wastewater biorefinery.

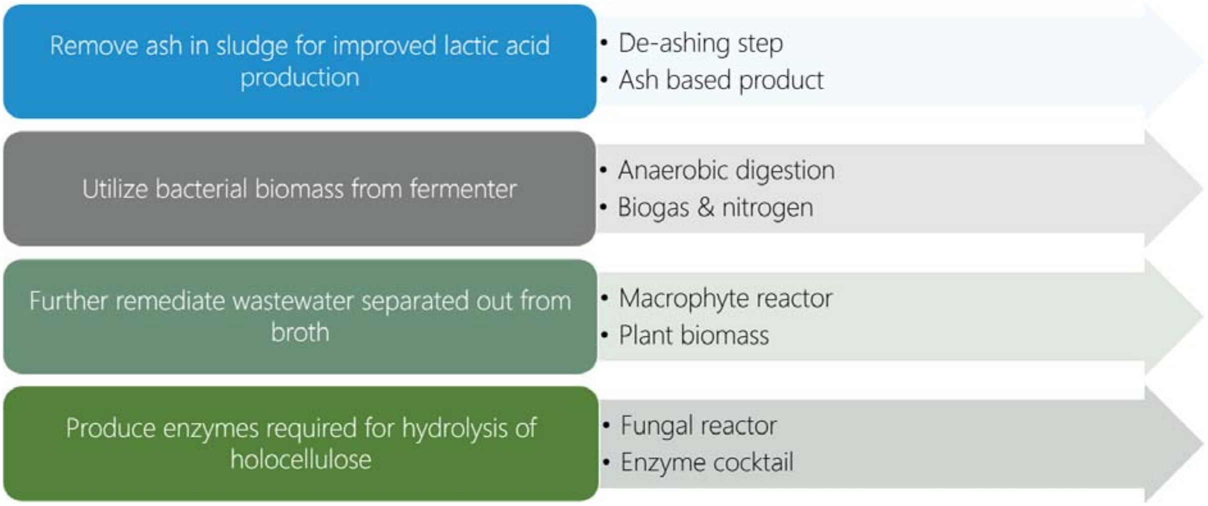


Figure 7-11 Aspects of the lactic acid production process that require addressing with the proposed solution and its associated product. Note that water forms a non-negotiable product of the process, with its quality a key indicator too

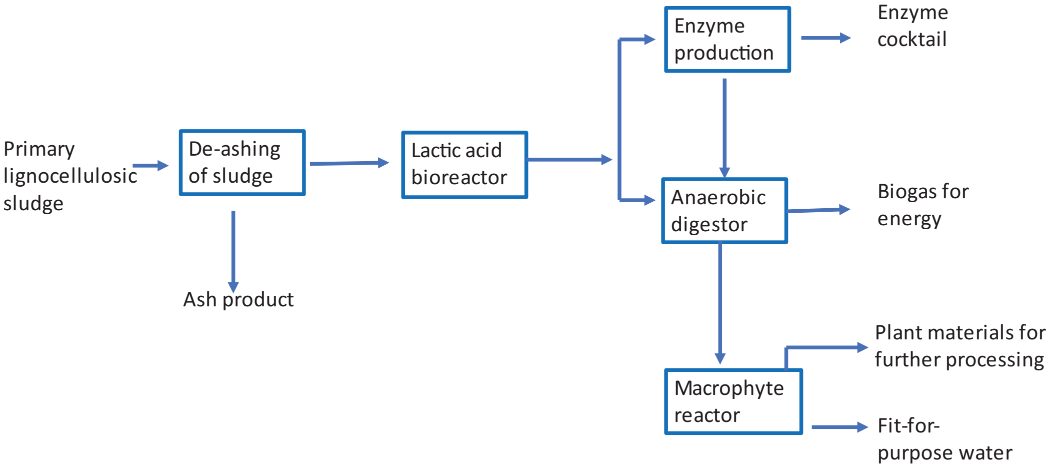


Figure 7-12 Framing the lignocellulosic wastewater biorefinery with lactic acid as the anchor product.

7.2.1 The proposed process units forming the lignocellulosic wastewater biorefinery

7.2.1.1 *Improving primary product production: deashing*

Referring to Table 7-1, a large amount of ash present in the sludge was noted. As will be discussed in Section 7.3, one of the factors that limit the productivity of the lactic acid process is the substrate concentration achievable in the reactor due to inadequate mixing at solids loading exceeding 15%(w/v). The ash can account for as much as half of the solids present in the process and increases the viscosity of the feed to the bioreactor. There are other ways in which the presence of ash impacts the efficiency of the process, including the adsorption of the enzymes responsible for the hydrolysis of the fibres onto the ash particles resulting in increased enzyme costs. Removal of the ash from the sludge before it enters the lactic acid production unit allows it to be processed into a secondary product of the wastewater biorefinery. Ash recovered from the pulp and paper industry has found application in more than one industry, including in construction as a cement filler (Fava et al. 2011) and in agriculture as a soil amendment (Chen et al. 2014a).

7.2.1.2 *The core process: lactic acid production*

Lactic acid is produced from glucose and xylose, the monomers of cellulose and hemicellulose (Section 7.3); this means that before the bioreactor, the fibres need to be hydrolysed. Thus, the core process for the bioproduction of lactic acid, in fact, consists of two processes: hydrolysis and fermentation. There are several options for the configuration of these processes, and the most efficient solution for this feedstock is best determined experimentally. The two main options are separate hydrolysis and fermentation (SHF) and simultaneous saccharification and co-fermentation (SSCF). In SHF, the cellulose and hemicellulose are broken down to glucose and xylose by enzymes in a separate reactor, followed by a bioreactor dedicated to fermenting the sugars to lactic acid. In SSCF, these two consecutive reactions occur concurrently in one bioreactor. There are benefits and drawbacks to each configuration. This will be explored in detail in Section 7.3.2.

7.2.1.3 *Possible on-site production of enzymes for lactic acid production*

The hydrolysis reaction, which produces the monosaccharides from the lignocellulosic feed, is catalysed by fungal enzymes collectively referred to as lignocellulases. The microbiology behind this process is discussed in Section 7.4. There are two ways in which the wastewater biorefinery can address the enzyme requirement of the hydrolysis step: either by buying in an enzyme cocktail from suppliers such as DuPont or Novozymes or by producing enzymes on-site. The enzymes have been shown to be one of the primary cost contributors in biorefineries (Guo et al. 2017) and can account for 25 to 30% of the operational cost of producing biofuels from 2nd generation feedstocks (Valdivia et al. 2016). Table 7-4 lists the most common enzyme manufacturers and their cellulase complexes currently available.

Table 7-10 List of commercial enzyme cocktails for the hydrolysis of lignocellulosic material

Enzyme cocktail	Manufacturer
Accellerase 1500, Accellerase Duet	DuPont
Cellic® CTec3, Celluclast 1.5L	Novozymes
Palkanol MBW	MAPS Enzymes
Spezyme CP, GC220	Genencor (now DuPont)

The alternative, on-site production of cellulase, was investigated by the National Renewable Energy Laboratory (NREL), and their calculated cost of enzymes is $6,16/kg protein. Figure 7-5 shows the simplified flow diagram of the on-site enzyme production facility. In this case study, it is proposed that cellulase be produced on-site using xylose as substrate. The feasibility of this proposal will be tested through experimentation and flowsheet development.

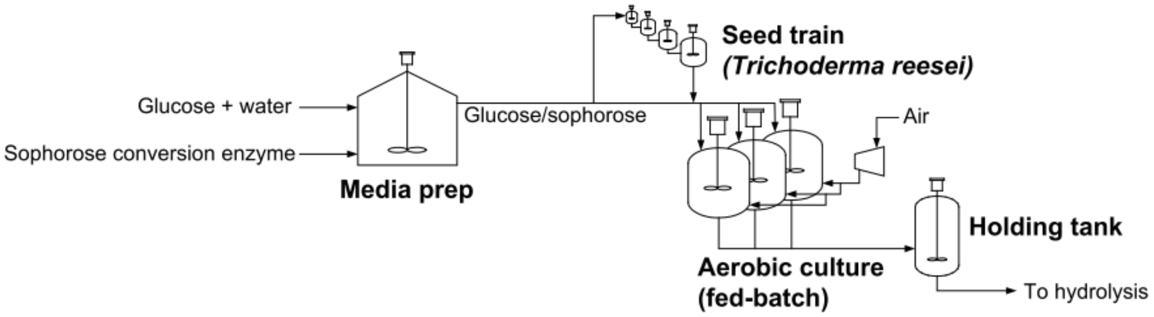


Figure 7-13 Simplified flow diagram of enzyme production (Davis et al. 2018)

7.2.1.4 *Utilising the core process waste: anaerobic digestion for energy production*

The lactic acid-free broth leaving the core and secondary bioreactor train contains the microbial cells responsible for the fermentation of the sugars, enzymes responsible for the hydrolysis of the lignocellulose into sugars, and small amounts of unconverted lignocellulosic substrate. In order to utilise all carbon in the waste feedstock and the biomass fraction arising from bioprocess units, a product and process were needed that could remove all the organics, including recalcitrant compounds. Anaerobic digestion (AD) addresses this requirement (Section 7.5). In AD, organic carbon is converted to energy, facilitated by a microbial consortium in which different microbial groupings contribute to the four stages of the process: hydrolysis, followed by acidogenesis and acetogenesis and finally, methanogenesis (Yunqin et al. 2009). These stages interlink to produce biogas which is made up of methane and carbon dioxide. The biogas is often then processed in a combined heat and power (CHP) unit and converted into electricity and heat. The two energy forms can be used to provide heating for the primary bioreactor and the digester, which both operate at slightly elevated temperatures and to provide power for the parent mill and the wastewater biorefinery. The other stream exiting an AD unit, called the digestate, is made up of solid and liquid fractions, which are then separated. The liquid stream consists of treated water with low nutrient content, and the solid stream consists of undigested organics and biosludge, which can be converted to fertiliser or soil conditioner, depending on the carbon-to-nitrogen ratio, as demonstrated in Figure 7-6.

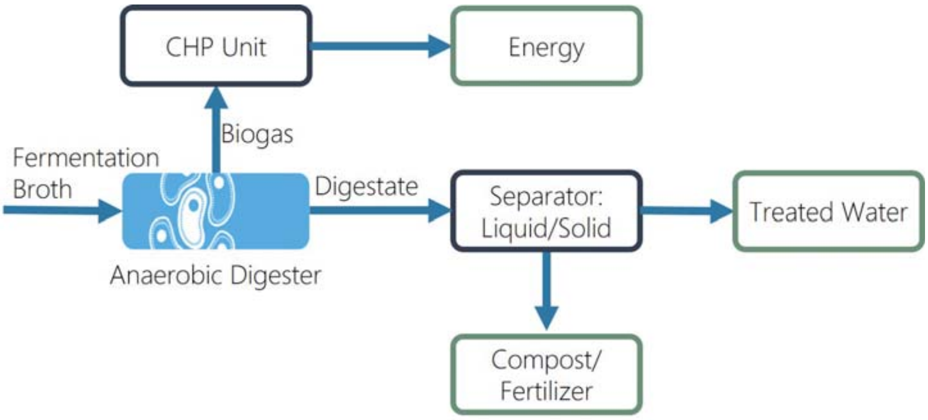


Figure 7-14 Streams flowing into and out of the anaerobic digester

7.2.1.5 *Production of compliant water: macrophyte reactor polishing*

The treated water separated from the solids in the digestate requires a polishing step to raise the quality, enabling reuse, either recycled to the parent facility or used outside the mill. Plants have been used in phytoremediation to treat contaminated water and soil (Md Yusoff et al. 2019). Constructed wetlands (CWs) are a phytoremediation system which is considered for water polishing due to their low environmental footprint and affordability (Md Yusoff et al. 2019). The macrophyte reactor is able to degrade or absorb organics, inorganics, metals and toxic compounds (Choudhary et al. 2011). CWs are used in different ways: as a stand-alone treatment system, as a polishing bioreactor or as an emergency backup treatment system for chemical plants (Department of Water Affairs and Forestry, 2007). The removal of contaminants is achieved by the simultaneous working of different mechanisms, which include sedimentation, filtration, adsorption, precipitation, microbial degradation and uptake and transformation by plants (Choudhary et al. 2011). While plants are mainly responsible for the uptake of nutrients, at their roots, they release oxygen which enables aerobic microbial degradation of pollutants (Choudhary et al. 2011). In this wastewater biorefinery, a CW will be employed to polish the water before it is reused.

7.2.2 **The proposed pulp and paper wastewater biorefinery flowsheet**

When combining all the units, the process flow diagram shown in Figure 7-7 is generated. The wastewater leaving the pulp and paper recycling mill enters the wastewater biorefinery, and the fit-for-purpose water, which is one of the wastewater biorefinery products, is returned for use in the parent mill.

The wastewater biorefinery consists of four bioprocesses with associated separation, pretreatment and purification steps. The wastewater from the mill is initially separated into sludge and liquid streams. The sludge is deashed and goes through acid pretreatment, with the cellulose stream going to the core two-stage bacterial bioreaction producing lactic acid. The xylose stream from the acid pretreatment is sent to the fungal bioreactor, producing enzymes for use in the hydrolysis stage of lactic acid production. The liquid separated from the mill wastewater, together with the waste from the lactic acid bioprocess, is sent to the anaerobic digester, which produces biogas, compost and improved water. This water goes to the macrophyte bioreactor, which produces the compliant water for return to the mill and plant biomass. The biomass, biogas, compost and ash may go to further processing for more specific uses.

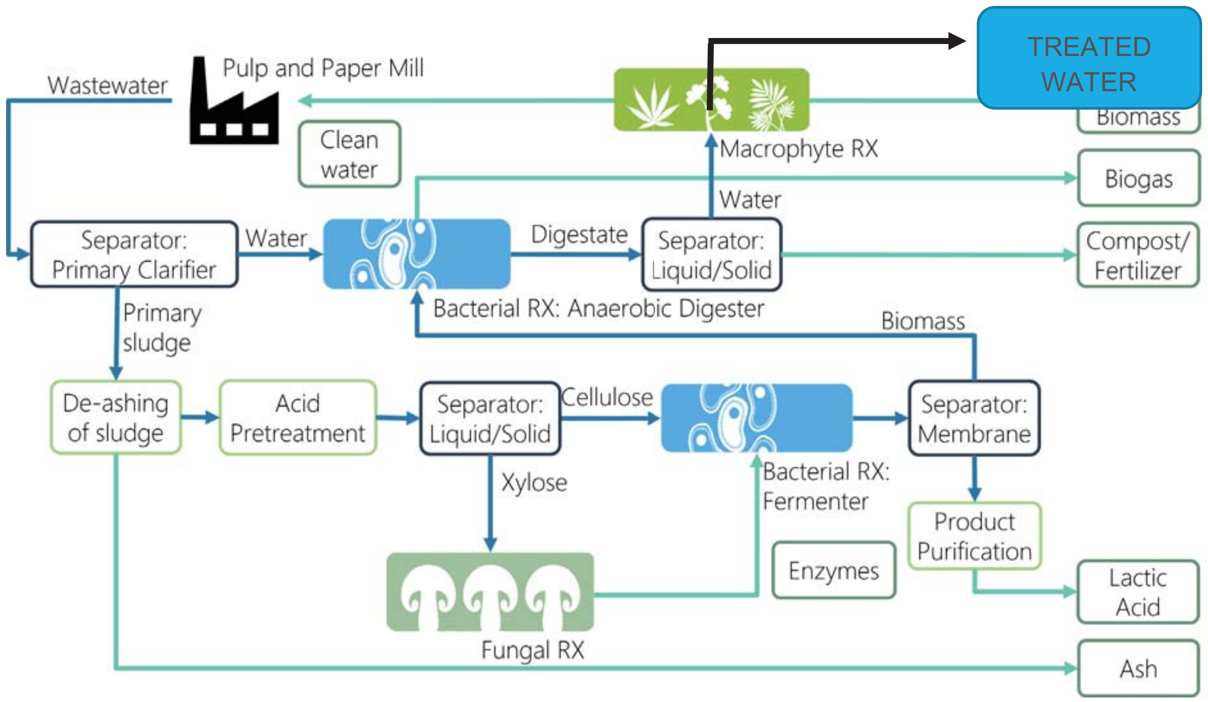


Figure 7-15 Diagram of proposed pulp and paper wastewater biorefinery

7.3 Lactic acid from a lignocellulosic stream

7.3.1 Lactic acid as a product

Lactic acid, the simplest hydroxycarboxylic acid, is a platform chemical used in several industries, the major ones being the food, pharmaceutical, health care and chemical industries (Daful et al. 2016). It also serves as an intermediate chemical for the production of acrylic acid, pyruvic acid and acetaldehyde, to name a few (Daful et al. 2016). A large part of the lactic acid produced is used to make polylactic acid (PLA), a biodegradable plastic with high tensile strength used in the packaging industry (Bapat et al. 2014).

In 2012 the global consumption of lactic acid was 259 000 tons and was expected to increase to 367 300 tons in 2017 (Jantasee et al. 2017). Lactic acid can be produced via chemical synthesis or microbial fermentation. Microbial fermentation is the preferred route, particularly because pure (L)+ or (D)- lactic acid is produced instead of a racemic mixture. It is also a more environmentally friendly process that uses renewable feedstock and has a lower energy required to deliver a highly pure product (Abdel-Rahman et al. 2013; Jantasee et al. 2017).

The fermentation of sugars to produce lactic acid is comparatively fast and has a high yield (Wessels et al. 2004). At the moment, the acid is produced from glucose, which makes up a large part of the production cost. This also competes with food and feed supply (Juturu and Wu, 2016). For this reason, lignocellulosic biomass, which is inexpensive and plentiful, is a desirable second-generation feedstock for lactic acid production. Lignocellulosic biomass includes dry grass, municipal solid waste, agricultural residues, woody forest feedstock and pulp and paper mill waste. It is mainly made up of cellulose, hemicellulose and lignin and is notoriously resistant to degradation (Tandon, 2015).

To utilise lignocellulosic biomass, two additional steps need to be added to the conventional lactic acid production process, namely pretreatment (hydrolysis) and enzymatic saccharification. The pretreatment step serves to break down the structure of the biomass so that it is more responsive to enzymatic saccharification. Several pretreatment methods have been established, including chemical methods (like acid and alkaline treatment), steam explosion, thermal pretreatment, wet oxidation and ammonia fibre explosion (AFEX).

In terms of the pretreatment of feedstock for fermentation, research has been done on several types of lignocellulosic biomass, such as sugarcane bagasse and corn stover. However, few studies consider the pretreatment of paper-based sludge (wastepaper, cardboard, recycled paper sludge, pulp and paper mill primary and secondary sludge). Several researchers state that it is not necessary to pretreat paper sludge due to the nature of the papermaking process (Kang et al. 2010; Lark et al. 1997; Lin et al. 2005; Schmidt and Padukone, 1997; Shi et al. 2015).

The lactic acid concentration reached in the fermentation depends on the amount of substrate added to the bioreactor. This, in turn, is limited by the maximum viscosity tolerated by the process. At high viscosities pumping and mixing becomes problematic. Prior deashing of the sludge increases the fraction of substrate in the sludge; therefore, a higher lactic acid concentration can be reached at the same solids loading when using deashed sludge. Another motivation for deashing the sludge is the increased enzyme efficiency. Ash in primary sludge consists of filler material (clay, TiO_2 and calcium carbonate) added during the papermaking step in the mill (Kang et al. 2010). These inhibit the enzymes in several ways, including adsorption. Chen et al. (2014b) found that every gram of clay adsorbs 3 to 5 mg of enzyme and calcium carbonate, about half as much. Nikolov et al. (2000) found that the fillers and additives added to paper form an ‘envelope’ around the fibres, which minimises the enzyme’s interaction with the cellulose. Kang et al. (2011) showed that they required 30% fewer enzymes when using the deashed sludge to achieve the same ethanol yield as sludge that has not been deashed.

Lastly, the calcium carbonate in the ash acts as a buffer in the sludge, and therefore, more acid is required to adjust the pH to five. Chen et al. (2014) showed that, following deashing, the amount of sulphuric acid required to adjust the pH of virgin Kraft mill primary sludge decreased from 0.40 to 0.07 ton/BDT sludge, and for recycled paper mill sludge, this decreased from 0.44 to 0.08 ton/BDT sludge. Deashing can be performed by chemical treatment (Marques et al. 2008) or flotation and screening (Chen et al. 2014b; Kang et al. 2011). Kang et al. (2011) achieved deashing by flotation with CO_2 gas, followed by screening with a 100 mesh screen. A compositional analysis of the sludge showed some loss of glucan and xylan during the deashing, but mostly ash was removed.

As mentioned earlier, after pretreatment, additional enzymatic saccharification is necessary to completely break down the hydrolysed lignocellulose into fermentable sugars. The critical enzymes needed for the successful hydrolysis of cellulose and hemicellulose include a combination of xylanases and cellulases. For the complete hydrolysis of cellulose to glucose, a combination of endoglucanases, exoglucanases and β-glucosidases is required (Venkatesh, 1997). This step further increases the cost of production and slows down the process.

Many different microorganisms have the capacity to produce lactic acid, including fungi, bacteria, cyanobacteria and microalgae (Abdel-Rahman et al. 2013). Amongst bacteria, the most prominent lactic acid producers are from the genus *Lactobacillus* and *Bacillus*. Strains that are part of the *Lactobacillus* genus are called “Lactic Acid Bacteria”, or LAB for short. LAB require complex media rich in nutrients, whereas *Bacillus* strains can ferment sugars in minimal media (Poudel et al. 2016) and are able to operate at higher temperatures. The most promising *Bacillus* strains are *B. coagulans, B. subtilis, B. licheniformis*, and *B. thermoamylovorans* (Poudel et al. 2016).

To achieve maximum lactic acid production, utilisation of both glucose and xylose is critical when using a lignocellulosic feedstock. This remains a major challenge due to carbon catabolite repression (CCR), in which glucose is used preferentially, owing to it inhibiting other pathways. CCR features in most lactic acid producers, causing reduced fermentation efficiency and increased production cost (Abdel-Rahman and Sonomoto, 2016). *B.coagulans* is known to utilise both glucose and xylose simultaneously, i.e. it is not catabolite repressed (Maas et al. 2008).

As expected, temperature and pH play a big role in the fermentation process, influencing cell growth, lactic acid concentration, yield and productivity. The acidic lactic acid product requires ongoing pH control to prevent the inhibition of cell growth. Most lactic acid-producing bacteria operate in the pH range of 5 to 7 (Wang et al. 2015). To control the pH, a neutralising agent must be added to the fermentation broth. $CaCO_3$, $Ca(OH)_2$, NaOH, KOH and NH_3 are frequently used (Poudel et al. 2016).

7.3.2 **Process Flow and Reactor configurations**

To produce lactic acid from lignocellulosic biomass, we can build on the copious research into ethanol production and early studies on lactic acid from woody biomass. Two methods have been used: separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF). With SHF, the enzyme-mediated hydrolysis step is performed in a separate vessel to the microbial fermentation reaction. SSF combines the two steps by adding the bacterial inoculum to the vessel containing the lignocellulosic hydrolysate (from pretreatment) and enzymes. As the enzymes break the lignocellulose down into sugars, bacteria ferment these into lactic acid. There are several advantages to using SSF over SHF, such as the use of only one reaction vessel (lowering capital expenditures), a more rapid processing time and increased productivity (Marques et al. 2008). The biggest benefit is the low sugar (hexose and pentose) concentration maintained since, as it is released by the rate-limiting saccharification step, it is directly fermented. This prevents substrate inhibition (Martinez et al. 2013), and enzyme productivity is not limited by feedback inhibition. Marques et al. (2008) demonstrated the superiority of SSF over SHF, reporting a high lactic acid yield of 0.97 $g_{\text{lactic acid}}/g_{\text{carbohydrates}}$ for SSF compared with 0.81 $g_{\text{lactic acid}}/g_{\text{carbohydrates}}$ for SHF when using recycled paper sludge, a commercial enzyme cocktail for hydrolysing cellulolytic and xylanolytic biomass and *Lactobacillus rhamnosus* ATCC 7469 for the fermentation step. The final lactic acid concentration and overall productivity were also higher with SSF than with SHF.

Generally, the lactic acid fermentation process is operated in batch mode, with associated low productivity due to long fermentation time, turn-around time and low cell density (Abdel-Rahman et al. 2013). Fed-batch, repeat-batch (or draw-and-fill) and continuous fermentation offer the potential for improved operation. Fed-batch operation refers to the further addition of nutrients and enzymes at certain intervals for the duration of the process, preventing nutrient limitation (Romaní et al. 2008). Repeat-batch fermentation refers to the process where a significant fraction of the cell culture from a previous fermentation batch is combined with fresh media, and fermentation commences again, reducing turn-around time (Wee et al. 2006). Continuous fermentation differs from batch fermentation in that it is an open system operated at a steady state. Figure 7-6 summarises the advantages and disadvantages of the different modes of operation. Unlike batch fermentation, continuous fermentation does not suffer from end-product inhibition, and the cells are kept in a stable physiological state, maintained by a constant growth rate optimised to achieve maximum productivity (Poudel et al. 2016). One drawback of continuous fermentation is that the system operates at a low cell density, and cell washout can happen easily. To enhance conventional continuous fermentation, high cell density (HCD) can be achieved by cell recycling (Pal and Dey, 2013) or cell immobilisation (Senthuran et al. 1997).

Table 7-11 Advantages and disadvantages of different operation modes for fermentation

Fermentation Mode	Advantages	Disadvantages
Batch	Simple operation High product concentration Reduced risk of contamination	Low productivity Substrate and end-product inhibition High turn-around time between run cycles
Fed-batch	Overcome substrate inhibition High product concentration High biomass concentration Extended production phase Increased productivity	End-product inhibition
Repeated-batch, also known as Draw-and-fill	Reduced turn-around time	Increased risk of contamination
Continuous	High productivity Control growth rates Steady operating conditions Less frequent shutdown	Incomplete utilisation of carbon source Increased risk of contamination Reduced biomass concentration (unless biomass retention is included) Susceptible to cell washout

In a survey of the limited literature published on lactic acid production from paper sludge, all studies used batch or fed-batch operation. Marques et al. (2017) used the data generated from their fed-batch reactor in which a membrane was used to recycle cells and remove products to set up a model on Superpro Designer (Intelligen, Inc.) that simulates continuous operation. Upon widening the search to include other lignocellulosic feedstocks, a number of papers reported continuous fermentation, but continuous SSF for lactic acid fermentation was not reported. A kinetic model has been developed for continuous SSF for the production of ethanol, which was verified by experimental data (South et al. 1995).

7.4 Enzymes from a lignocellulosic stream

There are numerous microorganisms that have been investigated and found to have the ability to break down lignocellulosic biomass; most of these are fungi or bacteria (Woo et al. 2014). The microorganisms produce a diversity of cellulolytic and hemicellulolytic enzymes under aerobic and anaerobic conditions (Wongwilaiwalin et al. 2010). Lignocellulose-degrading microorganisms are naturally present in wastes and take part in the composting process (Tuomela et al. 2000). Although both bacteria and fungi are known to degrade lignocellulosic biomass, fungi generally degrade lignin better than bacteria (Medina et al. 2017).

Fungi are highly active in degrading wood and are categorised into three fungal classes with the ability to degrade the lignocellulosic biomass: white-rot, brown-rot and soft-rot fungi(Manavalan and Heese, 2015). White-rot fungi degrade all the wood fraction, including the tough structure of the lignin, growing on both hardwood and softwood(Blanchette, 1995). There are many white-rot fungi species that have been demonstrated to produce ligninolytic enzymes, for example, *Trametes versicolor, Trametes pubescens, Phanerochaete chrysosporium,* and *Aspergillus niger* (Long and Sweet, 2006). These fungal species have all been exploited using different lignocellulosic materials and have shown high levels of efficient degradation (Aveiro and Janeiro, 2006; Galhaup and Haltrich, 2001; Ryan, Leukes and Burton, 2005)

There are two technologies that are currently applied for microbial enzyme production, namely Solid-State Fermentation (SoSF) and Submerged Fermentation (SmF). SmF technologies have been traditionally used for enzyme production; however, SoSF technologies have been more recently used to produce several enzymes (Rodr and Sanrom, 2005). SoSF, characterised by the absence or near absence of water, is more suitable for complex substrates and can be ideal for fungal growth since it mimics the natural conditions of fungal habitat (Rajwar et al. 2016).

7.4.1 Properties of lignocellulosic enzymes

7.4.1.1 *Cellulases*

Cellulose is the β-1,4-polyacetal of cellobiose (4-O-β-D-glucopyranosyl-D-glucose). It is a structural component of the primary cell wall of green plants and a linear polymer of glucose derived from D-glucose units (Shahzadi et al. 2014). It condenses through β (1- 4)- glycosidic bonds, usually set in microcrystalline structures, making its hydrolysis very difficult under natural conditions (Dyk and Pletschke, 2012). Cellulose accounts for about 50% of all the carbon utilised by plant biomass during photosynthesis yearly (Chen, 2006). In nature, cellulose is typically hydrolysed by microorganisms, mainly fungi and bacteria. Cellulases are a group of enzymes that can degrade cellulose; these proteins are composed of a complex structure and can degrade cellulose. These enzymes include endoglucanase, exoglucanase, cellobiohydrolase and β-glucosidase.

7.4.1.2 *Hemicellulases*

Hemicellulases are either glycoside hydrolases or carbohydrate esterases and are classified into families based on their activity and homology of primary sequence(Cragg et al. 2015). The hydrolysis of glycosidic bonds is carried out by glycoside hydrolases enzymes, whereas carbohydrate esterases enzymes cleave the ester linked acetate and ferulic acids side chains. The structure of hemicellulose is heterogenous and thus requires several enzymes to hydrolyse(Chen HZ, 2006). Enzymes that can hydrolyse hemicellulose are endo-β-1,4 xylanase, exo-β-1,4-xylosidase, exo-β-1,4 mannosidase, endo-β-1,4-mannanase, α-Glucuronidase, α-Galactosidase, endo-galactanase, α-L-arabinofuranosidase, acetyl xylan esterases, Acetyl mannan esterase, ferulic and p-cumaric acid and esterases (Zhao et al. 2016).

7.4.1.3 *Lignase*

Ligninolytic enzymes are used for delignification; these enzymes increase the exposure and accessibility to both cellulose and hemicellulose. One of the advantages of these enzymes is the recovery of valuable phenolic compounds found in lignin degradation. (Liguori and Faraco, 2016). Ligninolytic enzymes are categorised into two clusters laccase and peroxidases (Krause et al. 2003). The total peroxidases are divided into lignin peroxidase (LiP) and manganese peroxidase (MnP). The LiP enzyme is characterised by its ability to degrade aromatic structures such as methoxybenzenes and veratryl alcohols(Rodrigues et al. 2008). Another characteristic of LiP is its high redox potential. LiP enzymes are a glycosylated monomeric of 40 kDa with 343 amino acids (Martínez, 2002).

Manganese peroxidase are glycoproteins with a molecular weight ranging from 32-62.5 kDa, with an estimated number of 350 amino acids (Plácido and Capareda, 2015). MnP is characterised by heminic group and helixes structures, and this is the feature that distinguishes MnP from other peroxidases (Martínez, 2002). Laccases are one of the well studied enzymes belonging to the blue multicopper ligninolytic oxidases group (Thurston, 1994). These enzymes are mostly extracellular, existing as either monomers or homodimers with the range of molecular weight of the laccase enzyme monomer 60–80 kDa, with carbohydrates (Mayer and Staples, 2002; Thurston, 1994). Interest in laccases has increased because of their potential use in the detoxification of pollutants and bioremediation of phenolic compounds.

7.4.2 Applications of lignocellulosic enzymes

Lignocellulosic enzymes are used as a biotechnological tool (and thus applied in various agricultural, food, chemical, fuel, animal feed, laundry and pulp and paper industries (Howard et al. 2003)).

Table 7-12 Industrial enzyme application (Kirk et al. 2002)

Industry	Enzyme class	Application
Detergent	Protease Amylase Lipase Cellulase Mannanase	Protein stain removal Starch stain removal Lipid stain removal Lipid stain removal Cleaning, colour clarification, anti-redeposition (cotton)
Starch and fuel	Amylase Amyloglucosidase Pullulanase Glucose isomerase Cyclodextrin-glycosyltransferase Xylanase Protease	Starch liquefaction and saccharification Saccharification Saccharification Glucose to fructose conversion Cyclodextrin production Viscosity reduction (fuel and starch)
Food	Protease Lipase Lactase Pectin methyl esterase Pectinase Transglutaminase	Milk clotting, infant formulas (low allergenic), flavour Cheese flavour Lactose removal (milk) Firming fruit-based products Fruit-based products Modify visco-elastic properties
Baking	Amylase Xylanase Lipase Phospholipase Glucose oxidase Lipoxygenase	Bread softness and volume, flour adjustment Dough conditioning Dough stability and conditioning (*in situ* emulsifier) Dough stability and conditioning (*in situ* emulsifier) Dough strengthening Dough strengthening, bread whitening
Animal	Phytase Xylanase Glucanase	Phytate digestibility – phosphorus release Digestibility Digestibility
Beverage	Pectinase Amylase Glucanase Acetolactate decarboxylase	Depectinisation, mashing Juice treatment, low-calorie beer Mashing Maturation (beer)
Textile	Cellulase Amylase Pectate lyase Catalase Bleach Laccase Bleaching Peroxidase	Denim finishing, cotton softening De-sizing Scouring Bleach termination Bleaching Excess dye removal
Pulp and paper	Lipase Protease Amylase Xylanase Cellulase	Pitch control, contaminant control Biofilm removal Starch-coating, de-inking Bleach boosting Deinking, drainage improvement, fibre modification
Organic synthesis	Lipase Acylase Nitrilase	Resolution of chiral alcohols and amides Synthesis of semisynthetic penicillin Synthesis of enantiopure carboxylic acids
Fats and oils	Lipase Phospholipase	Transesterification Degumming, lysolecithin production

7.5 Products for recalcitrant components

The bioproducts produced from a lignocellulosic stream will always leave a stream of unreacted or recalcitrant compounds. In the wastewater biorefinery, these are not considered waste but, where appropriate, are sent to another bioreactor train to produce further products simultaneously with improving the water stream towards the compliant water product. The most mature technology for this stage of the biorefinery is in the production of energy, as this has historically been part of the wastewater treatment scenarios. In a wastewater biorefinery, energy production is, therefore, a key option for valorising and removing the components unused by the bioproduct production units. However, it is worth considering the potential of other possibilities for this stream so that the final flowsheet is more informed, possibly pointing towards future investigation for preferred routes.

7.5.1 Energy as a product for recalcitrant components

7.5.1.1 *Anaerobic digestion*

Anaerobic digestion (AD) is the process in which organic matter is broken down by microorganisms in the absence of oxygen, as shown in Figure 7-8. This breakdown of organic matter results in the production of biogas (Chynoweth et al. 2000). The AD process allows for the removal of nutrients and organic compounds, effectively improving the quality of the effluent and digestate. The AD process not only results in the production of biogas and improved quality effluent but is also associated with the production of Volatile fatty acids (VFA's) (Huang et al. 2016).

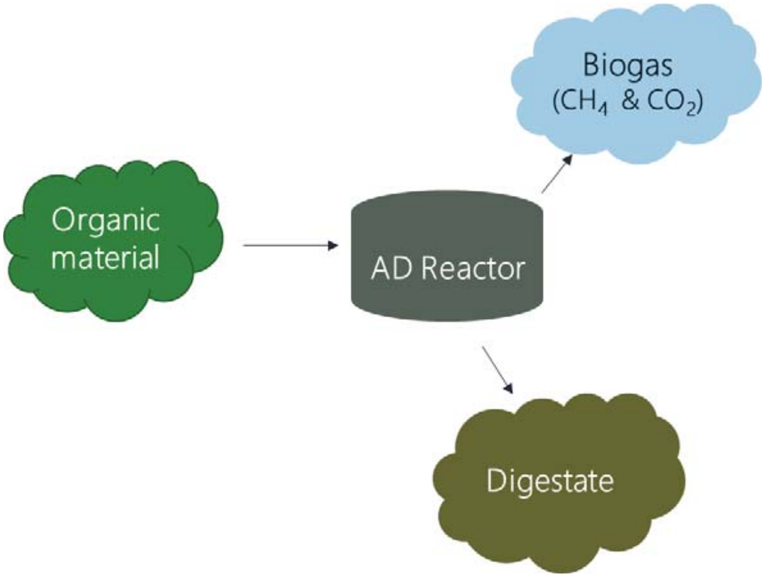


Figure 7-16 Simplified anaerobic digestion process

The biogas produced during anaerobic digestion is produced in the form of methane (CH_4) and carbon dioxide (CO_2); however, in some cases production of hydrogen (H_2) can be observed. In most cases, CH_4 is the desired form of biogas and comprises approximately 60% of the biogas produced (Chynoweth et al. 2000). It is possible to optimise methane production in the AD process by optimising reaction conditions favouring methanogenesis. The generated biogas can be utilised for various purposes, including vehicle fuels, heat and electricity (Mao et al. 2015).

The other products of the AD process have also been repurposed. For example, VFAs may be used as a main product or as an intermediate resource in other processes, such as polymer production (Van Loosdrecht and Brdjanovic, 2014). The digestate produced is rich in nutrients such as nitrogen (N) and phosphorus (P). As a result, the digestate may be used as fertiliser; however, this is dependent on the nutrient concentration. The digestate can be safely used as fertiliser at low nutrient concentrations; however, high nutrient concentrations may result in eutrophication (Huang et al. 2016).

7.5.1.2 *Microbiology of AD*

The AD process is comprised of a series of sub-processes that result in the production of several bioproducts. The sub-processes are hydrolysis, acidogenesis and acetogenesis and methanogenesis, as demonstrated in Figure 7-9 (Mao et al. 2015).

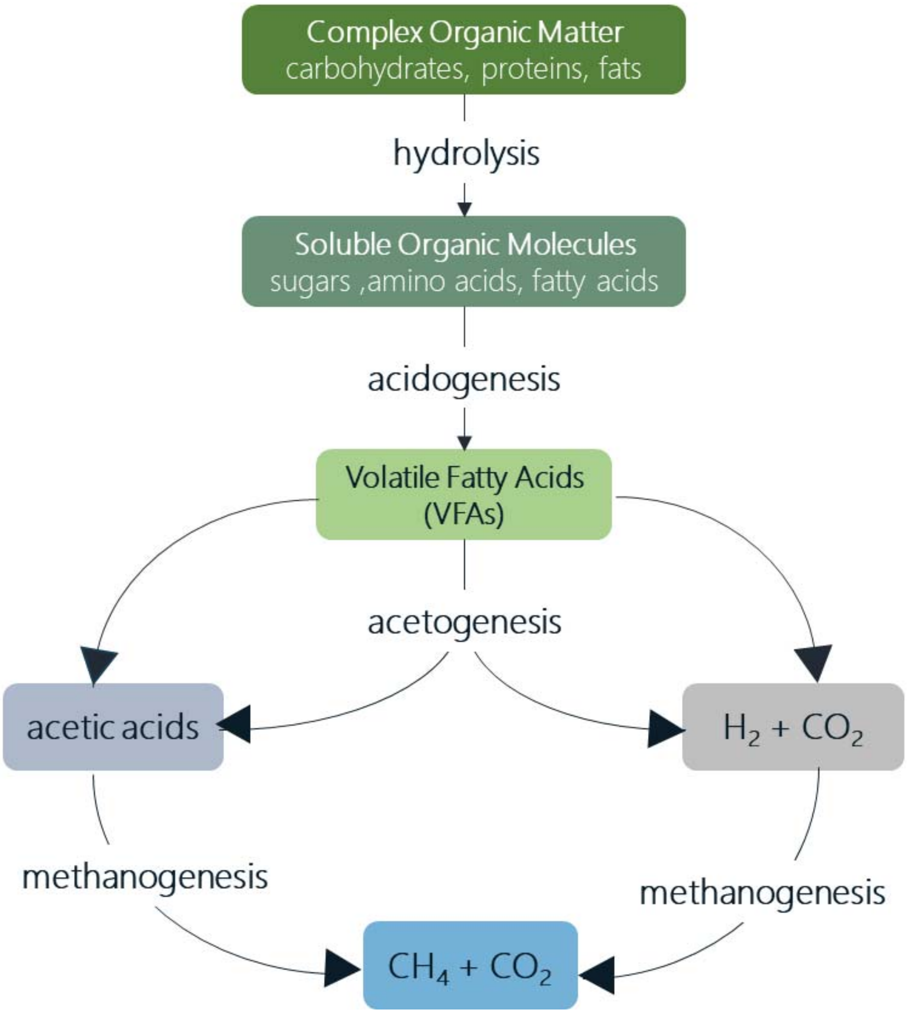


Figure 7-17 Biological steps involved in anaerobic digestion

Hydrolysis is the first step in the AD process and is often referred to as the rate-limiting step. Hydrolysis involves the breakdown of complex organic polymers such as carbohydrates, proteins and fats into less complex monomers. Hydrolytic microorganisms secrete enzymes which facilitate the breakdown of organic material. The products of this process include sugars, amino acids and long-chain fatty acids (LCFAs) (Lee et al. 2014). The hydrolysis step is largely dependent on substrate composition; hence it is considered the rate-limiting step. (Chernicharo et al. 2015).

Following hydrolysis, the monomers, specifically sugars, amino acids and LCFAs, are further processed through acidogenesis. Acidogenic microorganisms break down the products of hydrolysis into volatile fatty acids (VFAs) such as acetate, propionic and butyric acids (Abbasi et al. 2012; Lee et al. 2014). In some cases, VFAs are preferred as the final product. In this case, the acetogenesis, which would be the next step in the process, is left incomplete (Van Loosdrecht and Brdjanovic, 2014).

In the case where VFA production is not the desired outcome, acetogenesis would be allowed to occur. Acetogenesis is the further breakdown or consumption of VFAs produced from acidogenesis by acetogenic microorganisms. This results in the production of acetic acid, carbon dioxide and hydrogen (Abbasi et al. 2012). This is followed by the last step in the AD process, known as methanogenesis. In this process, strictly anaerobic methanogenic microorganisms consume the acetic acid, carbon dioxide and hydrogen produced in the previous step. The result of this consumption is the production of methane (Abbasi et al. 2012). In many cases, the aim of utilising the AD process is to produce methane; however, as mentioned above, VFA production is also prioritised in some cases.

7.5.1.3 *Benefits of Anaerobic Digestion*

There are many benefits associated with Anaerobic digestion, the first of which is the production of useful bioproducts. Waste that was previously viewed as useless waste can be treated to produce products that are useful in many industries, while remediation of wastewater occurs.

Anaerobic digestion is also considered a more economical alternative to other wastewater treatment methods. One of the main benefits, however, is that AD is a more environmentally friendly treatment method requiring less energy and generating less pollution and contamination (Kamali and Khodaparast, 2015).

7.6 Concluding remarks regarding the potential of lignocellulosic streams

In this case study, an integrated pulp and paper wastewater biorefinery was built around harnessing the resources contained with a combined recycling mill effluent. By adhering to the principles of our wastewater biorefinery concept, the traditional wastewater treatment system was substituted with multiple biorefinery units. The main process unit – a bioreactor, transformed the carbon contained within the lignocellulosic biomass to lactic acid, a platform chemical of high-value. Since the residual waste stream still contained a significant amount of organic material, an additional bioreactor in the form of an AD was incorporated to generate biogas, an energy product. To valorise the xylose stream remaining after pre-treating the feedstock, a fungal reactor was added to produce lignocellulolytic enzymes, which can be used on-site in the pretreatment of the lignocellulosic biomass feedstock itself. Finally, a macrophyte reactor was added to clean the remaining effluent to generate a “fit-for-purpose” water stream, which can be used in the recycling mill or in the biorefinery unit system itself.

By concomitantly generating multiple bioproducts alongside treated water, the recycling mill can be transformed into a dynamic and flexible wastewater biorefinery system. However, due to the nature of the feedstock being a dilute stream containing recalcitrant compounds, each unit must be carefully selected and designed to ensure optimum performance combined with feasible techno-economics and minimal environmental impacts.

8 Experimental proof of concept for products from lignocellulosic wastewater

In this chapter, preliminary bench-scale studies are presented to demonstrate the proof of concept for the integrated pulp and paper wastewater biorefinery introduced in Chapter 7 by focusing on lactic acid, lignocellulolytic enzymes and biogas production.

8.1 Lactic acid from lignocellulose

The focus of the experimental work is to answer some of the questions that arise from the literature review of current lactic acid production methods. The work can be divided into three major sections, as shown in Figure 8-1. The first focuses on the fermentation capacity of Bacillus coagulans DSM 2314, the second on the enzymatic hydrolysis of pulp and paper sludge, and the third section on reactor configuration and operation.

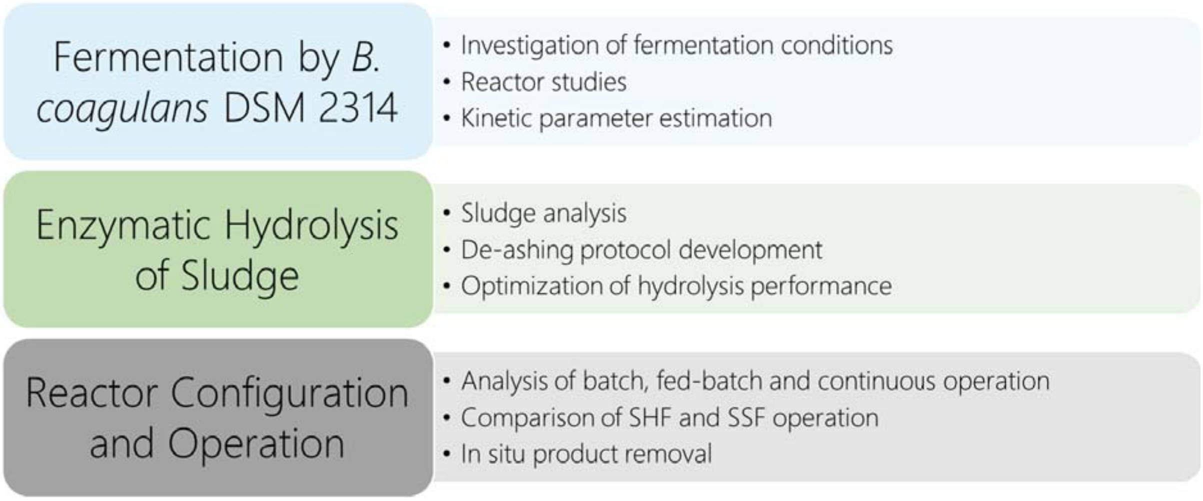


Figure 8-18 Lactic acid from lignocellulose: Initial growth rate experiments

8.1.1 Study of fermentation conditions: Fermentation conditions

Bacillus coagulans DSM 2314 can ferment glucose and xylose under both aerobic and anaerobic conditions. For lactic acid production, the fermentation must proceed under anaerobic conditions. The difference in growth rate and product formation rate was investigated under aerobic and anaerobic conditions.

8.1.1.1 *Method for study of fermentation conditions*

For the aerobic experiment, 500 mL shake flasks were used with 100 mL reaction medium. The medium consisted of Tryptone Soy Broth (TSB) with 40 g/L glucose added after autoclaving. To increase the buffer capacity, a 100 mM phosphate buffer was added, and the resulting initial pH was 7. After adding a 10% inoculum, the flasks were placed in an incubator rotating at a speed of 120 rpm with the temperature controlled at 50°C. Samples were taken at regular intervals, and the absorbance at 660 nm and the pH were measured. The same conditions were used for the anaerobic experiments, except 100 mL crimp-sealed serum bottles were used, and sampling was done with a needle to maintain anaerobic conditions. Both experiments were done in triplicate.

8.1.1.2 *Results of the study of fermentation conditions*

Figure 8-2 shows the change in OD over time for the batch shake flask experiment. For growth under aerobic conditions, the OD increased to a higher number than for anaerobic conditions; the pH bottomed out at 4.5 for both conditions, which indicates that this is the minimum pH at which the bacterium can grow. The fact that the pH dropped quicker in the anaerobic run is indicative of lactic acid forming rather than aerobic growth metabolites. More energy is released from glucose metabolism for cell synthesis during aerobic growth, as indicated by the higher growth rate and final OD reached. From these results, it is clear that pH control is necessary to sustain growth for longer periods due to the high amounts of acid being produced as part of the bacteria metabolism.

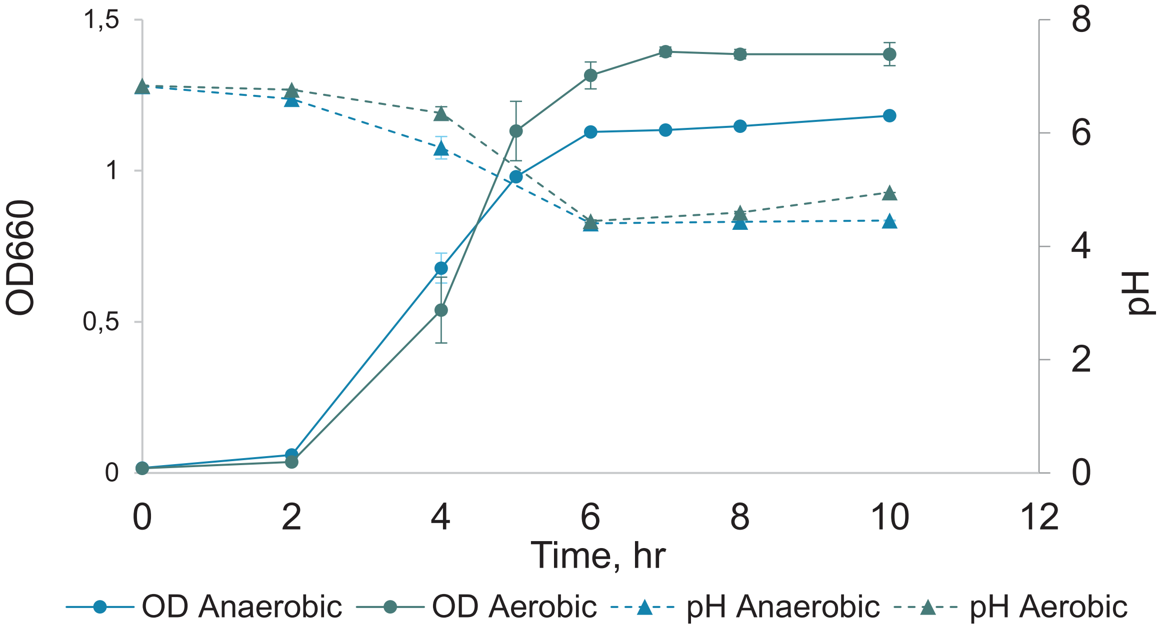


Figure 8-19 Growth curve for *B. coagulans* DSM 2314 in TSB, pH-controlled only by a buffer.

8.1.2 Lactic acid from lignocellulose: Reactor studies

To determine the maximum amount of lactic acid that can be produced in a system where the pH does not limit growth, bioreactors with pH control were used.

8.1.2.1 *Impact of pH Control*

8.1.2.1.1 *Method*

The CeBER laboratory Infors™ Sixfors™ reactors were used; the working volume was 250 mL. The inoculum was prepared in two stages, first 50 mL Tryptone Soy Broth (TSB) was inoculated with the contents of a thawed cryovial, and after 24 hours, 10 mL of the pre-inoculum was transferred to 100 mL TSB. After 4 hours, 25 mL of the inoculum was added to each reactor which had been filled with 225 mL medium. The TSB medium in the bioreactor was supplemented with a concentrated sugar solution to reach a final concentration of 40 g/L glucose or xylose after mixing. The medium was buffered to a pH of six using a 150 mM phosphate buffer. The pH was controlled by the addition of 3 M NaOH. The reactors were operated under anaerobic conditions by sparging with nitrogen gas before the start of the experiment and thereafter after sampling. An agitation rate of 150 rpm and temperature of 50°C was used, and to avoid moisture loss, a condenser supplied with coolant at 1°C was placed on the vent line. 1 mL samples were withdrawn from the reactors at regular time intervals and were used to measure the absorbance at 660 nm and the pH to ensure that the pH meter in the reactor was still accurate. Of each sample, 0.6 mL was centrifuged at 13 000 rpm for 10 minutes, and the supernatant was analysed for sugars and lactic acid using high-performance liquid chromatography (HPLC). The experiments were run in duplicate and stopped after the OD_{660} reached the stationary phase.

8.1.2.1.2 *Results*

Controlling the pH in the reactor adds complexity and cost to the fermentation; therefore, an experiment was done to compare biomass formation with and without pH control; the results are shown in Figure 8-3. The biomass concentration is directly related to the amount of lactic acid produced, both during growth and in the stationary phase, since it is metabolised for energy during the anaerobic Embden-Meyerhof-Parnas pathway. In this experiment, glucose was the carbon source. The total biomass formed under pH-controlled conditions is more than double that without pH control. Not only that, but the rate at which biomass is formed is also negatively influenced toward the end of the experiment, where no pH control was applied. The pH-controlled reactor run reaches an OD_{660} close to the final OD_{660} of the pH-uncontrolled run after approximately four hours, whereas the pH-uncontrolled run takes another two hours to reach the stationary phase. It is evident from these results that controlling the pH is invaluable for achieving a high biomass concentration and, therefore, for lactic acid production.

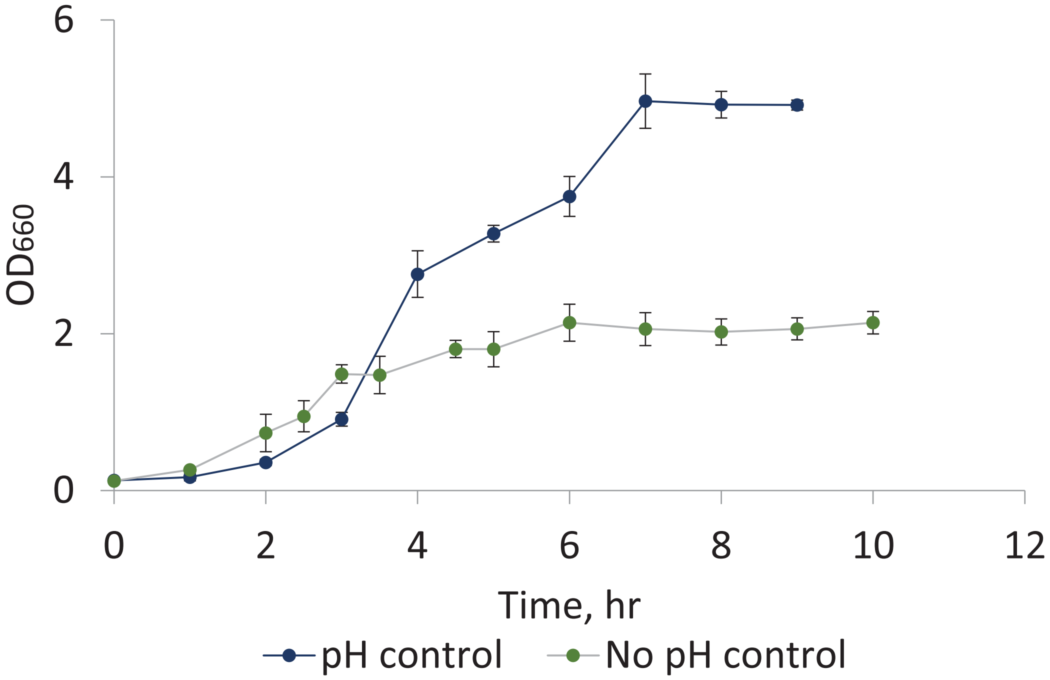


Figure 8-20 Comparison of the growth rate and extent of a reactor run with pH control and one without

Figure 8-4 shows the glucose consumption and lactic acid production for the pH-controlled reactor run. Glucose consumption continued past the stationary phase, and after 24 hours, a final sample was taken (data not shown), and no glucose was detected. The continued consumption of glucose past the stationary phase can be ascribed to cellular metabolism for the release of the energy required to maintain the cells. The lactic acid yield of 73% was obtained with a final lactic acid concentration after 24 hours of 37.7 g/L. The productivity in the first 11 hours was 2.76 g/L/h. When comparing these values with what has been reported for other lactic acid bacteria, the productivity is reasonable, but the yield is lower than expected, suggesting further optimisation.

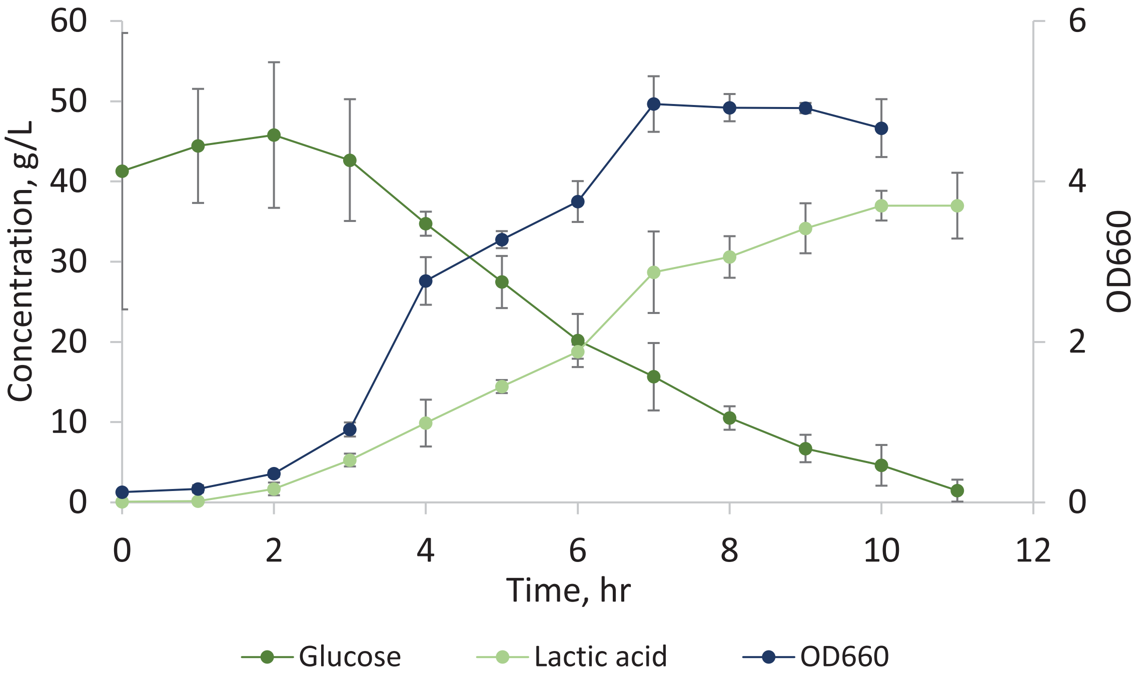


Figure 8-21 Growth curve for Bacillus coagulans DSM 2314 using glucose as substrate under anaerobic conditions and automated pH control through base addition

8.1.2.2 ***Impact of Carbon Source***

8.1.2.2.1 *Method*

The same reactor protocol was followed as with the other experiments, except xylose instead of glucose was added as the substrate in one of the experiments. The pH was also controlled at 6.

8.1.2.2.2 *Results*

Figure 8-5 shows the growth curves for glucose and xylose as carbon sources; xylose was metabolised at a slower rate than glucose, but at the end of growth, the same amount of biomass was formed. From this, it can be deduced that the limiting factor for overall biomass production is not the type of carbon source or metabolic pathway utilised.

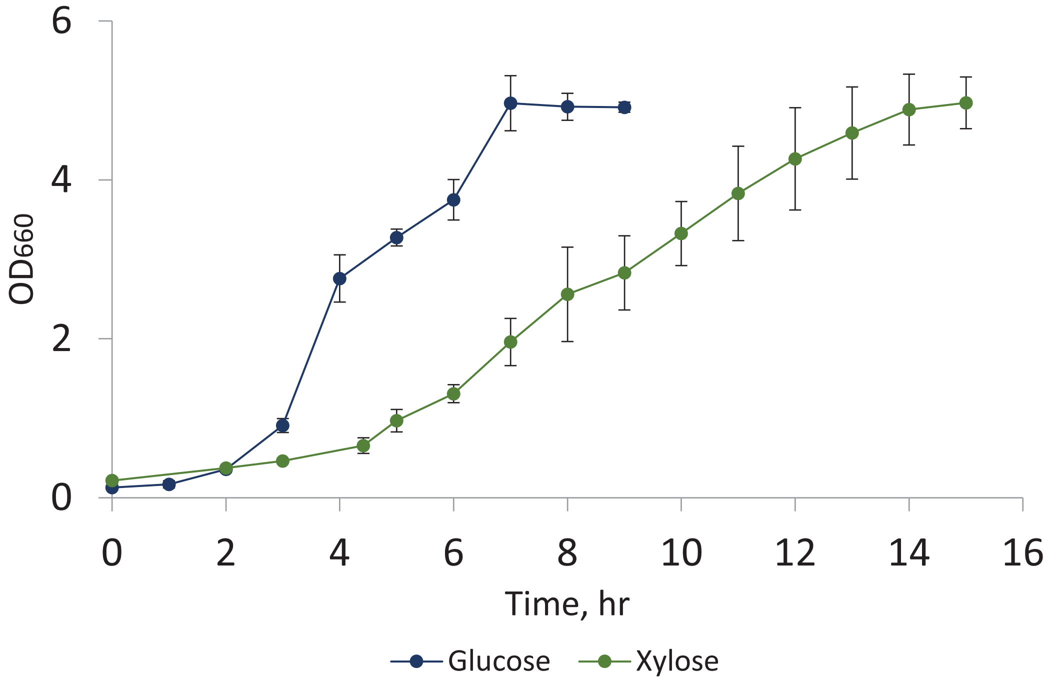


Figure 8-22 Growth curve for a reactor run with glucose as substrate and one with xylose as substrate, both runs were pH-controlled

A bioreactor run without pH control was done to confirm previous findings that this bacterium does not exhibit carbon catabolite repression (CCR). Figure 8-6 shows these results. The amount of lactic acid produced, and the growth rate for the mixed sugars is much lower than for the bioreactor runs done with single sugars (Figure 8-7). The cells were viewed under a microscope, and they appeared elongated, indicating that they were stressed. This is unexpected and needs to be investigated further.

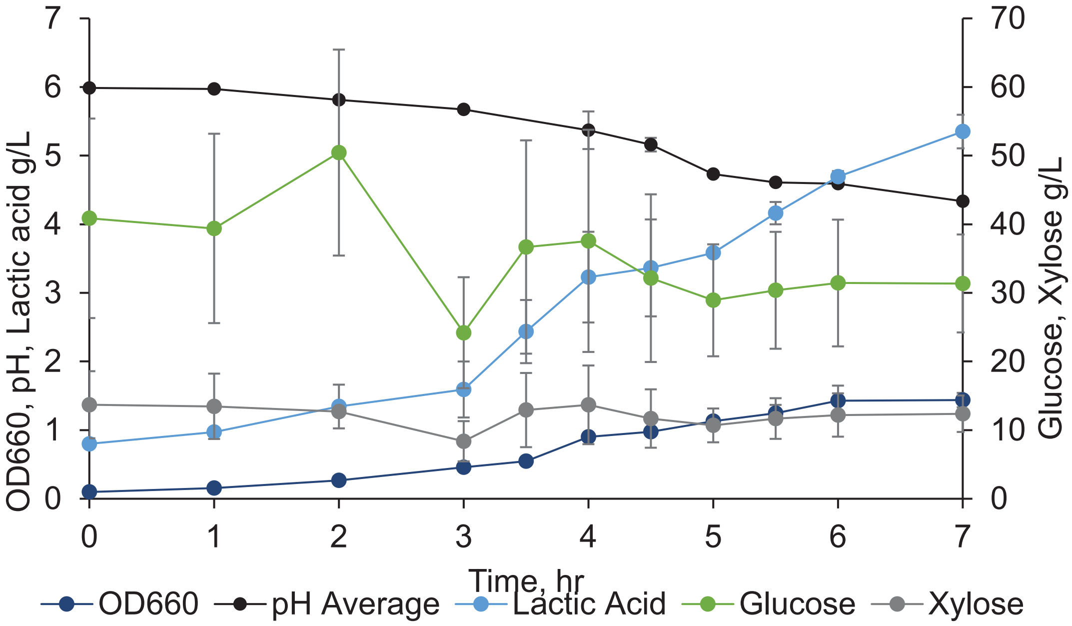


Figure 8-23: pH-uncontrolled reactor run with 75% glucose and 25% xylose as carbon source

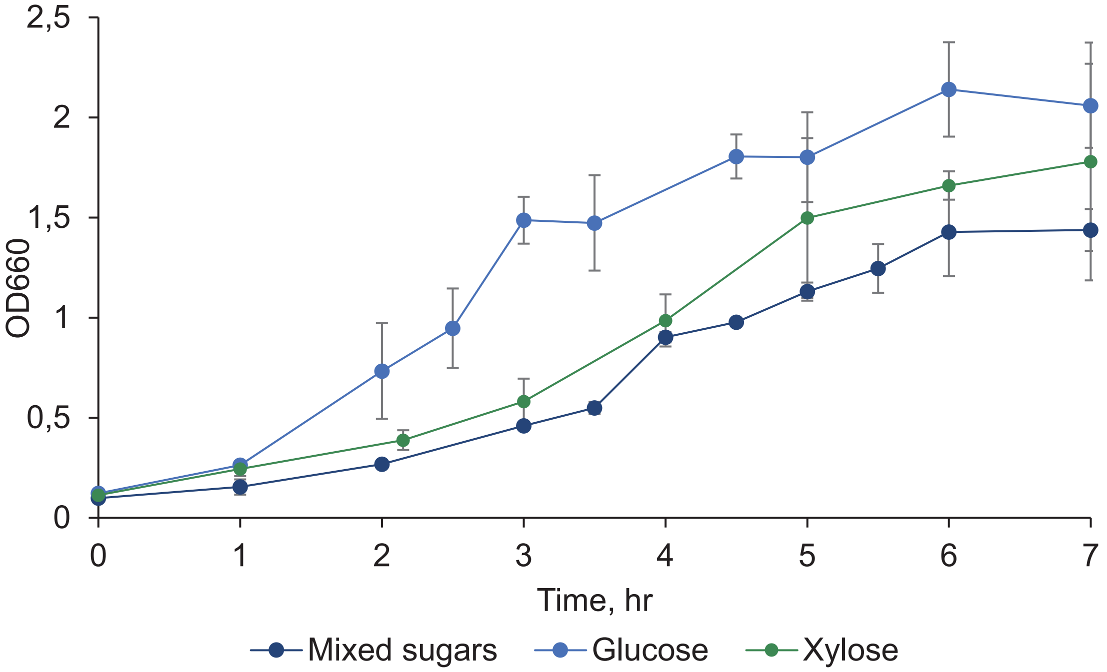


Figure 8-24 Change in optical density of fermentation broth with different carbon sources

8.1.3 Lactic acid from lignocellulose: Lactic acid as an inhibitor

Lactic acid acts as an inhibitor during the fermentation of sugars by *Bacillus coagulans* DSM2314. The exact mechanism of inhibition is still unclear. It is important to understand the extent of the inhibition since it has an impact on the maximum lactic acid concentration that can be reached during fermentation. The acidic nature of the product leads to a drop in the pH of the broth, which inhibits the bacterium, but the lactic acid ion also inhibits its growth. The impact of the inhibition by the lactic acid ion was tested by varying the amount of lactic acid in the broth while keeping the initial pH constant.

8.1.3.1 *Multiwell plate experiments for lactic acid inhibition*

8.1.3.1.1 *Method*

Multiwell plates are useful to determine the impact of increasing or decreasing a certain parameter over a range of values. Van der Pol et al. (2016) used 96-well plates to rapidly screen for the impact of pretreatment by-products on the fermentation of lignocellulose to lactic acid. In this work, 12-well plates were used to assess the inhibitory influence of lactic acid on the fermentation of glucose to lactic acid with *B. coagulans* DSM2314.

The 12-well plates were prepared with 1600 μL media and 400 μL inoculum to make a final volume of 2000 μL in each well. The media was made up in such a way that after adding the inoculum, the concentration of tryptone, soy peptone, sodium chloride and glucose was 15, 5, 5 and 20 g/L. A 100 mM potassium-phosphate buffer set at a pH of six was also added to the reaction media. The inoculum train was the same as that of the reactor studies.

The absorbance at 660 nm was measured at the beginning and after four hours. The plates were kept under anaerobic conditions at 50°C in a container placed on a rotary platform shaking at 150 rpm. Five different “levels” were evaluated against a “base case” in which the initial lactic acid concentration was 0 g/L. Each level occupied four wells. Most growth was expected in the base case; each level’s performance was reported as a percentage of the base case according to Equation 8-1.

$$\Delta\,(\%) = \frac{OD_{660f} - OD_{660i}}{OD_{660f,b} - OD_{660i,b}}\,.100 \qquad \text{Equation 8-1}$$

8.1.3.1.2 *Results*

Lactic acid has a negative impact on the growth rate of *Bacillus coagulans* DSM2314, as shown in Figure 10-6 and at an initial concentration of 12 g/L, the growth is completely inhibited. The value of removing lactic acid from the reactor as it is being produced can be seen in these results.

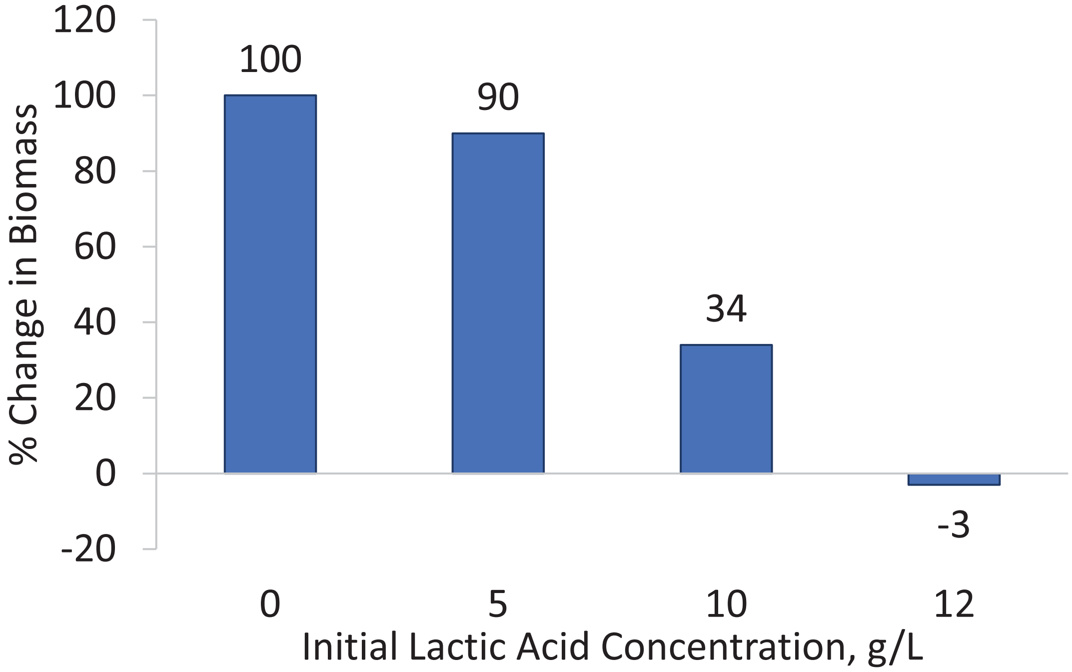


Figure 8-25 Percentage change in OD_{660} after 4 hours reaction time of wells spiked with lactic acid at the start of the experiment

8.1.3.2 ***Serum Bottle Experiments for lactic acid inhibition***

8.1.3.2.1 *Method*

Building on the multiwell plate experiments, kinetic data was generated; serum bottles with a working volume of 80 mL were used to generate growth curves for three levels of initial lactic acid concentration in the reaction media. The same media was prepared, with the only difference being that the initial glucose concentration was increased to 40 g/L. The inoculum train was also prepared in the same way, and 1 mL samples were taken at regular intervals. The experiment was done in triplicate.

8.1.3.2.2 *Results*

The rate of growth is negatively impacted by an increase in the lactic acid present in the broth. The lowered growth rate is evident from the slower increase in OD_{660} observed in Figure 8-9 and is confirmed by the delayed drop in pH, which is an indicator of lactic acid production. The final lactic acid concentration for initial lactic acid concentrations of 0, 5 and 10 g/L were 4.5, 10.3 and 16.8 g/L; note that the final amount of lactic acid is not the same for the different scenarios, but the final pH is. Across all the pH-uncontrolled experiments, the pH stabilises at 4.5. This may point to the concentration of protons rather than free lactate anions being the limiting factor in pH-uncontrolled experiments.

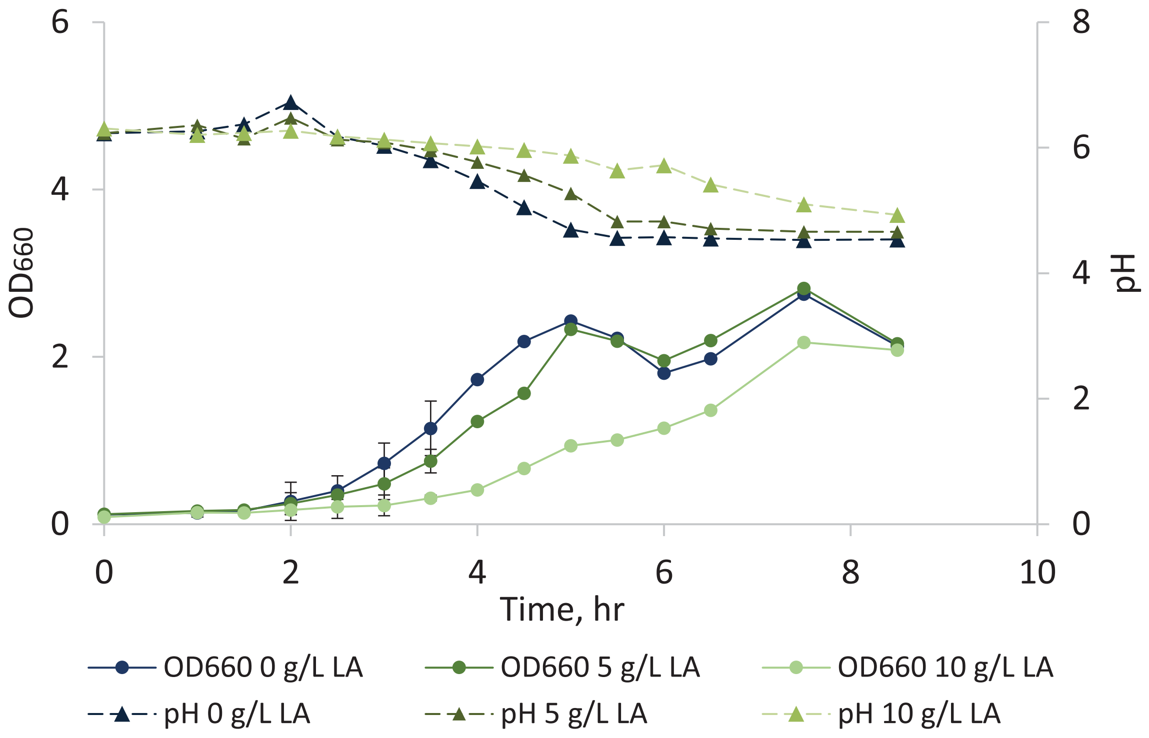


Figure 8-26 Impact of lactic acid on growth rate and biomass yield

8.1.4 Production potential for lactic acid from a South African recycling mill

Lactic acid is proposed here as a primary product to be produced from the fibres present in the wastewater from a recycling mill. The first step in testing the viability of this proposal is to calculate the amount of lactic acid that can theoretically be produced from the wastewater produced per ton of mill product. The "lactic acid potential" (LAP) was calculated in five steps: wastewater generation, ash removal, hydrolysis, fermentation and product purification. The yield and other parameters assumed for each of the steps are given in Table 8-1. The average wastewater flowrate for paper mills reported in NatSurv 12 (Van Der Merwe-Botha et al. 2017) was used as the basis, and a solids content of 5% was assumed for the wastewater; this value was taken from Krigstin and Sain (2006). This calculated sludge rate of 610 kg/ton product calculated is relatively close to the 406 kg/ton product reported by Scott and Smith (1995).

Table 8-13 Parameter values used in the calculation of lactic acid potential per ton of product from a recycling mill

Parameter	Value	Reference
Wastewater flow rate	12.2 m³/ton	NatSurv 12 (Van Der Merwe-Botha et al. 2017)
solids in wastewater	5%	Krigstin and Sain (2006)
Ash	60.1%	Average calculated from different literature sources
Cellulose	26.2%	
Hemicellulose	4.5%	
Lignin	5.1%	
Ash removal	90%	Robus (2013)
Cellulose loss	9%	Robus (2013)
Hemicellulose loss	9%	Assume hemicellulose loss is the same as that of cellulose
Hydrolysis yield, cellulose	92.3%	Chen et al. (2014a)
Hydrolysis yield, hemicellulose	98.7%	Chen et al. (2014a)
glucose kg/ton product	149 kg/ton	Calculated
xylose kg/ton product	27.4 kg/ton	Calculated
total sugars	176.4 kg/ton	Calculated
Fermentation yield	92.0%	Van der Pol et al. (2016)
Lactic acid kg/ton product	162.3 kg/ton	with 10 g/L yeast extract and 20 g/L peptone, pH 6, 50°C
Recovery	95%	Su et al. (2013)
Lactic acid recovered kg/ton product	154.1 kg/ton	

The fermentation yield used in this calculation was taken from Van der Pol et al. (2016), where *Bacillus coagulans* DSM2314, among other strains, was used to test the impact inhibitors have on bacteria during the fermentation of sugars to lactic acid. For this calculation, the fermentation yield achieved in the absence of such inhibitors was used since no inhibitors are expected to be present in this case. The acidification step in the proposed flowsheet will be mild and strong acid will not be used. In terms of lactic acid recovered from the broth, the reactive distillation with ethanol studied by Su et al. (2013) was used in the calculations. The flow of the substrate and product is visualised in Figure 8-10.

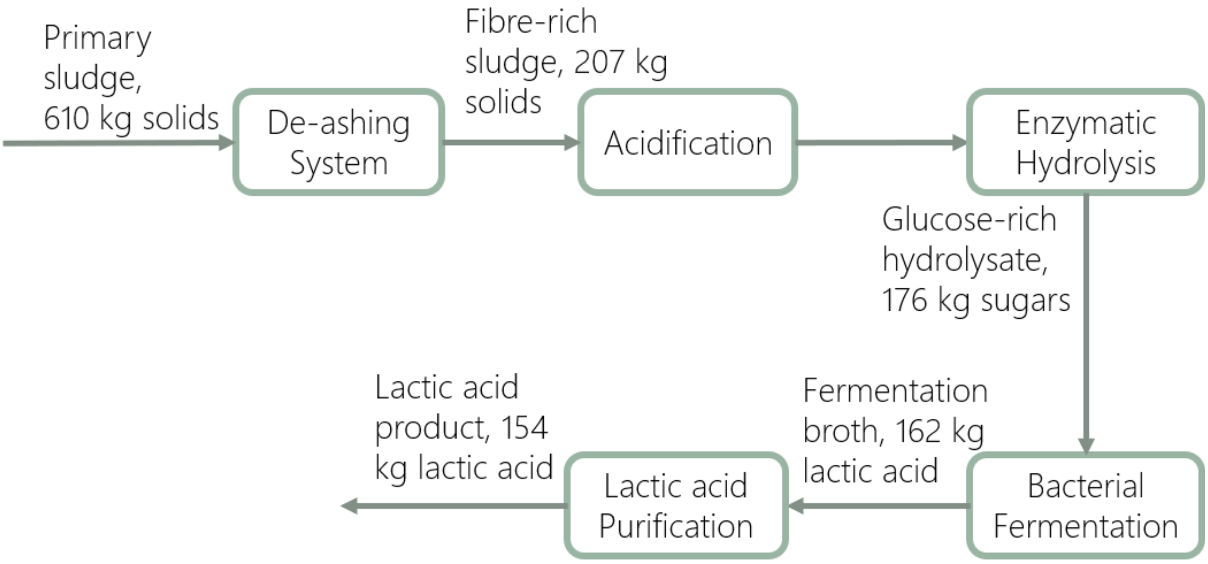


Figure 8-27 Block flow diagram showing the lactic acid potential in the wastewater of a recycling mill

To test the sensitivity of the LAP, the wastewater flow rate and the fraction of ash in the sludge were varied. As expected, increasing the ash content of the solids fraction of the wastewater has a negative impact on the LAP, whereas increasing the wastewater flow rate increases the LAP. The LAP is slightly more sensitive to variations in the ash content, it should be stated that the other parameters, such as the solids content of the wastewater, were kept constant for these calculations. Should the solids content of the wastewater be lowered to 406 kg/ton product, the number reported by Scott et al. (1995), the LAP is decreased to 116 kg/ton product.

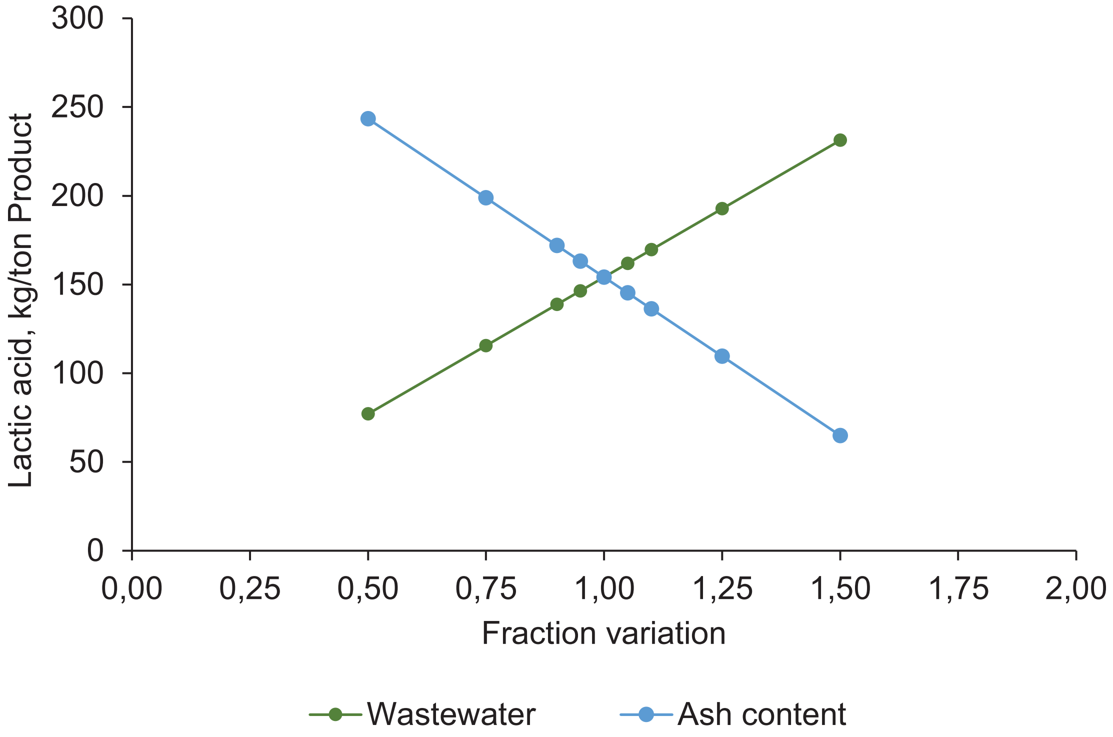


Figure 8-28 Sensitivity of LAP to changes in wastewater flow rate and Ash content of solids in wastewater

8.2 Energy products from recalcitrant components

8.2.1 Factors affecting anaerobic digestion (AD)

In order to make use of AD as a unit in a wastewater biorefinery, it is important to understand the anaerobic digestion process and the factors affecting anaerobic digestion. There are several factors that affect the AD process, which need to be experimentally optimised based on the combination of the feed stream and desired product. Factors affecting the optimisation within the wastewater biorefinery include temperature, pH, substrate composition and nutrient requirements (Mao et al. 2015).

8.2.1.1 *Temperature*

Temperature plays a significant role in the AD process affecting the various processes (Section 0). The three most common categories in which AD processes are carried out are psychrophilic (0-20°C), mesophilic (25-40°C) and thermophilic (≥45°C) (Mao et al. 2015; Rajeshwari et al. 2000). Mesophilic AD and thermophilic AD are more commonly used than psychrophilic AD.

An increase in temperature, still within the microbial tolerance, allows for increased microbial activity. Increased temperature also favours process kinetics by increasing the rate of hydrolysis. The improved process kinetics result in reduced hydraulic retention time (Harrison et al. 2019; Rajeshwari et al. 2000), while the increased microbial activity enables the handling of higher retention times (Harrison et al. 2018). The temperature has also been shown to play a role in pathogen inactivation. Thermophilic processes have been shown to be more effective at pathogen inactivation compared to mesophilic processes (Sassi et al. 2018).

There are, however, some disadvantages associated with the increased temperatures used in thermophilic AD. For example, the increased temperatures are associated with acidification which results in VFA accumulation. A decrease in temperature has been shown to have the opposite effect resulting in decreased VFA production rate (Mao et al. 2015). Reduced stability, as well as reduced quality, have also been reported for thermophilic processes (Mao et al. 2015).

8.2.1.2 ***pH***

Another important factor in the AD process is pH. The pH in the bioreactor must be maintained at favourable ranges, dependent on the desired product (Rajeshwari et al. 2000). In the case where methane production is the main aim of the AD process; the pH would be maintained at the optimal range, promoting methanogenesis. Methanogenic bacteria thrive in pH ranging from 6.8-7.2. Lower pH favours acidogenic microorganisms, which results in VFA accumulation and reduced methane production (Mao et al. 2015; Rajeshwari et al. 2000). A decrease in pH is often observed during the AD process, and to maintain a stable pH for biogas production, it is necessary to add a source of alkalinity. Rajeshwari et al. (2000) demonstrated that sodium bicarbonate might be used.

8.2.1.3 ***Substrate composition and the rate-limiting step***

The substrate composition and nature of the substrate play a significant role in the determination of the rate-limiting step in the AD process. The current opinion is that hydrolysis is generally the slowest step in AD, making it the rate-limiting step (Chernicharo et al. 2015; Speece, 1983). When substrates are more difficult to digest, such as grease, lipids, cellulose and lignin, which are often present in wastewater, the hydrolysis step is usually the rate-limiting step (Chernicharo et al. 2015).

In cases where the wastewater fed into the AD reactor is not rich in complex substrates such as cellulose and lignin, the breakdown of the substrate is no longer as slow. In this case, methanogenesis is identified as the rate-limiting step (Speece, 1983). However, the feed stream for the pulp and paper wastewater biorefinery AD consists mostly of complex components, including res, such that hydrolysis will most likely be rate-limiting.

8.2.1.4 ***Nutrient requirements***

As with any living organism, the microorganisms involved in the AD process require nutrients in order to survive and display maximum activity; these include both macronutrients and micronutrients such as nitrogen, phosphorus, sulphur, potassium, calcium, magnesium, iron, nickel, cobalt, zinc, manganese and copper (Rajeshwari et al. 2000).

Nitrogen is one of the most basic nutrients required. The required nitrogen is presented as a C:N ratio in literature. C:N ratios that have been shown to be effective in carbohydrate degradation range from 20-32, although methanogenic microorganisms have been shown to tolerate higher ratios. (Mao et al. 2015). Optimisation of the C:N ratio also assists in avoiding ammonia build-up and resultant inhibition. Increased C:N ratios mean decreased nitrogen availability which limits cell biomass (Harrison et al. 2018; Mao et al. 2015). Where the nutrient content of the wastewater may not be sufficient to sustain microbial growth, particularly where the C:N ratio lies outside of the optimal range (Harrison et al. 2019), supplementation may be required. This applies to the other required nutrients as well.

8.2.1.5 *Hydraulic Retention Times and Organic Loading Rate*

Hydraulic retention time (HRT) is defined as the time required for the complete degradation of the substrate; this is also the time the substrate (liquid phase) spends in the reactor. HRT can be defined by Equation 8-2.

$$\text{HRT} = V/v \text{ (days)} \qquad \text{Equation 8-2}$$

Where *V* is the working volume of the reactor (m^3) and v is the volumetric flow rate of the feed (m^3/day) (Harrison et al. 2019; Lee et al. 2014b; Speece, 1983)

The HRT is influenced by the substrate composition as well as the organic loading rate. It often takes a few weeks to reach an effective HRT (Mao et al. 2015). An optimal and effective HRT is essential, this is because a short HRT results in VFA accumulation, while an overly extended HRT is associated with decreased digester component utilisation (Mao et al. 2015). The minimal HRT influences capital cost as it determines the reactor size and volume (Speece, 1983).

The time that the solid substrate spends in the reactor is referred to as the solid or biomass retention time (SRT) (Lee et al. 2014; Speece, 1983). The SRT is used to describe a system with discrete solid and liquid phases (Harrison et al. 2019). The SRT is comparable to the HRT in the case where freely suspended biomass is utilised, which is not ideal for the AD process. A sufficiently long SRT coupled with the minimum HRT is required to allow for hydrolysis during the AD process (Lee et al. 2014)

The organic loading rate (OLR) is the amount, in mass, of organic matter supplied to the bioreactor per unit reactor volume per day (Harrison et al. 2018). The OLR can be defined in terms of volatile solids (VS) and chemical oxygen demand (COD) (Lee et al. 2014). The mass of VS is usually used to represent the mass of biodegradable organic matter for solid waste treatment systems, while COD is used in the case of wastewater treatment systems. Equation 8-3 is used to describe the relationship between the COD, HRT and OLR (Harrison et al. 2019).

$$\text{OLR} = \frac{COD\ (\frac{kg}{m3})}{HRT\ (days)} \qquad \text{Equation 8-3}$$

8.2.1.6 *Inhibition of anaerobic digestion*

Inhibition of AD is a problem and can affect reaction stability (Chen et al. 2008). Inhibition is often caused by AD-inhibitory elements that are present in the substrate or wastewater being treated. Some of the most common inhibitory elements include ammonia, sulphide, long-chain fatty acids (LCFAs), metal toxicity, aluminium, calcium, potassium and sodium and heavy metals (Chen et al. 2008). It is important to account for these factors when carrying out AD experiments. Methods which may be used to alleviate inhibition include co-digestion of waste feed, enhancing microbial adaptation to inhibitory elements, and attempting to eliminate the inhibitors from the feed (Chen et al. 2008).

8.2.2 Experimental Approach

An experimental approach detailing the stepwise approach of wastewater characterisation, reactor design, biomethane potential assays and the USAB experiments is detailed in Figure 8-12.

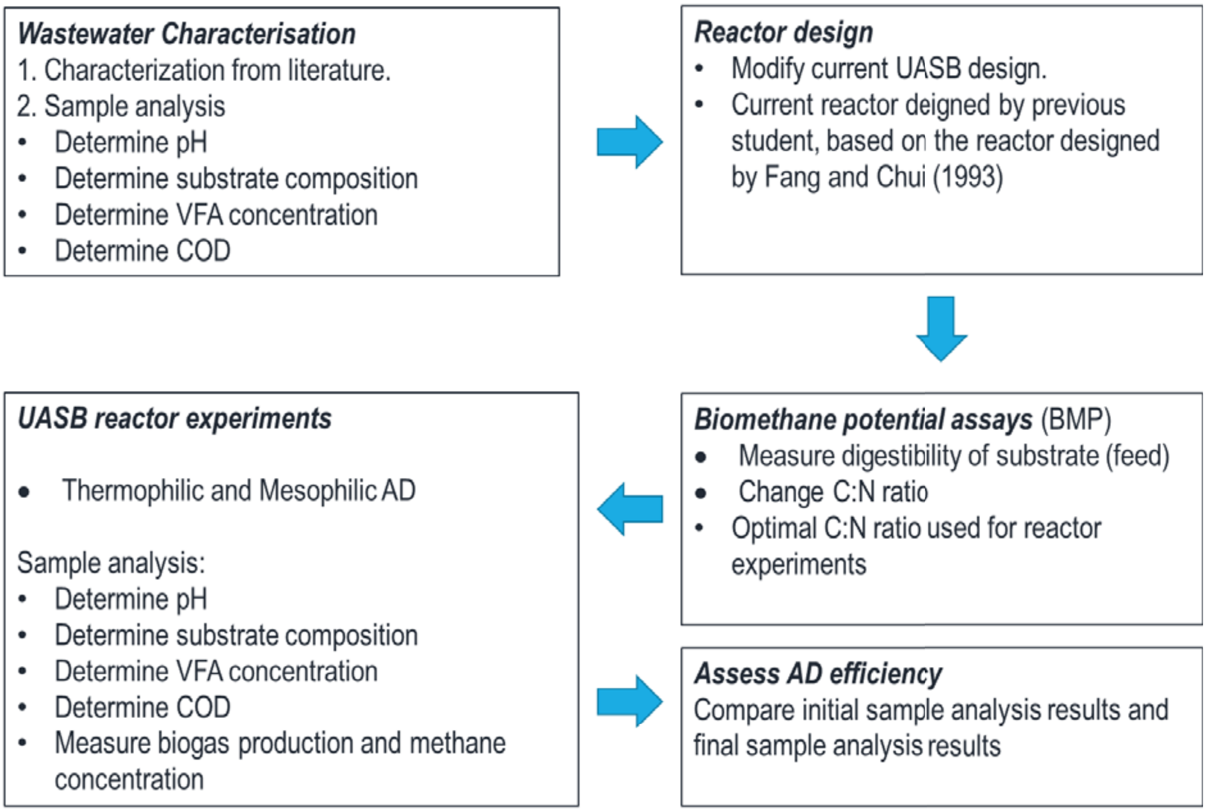


Figure 8-29 Block figure illustrating the experimental approach

8.2.3 UASB reactor experiments

8.2.3.1 *Experimental Approach*

8.2.3.1.1 *Reactor design and operation*

An up-flow anaerobic sludge blanket was used to investigate the distribution of influent COD for synthetic pulp and paper wastewater to CH_4 using AD. The decision to use the UASB reactor for these experiments was based on a brief literature review which showed that this reactor was the most widely used for AD wastewater treatment (Chernicharo et al. 2015).

The UASB reactor designed by a previous CeBER MSc student (Stott, 2022), reported in the WRC project K5/2473 (Harrison et al. 2019), was used in these experiments. The design was modified slightly to improve reactor performance. Reactor modifications included a change in aspect ratio which resulted in a wider and shorter reactor. Another modification was the addition of two sets of baffles to prevent sludge accumulation in the GLSS or upper section of the reactor (Bobade and Lomte 2015; Caixeta et al. 2002).

Figure 8-13 illustrates the reactor design, while Table 8-2 shows the reactor dimensions. Two identical 4.5L reactors were used in the experiments.

Table 8-14 Reactor dimensions

Reactor body	Inner diameter	105mm
	Height	471mm
	Outer diameter	110mm
Gas-Liquid-Solid Separation	Inner diameter	105mm
	Height	216mm
	Outer diameter	110mm

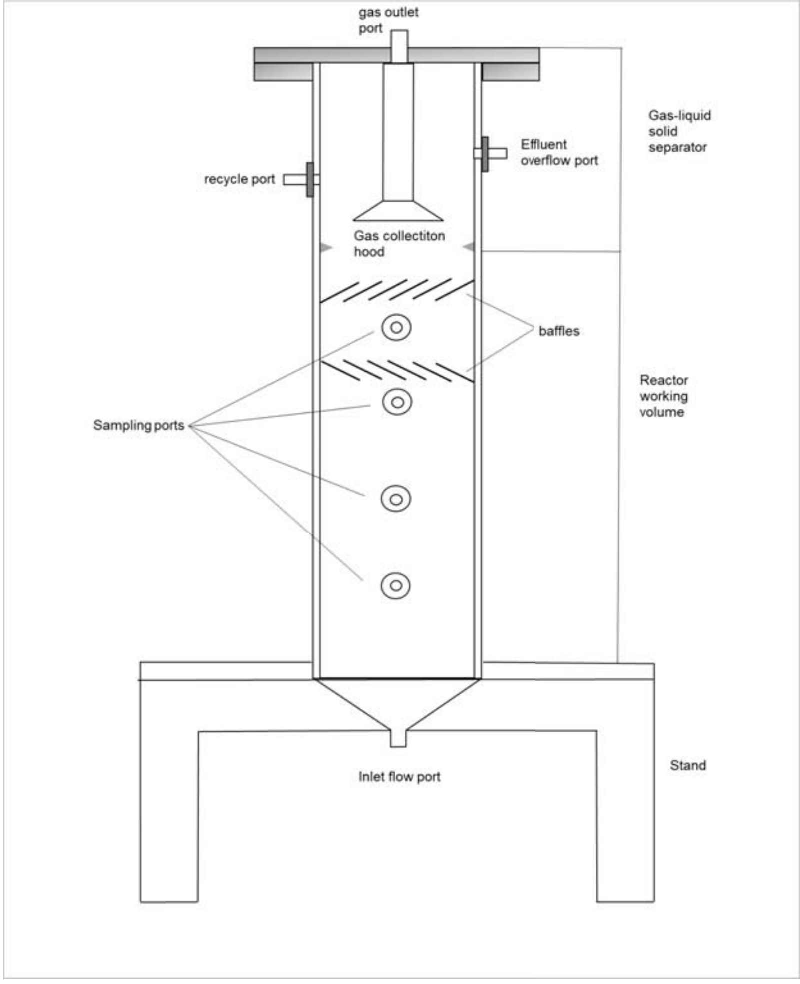


Figure 8-30 Diagram showing the modified UASB reactor

The reactors were inoculated with granulated sludge obtained from Talbot &Talbot, located in Pietermaritzburg (Kwa-Zulu Natal). Sludge granules were dark brown in colour and well-defined, as shown in Figure 8-14

Figure 8-31 Granulated sludge was used as the inoculum for the AD reactors

Inoculation was carried out at a ratio of 1:1 for inoculum: feed. Following inoculation, reactors are sealed and sparged with nitrogen to create an anaerobic environment.

Experiments were carried out under mesophilic conditions (37°C) for 350 days. OLR was increased gradually throughout the experiment. The initial stage of the project, which is also referred to as the acclimatisation stage, involved the gradual increase of the OLR from 2.3g /L/day - 5.9 g/L/day. This increase in OLR was achieved by increasing the pump flow rate while keeping the COD concentration constant. Influent and effluent COD was measured to assess COD removal efficiency, while the methane concentration in the gas produced was measured to assess methane production. After the acclimatisation stage, the OLR was increased by increasing the COD while keeping the pump flow rate constant.

8.2.3.2 ***Feed preparation***

The food composition described by Fang and Chui 1993 was used as a reference for the feedstock composition for this study. However, Fang and Chui 1993 describe the feedstock composition as representative of domestic wastewater. Modifications were required to ensure that the feedstock represented pulp and paper wastewater. In order to achieve this, the feedstock composition was developed using the Fang and Chui composition as well as a second approach presented by Sperling and Chernicharo 2005. The second approach involves using a theoretical approach to calculate the nutrient requirement (Sperling and Chernicharo 2005). The results obtained from the literature-based pulp and paper wastewater characterisation were used to determine the nutrient composition. The second approach involved the addition of Microcrystalline cellulose (MCC) to represent the complex structures characteristic of pulp and paper wastewater. Synthetic pulp and paper media was prepared as detailed in Table 8-3.

MCC was used as a carbon source; however, due to its low digestibility, sucrose and glucose, which are readily biodegradable, were added as secondary carbon sources. Sucrose and glucose were selected as secondary sources for the reasons provided by Stott (Stott, 2022, Harrison et al. 2019), which included affordability, availability and high solubility. In addition to the carbon sources, yeast extract was utilised as a nitrogen source, and macro and micronutrients were added, as detailed in Table 8-3. Due to the importance of pH regulation, sodium bicarbonate, potassium dihydrogen phosphate and dipotassium hydrogen phosphate were added as buffers.

The organic solutions and macronutrients were sterilised by autoclaving at 120°C for 20 minutes. The feed was prepared daily by adding the sterilised organic solutions, macronutrients and macronutrients in 10 L feed bottles containing sterile deionised water to make up the feed. The pH of the feed was adjusted between 7 – 8 using 5mM NaOH.

Table 8-15 Composition of synthetic pulp and paper wastewater

Medium components	mg/l	Stock Solution
Calcium Chloride	1318.09	macronutrients
Magnesium Sulphate Heptahydrate	243.38	
Potassium dihydrogen phosphate	4.39	
Dipotassium phosphate	33.39	
Sodium Metasilicate	26.51	
Sodium Bicarbonate	942.76	
Aluminium chloride hexahydrate	7.16	Micronutrients
Ferric chloride	7.74	
Manganese (II) chloride	2.52	
Barium Chloride dehydrate	0.26	
Boric powder	21.79	
Chromium (III) sulphate	0.014	
Cobalt chloride	0.00044	
Copper Sulphate pentahydrate	0.004	
Ammonium molybdate	0.0009	
Nickel chloride	0.004	
Sodium Selenate	0.0005	
Sodium Metavanadate	0.002	
EDTA	3.34	
yeast extract	1250	Organics
acetic acid	250	
propionic acid	62.5	
glucose	350	
sucrose	350	
cellulose	2500	

8.2.3.3 ***Analytical techniques***

COD measurements

Total and soluble COD was measured daily or every second day throughout the experiment. Samples were centrifuged for the determination of soluble COD. The closed reflux colourimetric method (5220 D) (APHA,1999) was used for the analysis. COD reagents A (Merck 114679) and B (Merck, 114680) were used together with a digestion block and the spectrophotometer. Potassium hydrogen phthalate (PHP) was dissolved in de-ionised water and used as a standard. The 8500 mg-PHP/L, which corresponds with a COD of 10000 mg/l, was used to prepare a 10000 mg-COD/L stock. The standard was further diluted to prepare standards of 1000, 2000,4000,6000,8000 and 10000 mg-COD/L.

Following the manufacturer's instructions, 1.10 mL of Reagent A and 0.90 mL of Reagent B were mixed in glass COD vials. This was followed by the addition of 0.50 mL of the sample. De-ionised water was used as a blank. In order to reduce wastage and for economic purposes, the volumes of samples and reagents were halved. The vials were vortexed for 10 seconds and incubated in a heating block (HI 83980 COD reactor 2008 series) for 2 hours at a temperature of 150°C. The samples were left to cool at room temperature following the incubation period. Absorbance was then measured in a spectrophotometer at 605 nm. The COD results are presented as the percentage of soluble COD removed from the system, which is calculated as the difference between the influent and effluent soluble CODs, divided by the influent soluble. COD.

Gas production and composition

Wet Tip gas meters were used to determine the volume of gas produced in the reactor experiments. The method makes use of the principle of liquid displacement. The meters were calibrated at the beginning of the experiment and regularly throughout the experiment. The gas count readings were recorded on a daily basis. The time of reading was used to calculate biogas productivity. Following the gas count, a gas sample was collected using a syringe to assess the gas composition by Perkin-Elmer gas chromatography (GC).

A Perkin-Elmer Auto system GC equipped with a Supelco was column (1.2 mm x 37 m), and a flame ionisation detector (FID) Was used to assess the gas composition, specifically the methane fraction, in the biogas. The FID temperature was set at 280°C while the oven temperature was set at 50°C. Nitrogen was used as a carrier gas. The standards utilised contained 25% and 50% methane, and these were used to generate a standard curve. 50Ul of gas and standards was injected, and the fraction of methane was measured. The injections were carried out three times for each sample (WRC project K5/2473, Harrison et al. 2019)

VFA analysis

High-performance chromatography (HPLC) was used to measure the concentrations of lactic acid, acetic acid, propionic acid and butyric acid. A Waters Breeze two system equipped with a Bio-Rad Organics Acids ROA column and a UV (210 nm wavelength) detector was used. The system was run isocratically using a mobile phase of 0.1 M H_2SO_4 at a flow rate of 0.63L/min. A set of standards containing the VFAs mentioned above was prepared at concentrations ranging from 100-600 mg/L. These standards were used to prepare standard curves, which were used for the quantification of the VFAs measured. VFA analysis was completed upon completion of the run in BMP assays as well as in the reactor experiments. VFA analysis was also carried out intermittently in the reactor experiments.

pH measurements

The Jenway 3510 pH meter (Lasec) was used to measure the pH of the substrate before and after the BMP assays were completed. In the reactor experiments, the pH of the influent and effluent was measured daily

8.2.3.4 *Results and discussions*

The project began with a gradual increase in OLR from 2.3 to 8 g/L/day (Table 8-4), achieved by increasing the feed rate at a constant COD concentration. This was referred to as the start-up or acclimatisation phase. Influent and effluent COD, along with the methane content of biogas produced, were assessed and used to determine the impact of increasing OLR on COD removal efficiency and biogas production. Average COD removal of above 80% was observed in both Reactor A (RA) and Reactor B (RB) at the start-up OLR of 2 g/L/day (Table 8-4).

Table 8-16 Performance of UASB reactors during the acclimation stage of reactor experiments

Date	OLR (g/L/day)	HRT (h)	pH	Soluble COD removal (%)	Biogas composition (%CH_4)
2020-09-08	2.3	31.88	7.0 -7.16	>80%	63% RB
2020-10-14	3.7	20	7.0	>85%	50% RA and 74%
2020-11-01	4.8	15.18	6.9	>80%	68% RA and 62% RB
2021-02-02	6	11.9	6.8 – 7.0	>88%	69% RA and 60% RB
2021-03-10	8	11.9	6.9	>90	60% RA and 69% RB

A gas leak in RA was observed during the experimental start-up, which prevented the assessment of gas production and composition. The leak was sealed, and monitoring of gas production and composition was resumed. Monitoring of these parameters was carried out in RB without any operational issues.

Effluent pH and temperature were monitored throughout the experiment and used to assess reactor stability. The pH remained constant at 7.0 for both RA and RB during the start-up phase of the experiment. The temperature remained constant, at 37°C, for both reactors

The reactors were operated for a period of 350 days, including the start-up phase. Reactor performance was assessed throughout the project by monitoring the COD removal efficiency and methane production. Following the acclimation phase, the OLR was gradually increased starting at 12 g/L/day and increased gradually to reach an OLR of 36 g/L/day. To achieve this increase in OLR, the feed rate was kept constant while the COD was gradually increased.

The average COD removal efficiency during the starting OLR was 89.6% and 81.6% for RA and RB, respectively (Figure 8-15 and Figure 8-16). The COD removal efficiency in both reactors remained stable (observed COD removal efficiency ranged from 80% - 98% in RA and 75% - 98% in RB) over a steady increase in OLR (Figure 8-15 and Figure 8-16).

The impact of increasing the OLR on COD removal efficiency was assessed and indicated by the volumetric COD conversion rate (VCCR). A directly proportional relationship between the OLR and VCCR is observed in both RA and RB, as shown in Figure 8-15 and Figure 8-16. Increasing the OLR resulted in an increase in VCCR in both reactors throughout the experiment. The maximum VCCR is observed at the highest OLR of 36 g/L/day for RB; however, in RA, the maximum VCCR was observed at an OLR of 32 g/L/day.

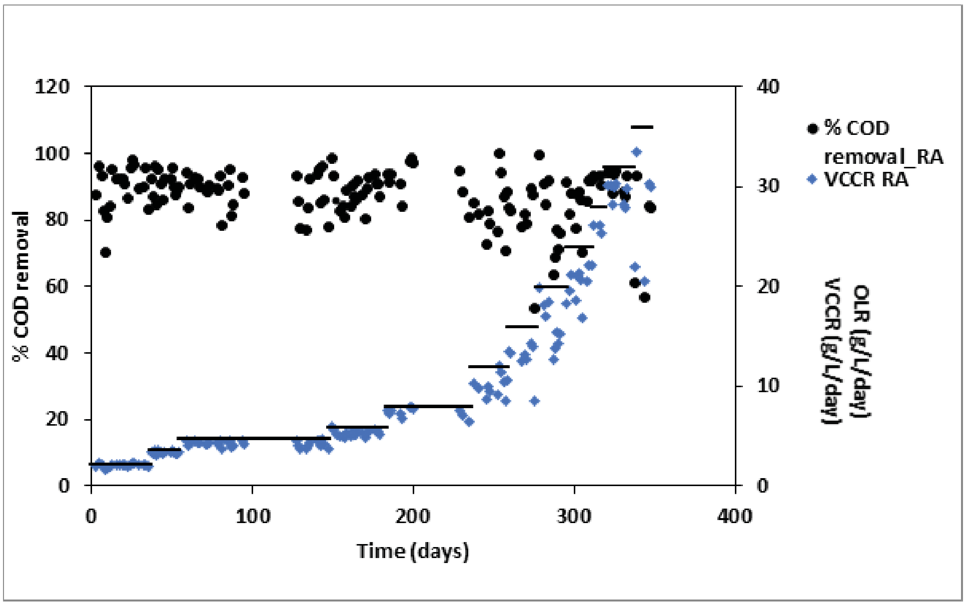


Figure 8-32 COD removal efficiencies from RA and associated volumetric COD conversion rate under various OLRs over 350 days

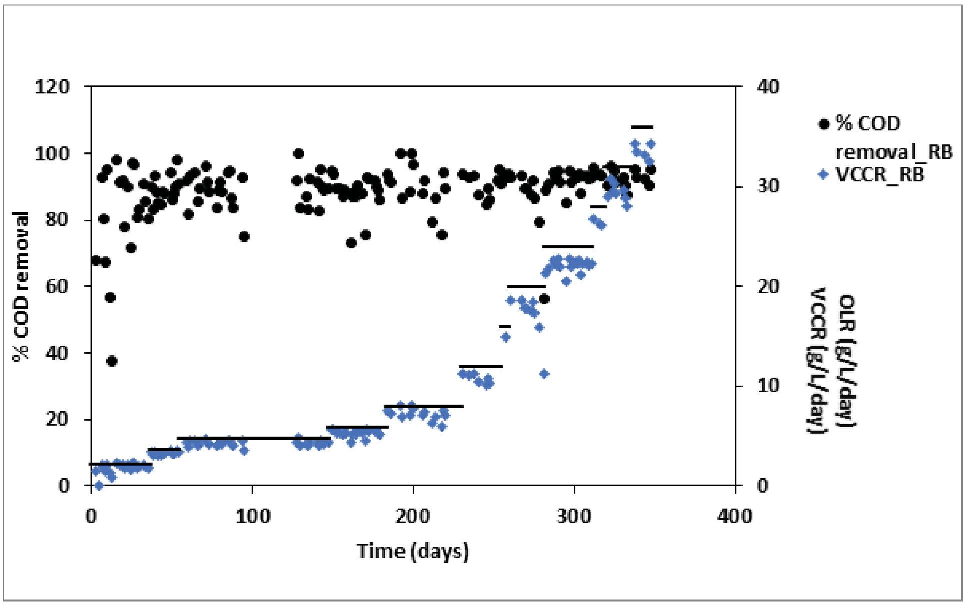


Figure 8-33 COD removal efficiencies from RB and associated volumetric COD conversion rate under various OLRs over 350 days

The effluent pH remained stable (pH ranged from 6.8-7.2 or both RA and RB) throughout the first 200 days of the experiment (Figure 8-17). The pH gradually increased after day 200, leading to a pH of 7.55 in RA and 7.6 in RB at an OLR of 36 g/L/day (Figure 8-17). The increase in pH is not associated with any clear changes in reactor performance with regard to methane production and COD removal efficiency. The temperature was monitored and used as the second measure of reactor stability. A decrease in temperature was observed; temperatures decreased to 30°C and 32°C for RA and RB, respectively (Figure 8-18).

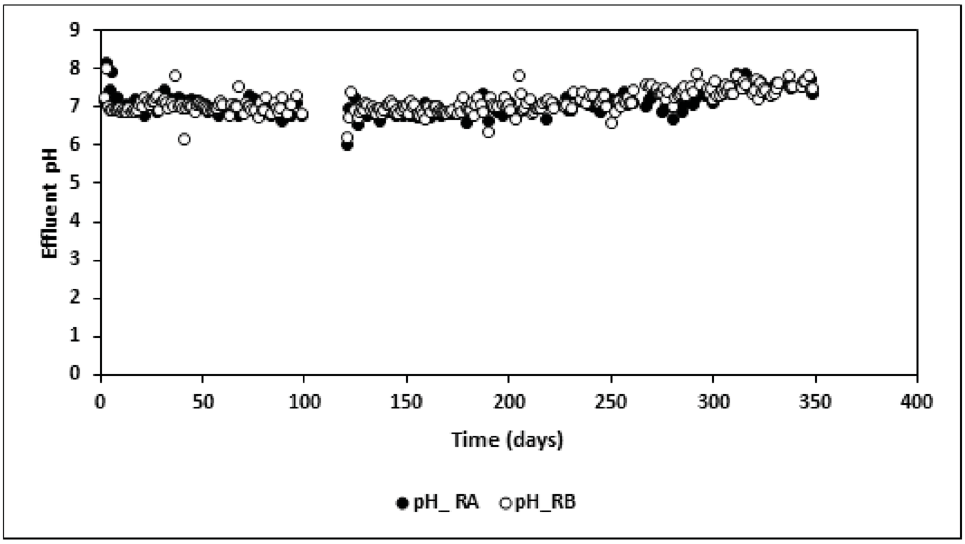


Figure 8-34 Effluent pH for RA and RB over a period of 0 to 350 days

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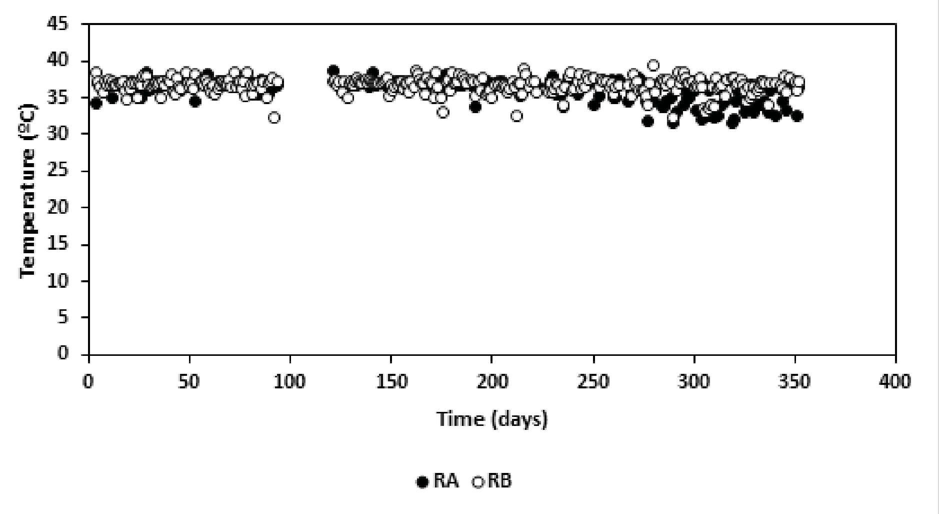

Figure 8-35 Temperature for RA and RB over a period of 0 to 350 days

Gradually increasing the OLR resulted in an increase in methane productivity for both RA and RB, as shown in Figure 8-19 and Figure 8-20. A slight drop in methane productivity was observed at OLRs of 12 g/L/day and 32 g/L/day in RA, while in RB, a decrease in methane productivity was observed at OLRs of 12 g/L/day and 24 g/L/day. Maximum methane productivity of 12.90 L/L/day at an OLR of 36 g/L/day for RA and 15.48 L/L/day at an OLR of 36 g/L/day (Figure 8-19 and Figure 8-20).

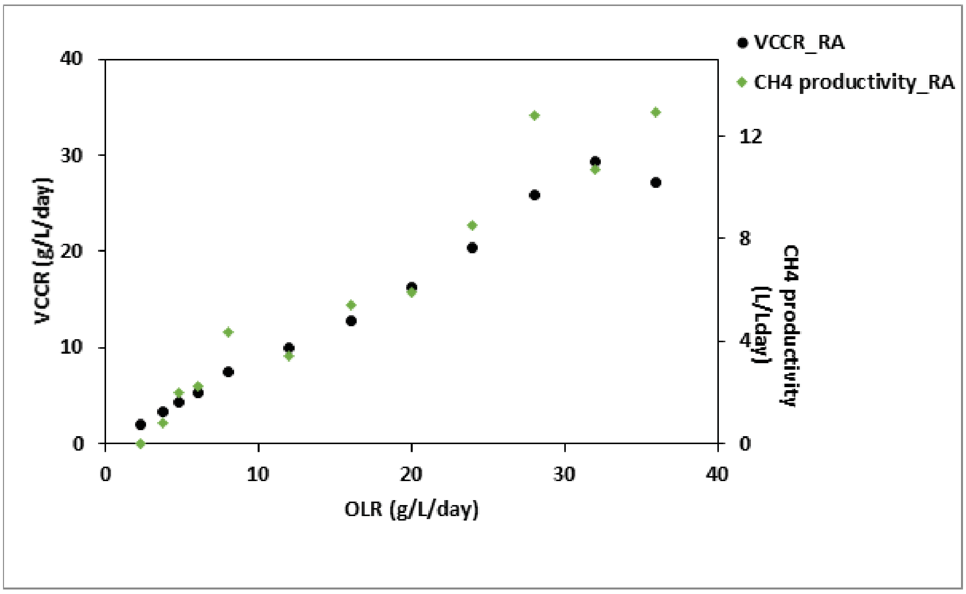

Figure 8-36 Volumetric COD conversion rate (g/L/day) and methane productivity per reactor volume (L/L/day) for RA at various OLRs (g/L/day)

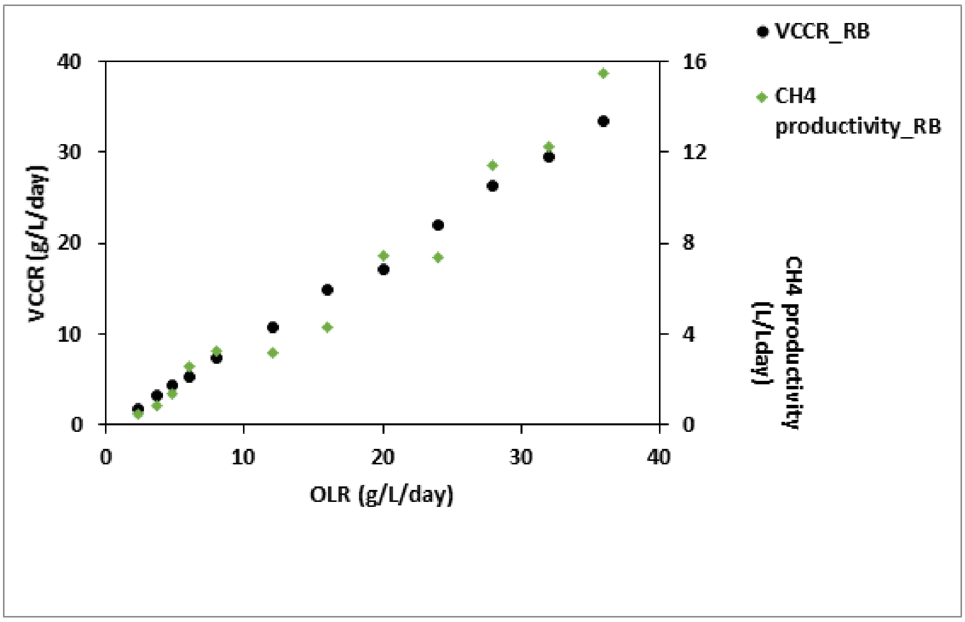

Figure 8-37 Volumetric COD conversion rate (g/L/day) and methane productivity per reactor volume (L/L/day) for RB at various OLRs (g/L/day)

8.2.3.5 ***Discussion***

UASB reactor studies were carried out to investigate the impact of Increasing the OLR on gas production and composition in a UASB reactor with pulp and paper wastewater as a substrate. The impact of the OLR on COD removal efficiency and volumetric COD conversion rates was also investigated. The experiments were also carried out to determine the optimal conditions for maximum methane production while maintaining reactor stability. Two UASB reactors were utilised in the study. Synthetic pulp and paper wastewater was used as feedstock. Upon the initial start-up of reactors, it was observed that the reactor lid was not sealed tightly, which resulted in incorrect gas measurements. The reactor lid was taken in for repairs; the reactor remained in operation using a temporary lid. RB displayed no operational issues at the start of the experiment. The reactors were started off at an OLR of 2.3 g/L/day, which is slightly lower than the starting OLR of 4 – 8 g/L/day recommended by Alphenaar (1994). The start-up phase for these studies did, however, involve a gradual increase in OLR to 8 g/L/day, which is within the recommended range. Despite the low starting OLR, the reactor performance was stable. Gas production and composition were not measured accurately in RA due to the slow gas leak. However, accurate measurements were observed from an OLR of 3.7 g/L/d.

Gas production and composition in RB were measured throughout the experiment with minimal issues encountered. Shortly after the reactors were inoculated, gas production was observed in both reactors, although measurements were not carried out in RA for the reasons stated above. Gas production increased as the OLR increased. The rate of methane production starts to decrease at an OLR of 34 g/L/day. The maximum methane yield of 0.58 L/g-COD was observed in RA at an OLR of 8 g/L/COD and 0.46 L/g-COD at the highest OLR of 36 g/L/day. Methane yields of 50-80% have been achieved in the AD of the pulp of paper wastewater (Li et al. 2012). The result observed in the study support these finding, as the maximum methane yield exceed 75% in both reactors.

The COD removal efficiency was consistent throughout the experiment for both RA and RB, with both reactors maintaining a removal efficiency of above 80%. COD removal efficiency has been reported to reach 75-90%, which supports the observation made in the study (Li et al. 2012). Average COD removal of 89% and 81% was observed in RA and RB, respectively, at the starting OLR of 2.3 g/L/day. A decrease in COD removal efficiency was observed towards the end of the experiment at an OLR of 36 g/L/day.

The reactors ran smoothly and remained stable for 200 days, after which the reactors became unstable, although methane yield and COD removal efficiency remained largely unaffected. Temperature and pH fluctuated slightly the longer the reactors were kept running.

Increasing OLR has been reported to be associated with reactor instability. High OLR results in increased hydrolysis/acidogenesis bacterial activity resulting in increased VFA production, which is associated with decreasing pH. In this study, stable pH suggested that the reactor instability was not due to VFA accumulation. This was supported by the low VFA concentrations observed throughout the study. Indeed stable operation was observed up to a maximum OLR of >35 g/L/day.

Part 3

Evaluating the potential for the valorisation of complex wastewater streams in wastewater biorefineries towards resource efficiency

9 Analysis of complex pulp and paper wastewater streams for potential in a wastewater biorefinery

As highlighted in Case Study 1, a biorefinery approach instead of traditional wastewater treatment would ensure that value-added products could be produced simultaneously with fit-for-purpose water and energy products. While the investigated stream in Case Study 1 was a relatively simple wastewater stream in terms of complexity and preliminary laboratory scale investigations, this section of the report we focus on more complex streams and the recalcitrant compounds they can contain in order to investigate how value addition targeting the holocellulose (cellulose and hemicellulose) and lignin components of lignocellulosic biomass together with remediated water, can be favoured instead of the usual wastewater treatment.

9.1 Selected streams

To evaluate the potential for the valorisation of complex P and P effluents, varied and complex P and P wastewater streams present in South African mills were selected in this study, as seen in Table 9-1. Streams with different characteristics are expected to be best suited to the production of different products (Chapters 4 and 5), and so require different methods of processing and different process flowsheets. The availability of data from the literature was also a determining factor in selecting the streams.

Table 9 1 Selected streams for Case Study 2

Stream	Reasons
Sulphite spent liquor (calcium-based) (Stream 1)	- High-concentration with high organic content - Medium complexity - Medium volume Increased accessibility to cellulose and hemicellulose due to the pulping method used. This may facilitate cheaper and easier pretreatment prior to processing into high-value bioproducts.
Pulp washing effluent (Kraft) (Stream 2)	- Small volume - Medium complexity - Medium concentration Carbon is less accessible than in the sulphur-spent liquor stream; hence pretreatment may be more difficult.
Bleaching ECF effluent (Stream 3)	- High volume - High complexity - Medium concentration with low organic content This stream should be evaluated for remediation.

9.1.1 Mass balance calculations

For the purposes of this study, it was assumed that the plant capacity was equivalent to the quantity of bleached pulp produced at the Ngodwana Mill (Sappi), i.e. 133 000 tpa (Macdonald, 2004). Information pertaining to the carbohydrate content of some streams was not available. To quantify the carbohydrate content of these streams, a basic mass balance was performed. These mass balances considered an assumed carbohydrate content of the feedstock (38% cellulose; 31% hemicellulose; 30% lignin

(Cabrera, 2017), balanced with an assumed carbohydrate content of the pulp product (70% cellulose; 26.9% hemicellulose; 3.1% lignin) and various other effluent streams provided from literature (Section 4.3). The water used for the pulp washing is assumed to be recycled water recovered from the rest of the P and P processing units, such as the condensates effluents.

Given the complexity of the bleaching stream, it was assumed that none of the bleaching effluents was recycled. To facilitate appropriate evaluations for each effluent stream, consistent stream composition data was required. Information for the carbohydrate content of some streams was unavailable and hence was calculated using a simple mass balance approach detailed below. The same method was used to calculate compositions for: the pulp washing (Kraft) stream (Stream 2), calcium and magnesium spent liquor streams and the O and E stage bleaching effluents (Streams 1 and 3). A pulp yield of 45% was assumed.

The assumptions shown in Table 9-2 were used to determine the mass flow rate of the carbohydrate constituents (assumed to be cellulose, hemicellulose and lignin) in the Kraft Pulp Washing stream. An example of these calculations is shown in Equation 9-1. A similar approach was used to determine the carbohydrate content of the other streams. (Table 9-3 and Table 9-4)

$$Cellulose_{Pulp\ wash} = Cellulose_{raw\ material} - Cellulose_{pulp\ product} - Cellulose_{other\ effluent} \qquad \text{Equation 9-1}$$

Table 9-17 Summary of assumptions made for mass balance calculations

Raw Material Composition (%) (Softwood)	
Cellulose	38
Hemicellulose	31
Lignin	30
Kraft Pulp Product Composition (%)	
Cellulose	70
Hemicellulose	27
Lignin	3.1
Dissolving Pulp Composition (%)	
Cellulose	93
Hemicellulose	4.5
Lignin	2.5
Known Effluents and Compositions	
Chip washing	
Carbohydrates (mg/L)	3210
Flowrate (m^3/yr)	13300
Debarking	
Carbohydrates (mg/L)	800
Flowrate (m^3/yr)	66500
Bleaching	
Lignin Content (mg/L)	50
Flowrate (m^3/yr)	4123000

Table 9-18 Process effluent flowrates (kg/h) of carbohydrates in stream 2

	Raw Material	Debarking	Chip Wash	Pulp Wash	Bleach Effluent	Kraft Pulp
Cellulose	14000	2.53	2.03	1810	582	11600
Hemicellulose	11500	2.06	1.65	6750	223	4470
Lignin	11100	1.99	1.60	10500	25.8	515

Table 9-19 Process effluent flowrates (kg/h) of carbohydrates in streams 1 and 3

	Raw Material	Chip wash	Ca	Mg	O	E	Dissolved Pulp
Cellulose	98900	2.37	1620	3670	298	298	93000
Hemicellulose	61100	1.47	17300	39300	8.46	8.46	4500
Lignin	57800	1.39	16900	38300	8.00	8.00	2500

9.1.2 Economic evaluation

To compare the economic performance of each respective process, an economic assessment of each pathway was performed. This assessment considered the calculated fixed capital cost (CAPEX) and operating costs (OPEX), as well as the revenue generated, calculations for which can be found in Appendix A. The discounted cash flow (DCCF) was calculated assuming a working capital of 10% of the WWBR CAPEX. A WWBR plant life of 25 years was assumed, with a discount rate of 12%, a tax rate of 28% and annual linear depreciation of 10% (Klein et al. 2017). The calculation of the DCCF facilitated the calculation of the internal rate of return (IRR) and the net present value (NPV).

Since the actual bioproduct recovery from downstream processing (DSP) is dependent on individual products, a DSP baseline estimate using the costs attributed to the downstream processing of bioethanol was used for the recovery and purification of the bioproducts. A goal seeks command was also used in Excel to determine the minimum product recovery required to reach the breakeven point for the respective process route. The breakeven point was defined as the point at which the internal rate of return is equal to the discount rate. This minimum product recovery, in conjunction with the net present value, was utilised as an indication of the most economically viable pathways.

9.2 Stream 1: Sulphite spent liquor

The decision pathway diagram for Stream 1 is provided in Figure 9-1. This diagram was compiled using the process considerations outlined in the following sections

9.2.1 Potential for valorisation

Moritz and Du (1996) report a cellulose accessibility of 66% in the sulphite pulping liquor effluent. Since hemicellulose is more easily hydrolysed than cellulose, it was assumed that all hemicellulose in the effluent stream exists in its hydrolysed form and thus requires no further pretreatment prior to processing. To further improve the accessibility of cellulose, maximising the utilisation of organic matter, pretreatment steps were evaluated. It is important to note that pretreatment, in this study, refers to detoxification and delignification. Lignin in this stream is assumed to exist completely in the form of lignosulphonates, which holds potential as a high-value bioproduct, further motivating the decision to consider this stream for valorisation. This stream is first sent through an evaporator to remove some water together with wood volatiles and produce a more carbohydrate-concentrated stream.

Table 9-5 shows the compound removal of the evaporator taken from the literature (Llano et al. 2017). The mass balance around the evaporator can be seen in Table 9-6. This was calculated based on the concentrations and total average volume flowrate (600 000 m^3/year) of calcium spent liquor stream i and component concentrations from Moodley et al. (2003), where the concentrations of the individual components were converted to flowrates using the total volume flowrate as seen in Equation 9-2. The amount of water in the feed and strong sulphite spent liquor (SSL) stream was based on Llano et al. (2017), which states that 10% of the feed is solid and 55% of the strong SSL stream is solid; thus, the remainder was assumed to be water.

$$Flowrate\left(\frac{kg}{h}\right) = Compound\ concentration\ \left(\frac{kg}{L}\right) \times total\ volume\ flowate\ \left(\frac{m^3}{yr}\right) \times 1000\ \left(\frac{kg}{m^3}\right) \div 8000\ \left(\frac{h}{yr}\right)$$

Equation 9-2

Table 9-20 Inhibitor removal ability of evaporator to produce strong SSL (Llano et al. 2017)

Compound	Removal Ability
Acetic Acid	53.0%
Methanol	95.3%
SO2 removal	28.6%

Table 9-21 Mass balance around the evaporator

	Feed (kg/hr)	Strong SSL (kg/h)	Water (kg/h)
Hemicellulose	2330	2330	0
Cellulose	176	176	0
Lignosulphonates	3530	3530	0
Phenols	30	13.7	16.3
Lignin Pre-cursors	2.48	2.48	0
Syringaldehyde	0.75	0.75	0
Free SO2	33.8	12	21.7
Combined SO2	163	58.1	105
Furfural	163	74.4	88.4
Acetic Acid	51.9	24.4	27.5
Water	58200	517	57700
Total	64700	6730	58000

9.2.2 **Detoxification methods**

The main processes investigated for the detoxification of the sulphite spent liquor were ion exchange, adsorption and overliming, as described in the study conducted by Llano et al. (2017). The ion exchange methods evaluated were both anionic (Amberlite IRA-96) and cationic (Dowex 50WX2). The adsorption methods considered were black carbon (BC) and activated charcoal (AC). Table 9-7 provides the removal efficiencies of the various methods, as detailed in Llano et al. (2017). The sugar loss was attributed to the loss of hydrolysed carbohydrates (hemicellulose) only.

Table 9-22 Detoxification removal efficiencies (Llano et al. 2017)

Method	Lignin Removal (%)	Phenol Removal (%)	Acetic Acid Removal (%)	Sugar Loss (%)	Furfural Removal (%)
Ion Exchange: Amberlite IRA-96	96	98	61	65	100
Ion Exchange: Dowex 50WX2	76	55	86	85	100
Adsorption: BC	76	67	77	42	100
Adsorption: AC	54	59	78	60	100
Overliming	38	37	29	6.0	71

Table 9-8 shows the product flowrates as a result of the various detoxification methods. The table was constructed by using the removal efficiencies in Table 9-6. It was assumed that there was no water loss experienced; thus, 100% of the water from the feed was reported to the product stream.

Table 9-23 SSL Flowrate (kg/h) results of various detoxification methods

	Feed	D1	D2	D3	D4	D5
Hemicellulose	2330	814	339	1360	937	2180
Cellulose	176	176	176	176	176	176
Lignosulphonates	3530	137	832	839	1610	2170
Phenols	13.7	0.26	6.2	4.56	5.66	8.7
Lignin Pre-cursors	2.48	2.48	2.48	2.48	2.48	2.48
Syringaldehyde	0.75	0.75	0.75	0.75	0.75	0.75
Free SO2	12	12	12	12	12	12
Combined SO2	58.1	58.1	58.1	58.1	58.1	58.1
Furfural	74.4	0	0	0	0	0
Acetic Acid	24.4	9.44	3.44	5.59	5.46	17.4
Water	517	517	517	517	517	517
Total Mass Flowrate	6730	1730	1950	2970	3330	5170

Key: D1: Ion Exchange using Amberlite IRA-96; D2: Ion Exchange using Dowex 50WX2; D3: Adsorption using Black Carbon; D4: Adsorption using Activated Charcoal; D5: Overliming

9.2.3 Applicable delignification methods

Ultrafiltration (UF) and nanofiltration (NF) were the two methods investigated for the delignification of the calcium spent liquor after the detoxification step. Table 9-9 outlines the membrane pore sizes and removal efficiencies. The UF (series) referred to in Table 9-9 comprises a 15 kDa membrane followed by a 5 kDa membrane and finally a 1 kDa membrane. It was assumed for delignification that the sugar loss was only because of hydrolysed hemicellulose; therefore, sugar loss was only calculated based on the hemicellulose content. Each product stream from detoxification (Table 9-8) was used as a feed for the various delignification methods in order to determine which combination would produce the highest carbohydrate content for the production of value-added products, using the lignin removal efficiencies and sugar loss percentages in Table 9-9. Table 9-10 to Table 9-14 present the results of the various delignification methods for each detoxification option. Similarly to the detoxification methods, it was assumed that there was no water loss to achieve maximum water recovery.

Table 9-24 Membrane removal efficiencies

Membrane Type	Lignin Removal (%)	Sugar Loss (%)
UF (15 kDa)[1]	44.7	17.9
UF (5 kDa)[1]	65.6	12.9
UF (1 kDa)[1]	45.7	5.10
UF (series)[1]	72.6	26.8
NF (200 Da)[2]	83.2	19.4

Key: 1: (Fernández-Rodríguez et al. 2015); 2: (He and Chen, 2020)

Table 9-25 Delignification flowrate (kg/h) results for Amberlite IRA-96

	UF (15kDa)	UF (5kDa)	UF (1kDa)	UF (series)	NF (200Da)
Hemicellulose	668	709	772	596	656
Cellulose	176	176	176	176	176
Lignosulphonates	76.1	47.2	130	101	111
Phenols	0.26	0.26	0.26	0.26	0.26
Lignin Pre-cursors	2.48	2.48	2.48	2.48	2.48
Syringaldehyde	0.75	0.75	0.75	0.75	0.75
Free SO_2	12	12	12	12	12
Combined SO_2	58.1	58.1	58.1	58.1	58.1
Furfural	0	0	0	0	0
Acetic Acid	9.44	9.44	9.44	9.44	9.44
Water	517	517	517	517	517
Total Mass Flowrate	1520	1530	1680	1470	1540

Table 9-26 Delignification flowrate (kg/h) results for Black Carbon

	UF (15kDa)	UF (5kDa)	UF (1kDa)	UF (series)	NF (200Da)
Hemicellulose	1110	1180	1290	994	1090
Cellulose	176	176	176	176	176
Lignosulphonates	464	288	796	614	676
Phenols	4.56	4.56	4.56	4.56	4.56
Lignin Pre-cursors	2.48	2.48	2.48	2.48	2.48
Syringaldehyde	0.75	0.75	0.75	0.75	0.75
Free SO_2	12	12	12	12	12
Combined SO_2	58.1	58.1	58.1	58.1	58.1
Furfural	0	0	0	0	0
Acetic Acid	5.59	5.59	5.59	5.59	5.59
Water	517	517	517	517	517
Total Mass Flowrate	2360	2250	2860	2380	2540

Table 9-27 Delignification flowrate (kg/h) results for Activated Charcoal

	UF (15kDa)	UF (5kDa)	UF (1kDa)	UF (series)	NF (200Da)
Hemicellulose	769	817	889	686	755
Cellulose	176	176	176	176	176
Lignosulphonates	891	554	1530	1180	1300
Phenols	5.66	5.66	5.66	5.66	5.66
Lignin Pre-cursors	2.48	2.48	2.48	2.48	2.48
Syringaldehyde	0.75	0.75	0.75	0.75	0.75
Free SO2	12	12	12	12	12
Combined SO2	58.1	58.1	58.1	58.1	58.1
Furfural	0	0	0	0	0
Acetic Acid	5.46	5.46	5.46	5.46	5.46
Water	517	517	517	517	517
Total Mass Flowrate	2440	2150	3200	2640	2830

Table 9-28 Delignification flowrate (kg/h) results using overliming

	UF (15kDa)	UF (5kDa)	UF (1kDa)	UF (series)	NF (200Da)
Hemicellulose	1790	1900	2070	1600	1760
Cellulose	176	176	176	176	176
Lignosulphonates	1200	747	2060	1590	1750
Phenols	8.7	8.7	8.7	8.7	8.7
Lignin Pre-cursors	2.48	2.48	2.48	2.48	2.48
Syringaldehyde	0.75	0.75	0.75	0.75	0.75
Free SO_2	12	12	12	12	12
Combined SO_2	58.1	58.1	58.1	58.1	58.1
Furfural	0	0	0	0	0
Acetic Acid	17.4	17.4	17.4	17.4	17.4
Water	517	517	517	517	517
Total Mass Flowrate	3810	3460	4920	3980	4300

9.2.4 Investigating product cluster

Rueda et al. (2014) proposed that ethanol, lactic acid, succinic acid, PHA (polyhydroxyalkanoates) and furfural are the most promising value-added products to be investigated for production from the sulphite spent liquor. As seen in Table 7-1, even though lactic acid was the top contender, both ethanol and succinic acid were also among the top three bioproducts suited for a WWBR (Section 7.1 in Chapter 7). As for PHAs, along with PLA (polylactic acid), it was listed as a promising bioplastic to be considered for the South African market. As such, the product list by Rueda et al. (2014) was assumed to be relevant bioproducts for a South African P and P WWBR since they fit the market and technical criteria.

There are various processes and pathways that could be utilised to produce these products, namely, simultaneous saccharification and fermentation (SSF), separate hydrolysis and fermentation (SHF) and thermochemical processes (for furfural production). Table 9-15 outlines the products available and mechanisms and process performances used in this investigation. A hydrolysis process is required to convert cellulose and hemicellulose to glucose and xylose, respectively. This is necessary to improve the effectiveness of fermentation since microorganisms digest glucose and xylose more easily than cellulose and hemicellulose.

SHF consists of separate hydrolysis and fermentation steps. This process is advantaged by the fact that separate stages facilitate the use of different optimal conditions for enzyme and microbial action, respectively. However, the accumulation of end-product in bulk limits results in enzyme inhibition which may affect process performance.

SSF combines both hydrolysis and fermentation into a single step. While this process is disadvantaged due to compromised operating conditions for both enzymes and microbes, enzymatic action is not inhibited due to the build-up of end-product in bulk. This is because hydrolysis end-product (simple sugars) are used up as they are produced in the fermentation process to produce the targeted bioproducts. SSF is reported to have a number of economic advantages over SHF; however, the selection between using SHF and SSF is process specific and depends on a number of operational factors (Waldron, 2010).

Table 9-29 Yields of various process options

Process	Mechanism	Product	Yield
Option 1: SHF			
Hydrolysis	Enzymes (glucanases and glucosidase)	Reducing sugars	43% conversion (cellulose to glucose)[1]
	Concentrated Acid	Reducing sugars	33.5% conversion (cellulose and hemicellulose to glucose and xylose); 33.9% removal (furfural); 33.0% removal (acetic acid)[2]
Fermentation	Yeast (Saccharomyces cerevisiae)	Ethanol	73% conversion glucose and xylose[1]
	Bacterial (mixed microbial culture)	PHA	30% conversion xylose[3]
Option 2: Thermal Conversion			
Biofine	H_2SO_4 catalyst	Furfural	1 mol xylose to 2.5 mol furfural[4]; 70% conversion xylose[5]
Option 3: SSF			
	Microbe: Yeast (*Saccharomyces cerevisiae*); Enzyme: glucanases and glucosidase	Ethanol	51% conversion glucose and xylose[6]
	Microbe: Bacteria (*Actinobacillus. succinogenes*); Enzyme: PEP carboxykinase	Succinic Acid	65% conversion glucose and xylose[7]
	Microbe: Bacteria (*Thermoanaerobacterium aotearoan*); Enzyme: phosphoketolase	Lactic Acid	83% conversion glucose and xylose[8]

Key: 1: (Moritz and Du, 1996); 2:(Llano et al. 2012); 3: (Queirós et al. 2014); 4: (Zhu et al. 2017); 5: (Cai et al. 2014); 6:(Moritz and Du, 1996); 7: (Alexandri et al. 2017); 8: (Yang et al. 2013)

Enzyme hydrolysis is favoured over acid hydrolysis since the product stream generated from the latter is rich in chemicals and requires further treatment. The main assumption was that all the hemicellulose from the initial waste water stream was converted to xylose, and only 43% of cellulose was converted to glucose (Moritz and Du, 1996).

Table 9-16 to Table 9-20 represent the different flowrates that were achieved for the value-added products using various pathways (pretreatment and conversion).

Table 9-30 Production flowrate (kg/h) results using Ion Exchange (Amberlite IRA-96)

	UF:15 kDa	UF:5 kDa	UF:1 kDa	UF: Series	NF
Ethanol (SSF)	400	421	454	364	394
Ethanol (SHF)	777	824	894	697	764
Succinic Acid (SSF)	510	537	578	463	502
Lactic Acid (SSF)	430	450	482	394	424
PHA (SHF)	154	164	178	138	152
Furfural (Thermo conversion)	748	794	865	667	735
Lignosulphonates	61.4	90.2	7.01	36.8	26.7

Table 9-31 Production flowrate (kg/h) results using Ion Exchange (Dowex 50WX2)

	UF:15 kDa	UF:5 kDa	UF:1 kDa	UF: Series	NF
Ethanol (SSF)	202	211	224	186	199
Ethanol (SHF)	341	360	390	307	335
Succinic Acid (SSF)	257	268	285	238	254
Lactic Acid (SSF)	236	244	258	221	233
PHA (SHF)	64.4	68.3	74.4	57.4	63.2
Furfural	312	331	361	278	306
Lignosulphonates	372	546	42.4	223	161

Table 9-32 Production flowrate (kg/h) results using Adsorption (Black Carbon)

	UF:15 kDa	UF:5 kDa	UF:1 kDa	UF: Series	NF
Ethanol (SSF)	628	663	717	567	618
Ethanol (SHF)	1280	1360	1470	1140	1260
Succinic Acid (SSF)	800	845	914	722	787
Lactic Acid (SSF)	652	686	739	592	642
PHA (SHF)	257	273	298	230	253
Furfural	1250	1330	1440	1110	1230
Lignosulphonates	375	551	42.8	225	163

Table 9-33 Production flowrate (kg/h) results using Adsorption (Activated Charcoal)

	UF:15 kDa	UF:5 kDa	UF:1 kDa	UF: Series	NF
Ethanol (SSF)	452	476	513	410	445
Ethanol (SHF)	891	944	1030	798	875
Succinic Acid (SSF)	576	607	654	522	567
Lactic Acid (SSF)	480	504	540	439	473
PHA (SHF)	178	189	205	158	174
Furfural	861	915	996	768	846
Lignosulphonates	719	1060	82.2	431	313

Table 9-34 Production flowrate (kg/h) results using overliming

	UF:15 kDa	UF:5 kDa	UF:1 kDa	UF: Series	NF
Ethanol (SSF)	974	1030	1120	875	957
Ethanol (SHF)	2040	2160	2350	1820	2000
Succinic Acid (SSF)	1240	1310	1420	1120	1220
Lactic Acid (SSF)	990	1040	1130	893	973
PHA (SHF)	414	440	479	369	406
Furfural	2010	2130	2320	1790	1970
Lignosulphonates	971	1430	111	582	422

9.2.5 Building decision pathway

A decision pathway (Figure 9-1)was built to facilitate the conversion of the hemicellulose, readily available in the SSL, to the products identified by Rueda et al. (2014) using the three process options identified in Table 9-15. Since the main inhibitors when working with bacterial strains for the production of succinic acid and Marcotullio (2013) are phenolic and lignosulphonates (Llano et al. 2017), the first stage focuses on eliminating phenolics, followed by a second stage of lignosulphonates removal to remove any residual lignosulphonates from the first stage. With regards to the yeast strains used in process options 1 and 3, it is assumed the de-toxification and de-lignification methods used for the bacterial strains will also remove significant amounts of furfural, which significantly impact the growth of yeast and ethanol yield and productivity (Mussatto and Roberto, 2004). This assumption is made based on the high furfural removal efficiencies presented in (Llano et al. 2017).

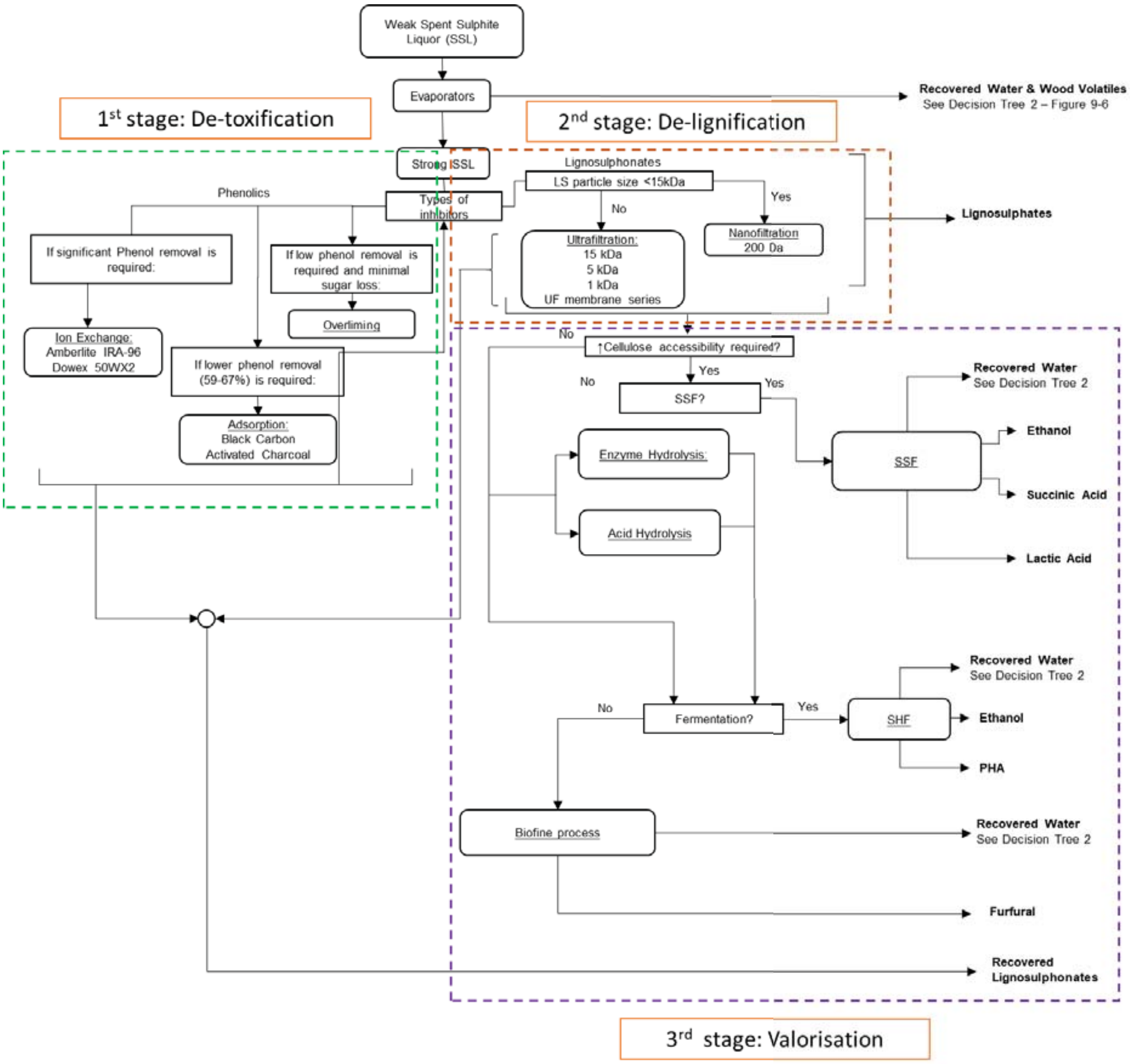

Figure 9-38 Decision pathway for calcium spent liquor from the dissolving pulp process, focused on valorisation potential based on the biological transformation of carbon resources using bacterial strains, with phenolics and lignosulphonates as the main inhibitors

9.2.6 Evaluation of pretreatment methods

The evaluation of pretreatment methods (combination of detoxification and delignification) considered the production rates of the various products from the different process pathways. Figure 9-2 shows the production of ethanol via the SSF using various combinations of pretreatment methods. The results for the other product pathways can be found in Section 0. The trend observed reveals that a combination of D5 (overliming) and UF (1kDa) methods achieve the highest production rates across all the products. Second to these production rates was the combination using D5 (overliming) and UF (5 kDa). Figure 9-3 shows the production rate of lignosulphonate using the various delignification methods (and overliming as a detoxification method), where UF and NF represent ultra and nanofiltration, respectively. Contrary to the value-added products produced, Figure 9-3 shows that pretreatment with UF (15 kDa) produces the most LS, followed by pretreatment with UF (5 kDa) and the series UF.

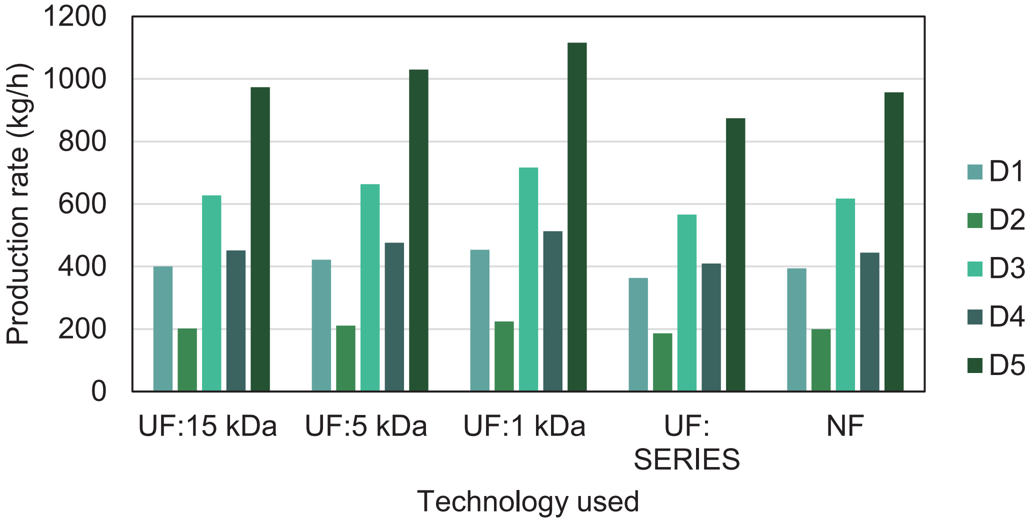

Figure 9-39 Ethanol produced from SSF using various pre-treatment combinations. D1 and D2 represent ion exchange using Amberlite IRA-96 and Dowex 50WX2. D3 and D4 are adsorption using BC and AC respectively while D5 is overliming

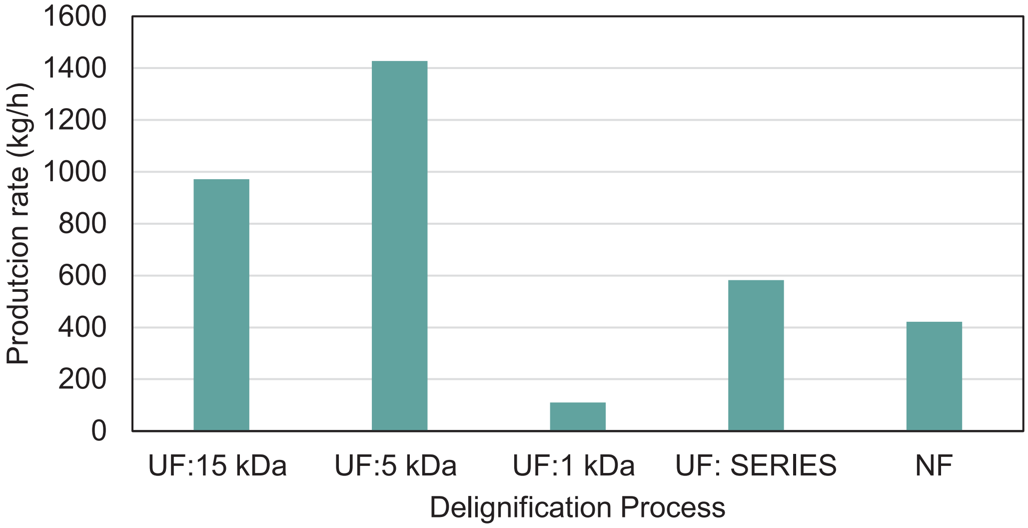

Figure 9-40 Lignosulphonates produced through various delignification methods using overliming as detoxification

9.2.7 Evaluation of potential pathways

The analysis of pretreatment methods described in Section 0 revealed that the overliming was the detoxification method which resulted in the greatest bioproduct generation. Ultrafiltration using 5kDa and 1kDa membranes resulted in the greatest production of sugar-based bioproducts and lignosulphonates, respectively. Hence ten potential pathways were evaluated to determine the most feasible processing routes, and these were compared to traditional WWT approaches. A techno-economic analysis was performed on both the combinations (D5+UF (5kDa) and D5+ UF (1kDa)) to determine which combination and which target bioproducts provided the most economically viable process routes.

Table 9-21 provides an overview of the key process areas identified within the potential pathways considered. Prior pretreatment steps (detoxification using overliming and delignification) were implemented to increase the accessibility of cellulose and hemicellulose for further processing, as well as to separate lignosulphonates from the effluent bulk. Calculations for the associated operating and capital costs for each process route can be found in Appendix A. The scope of this study did not include an evaluation of the downstream processing methods; however, to provide a more realistic view of the profitability of each route, baseline operating and capital costs for DSP were assumed to see Appendix A. These were based on the DSP costs attributed to the production of bioethanol; it is assumed that the production of finer biochemicals will incur greater DSP costs. Consequently, the returns reflected in the techno-economic analysis may be reduced when product-specific DSP costs are included.

Table 9-35 Potential pathways and key processing methods (Stream 1)

Pathway Number	Delignification Method	Bioproduct Processing Method	Target Product
1	UF: 1 kDa	SSF	Ethanol
2	UF: 5 kDa	SSF	Ethanol
3	UF: 1 kDa	SHF	Ethanol
4	UF: 5 kDa	SHF	Ethanol
5	UF: 1 kDa	SSF	Lactic Acid
6	UF: 5 kDa	SSF	Lactic Acid
7	UF: 1 kDa	SSF	Succinic Acid
8	UF: 5 kDa	Fermentation	PHA
9	UF: 5 kDa	Thermal Conversion	Furfural
10	UF: 1 kDa	Thermal Conversion	Furfural

An important stage to consider is the hydrolysis of the lignocellulose content. This can either be performed using an acidic or an enzymatic approach. Since hemicellulose hydrolyses more easily than cellulose, it is assumed that a large quantity of hemicellulose would have undergone hydrolysis during the dissolving pulping process. Hence hydrolysis for the SSL must target cellulose. While dilute acid hydrolysis is preferable for economic and environmental methods, to promote effective cellulose hydrolysis, a concentrated acidic hydrolysis method is recommended (Llano et al. 2012; Baruah et al. 2018). The generation of a highly acidic by-product stream is not preferable within a biorefinery system; hence hydrolysis in all pathways was assumed to be facilitated through an enzymatic approach.

Traditionally a bulk effluent stream arising from P&P processing is treated using an activated sludge (AS) system. Treatment using AS for volume flows equivalent to this stream would result in an annual operating cost of R4 120 000 with an associated capital cost of R6 426 000. While these costs are significantly lower than those of the pathways presented, the revenue-generating bioproducts present an attractive alternative for the processing of this wastewater stream.

Table 9-22 presents the outcomes of the techno-economic analyses performed for each pathway. A minimum product recovery was calculated using a goal-seek method in Excel. This minimum product recovery determines the minimum quantity of bioproducts which must be recovered to achieve the breakeven point for each processing pathway.

If one is to assume the full recovery of water, these pathways have the potential to save 0.5 million m^3 /yr water which amounts to an operational cost savings of R16.3 million per year (assuming R35/ kl of water).

Table 9-36 Summary of techno-economic analyses (Stream 1)

Pathway No.	NPV (MR)	Minimum Product Recovery
1	1.35	30%
2	0.653	14%
3	3.20	39%
4	2.33	24%
5	3.56	62%
6	3.75	38%
7	1.35	62%
8	1.14	18%
9	0.921	56%
10	0.866	88%

9.3 Stream 2 (Kraft Pulp Washing)

The decision pathway diagram for Stream 2 is provided in Figure 9-6. This diagram was compiled using the process considerations outlined in the proceeding sections

9.3.1 Potential for valorisation

In contrast to Stream 1, cellulose and hemicellulose in Stream 1 are not as easily accessible as calculated in Section 9.2.1. This is largely due to the difference in pulping method, and lignin is still bounded. Pretreatment is required firstly for delignification in order to increase the accessibility to both the cellulose and hemicellulose components to investigate potential conversion into value-added products. As such, for this particular stream, delignification is the first step required.

9.3.2 Applicable pretreatment Methods

Enzyme delignification, coagulation and electrocoagulation were the delignification methods investigated for this stream. Coagulation methods comprised polyaluminium chloride and copper sulphate processes. Electrocoagulation methods analysed included aluminium electrodes, iron electrodes as well as a combination of both. Chemical coagulation produces an undesirable chemical waste stream which requires further treatment. Table 9-23 presents the pollutant removal efficiencies of various delignification methods. It was assumed that the COD removal constituted the cellulose, hemicellulose and sulphide present in the stream. Table 9-4 gives the product flowrates for each delignification method that was considered. It was assumed that 100% of the water reported to the product stream.

Table 9-37 Delignification methods and efficiencies for stream 2

Process Type	Lignin Removal (%)	COD Removal (%)
Enzyme Delignification[1]	60.0	-
Coagulation: Polyaluminium chloride[2]	83.0	83.0
Coagulation: Copper sulphate[2]	76.0	76.0
Electrocoagulation: Iron node, aluminium cathode[2]	78.5	85.0
Electrocoagulation: Aluminium electrode[3]	80.0	70.0
Electrocoagulation: Iron electrode[3]	92.0	55.0

Key: [1](Chandra Rajak and Banerjee, 2015); [2](Azadi Aghdam et al. 2016); [3] (Uğurlu et al. 2008)

Table 9-38 Flowrates for various delignification methods (kg/h)

Component	Feed	DL	C2	C3	E1	E2	E3
Hemicellulose	5650	5650	961	1360	848	1690	2540
Cellulose	4410	4410	749	1060	661	1320	1980
Lignin	9060	3620	1540	2180	1950	1810	725
Sulphides	10.8	10.8	1.84	2.59	1.62	3.24	4.86
Water	22400	22400	22400	22400	22400	22400	22400
Total Mass Flowrate	416000	36100	25700	27000	25900	27300	27700

Key: DL: Enzymatic delignification, C2: coagulation using polyaluminium chloride, C3: coagulation using copper sulphate, E1: electrocoagulation using iron anode, aluminium cathode; E2: electrocoagulation using aluminium electrode; E3: electrocoagulation using an iron electrode.

To determine the accessibility of cellulose in the pulp washing stream prior to and post enzymatic delignification, the following calculations were performed.

Chandra Rajak and Banerjee (2015) report cellulose and hemicellulose concentrations of 387 mg/g and 290 mg/g of untreated lignocellulosic feedstock, respectively. Of these compounds, 67.5 mg/g are present in a reducing sugar form. It was assumed that the reducing sugar portion represents the portion of lignocellulosic material which is fully accessible to enzymatic action.

The original concentration of reducing sugars within the lignocellulosic material in the kraft pulp washing stream was found using the aforementioned information as well as the cellulose and hemicellulose compositions calculated for this stream (See Section 9.1). This calculation is represented by Equation 9-3.

$$[Reducing\ sugar] = [Hemicellulose]_{pulp\ wash} \cdot \frac{[Reducing\ sugar]_{reported}}{[Hemicellulose]_{reported}} = 68.8\frac{mg}{g}$$

Equation 9-3

The final concentration of reducing sugars was calculated in the same manner as presented in Equation 9-3, however the final (after enzyme delignification) reported concentrations of reducing sugars (462 mg/g) were used in conjunction with the concentrations of cellulose for the reported and pulp wash streams (387 mg/g and 230 mg/g respectively). This resulted in a final reduced sugar concentration of 249 mg/g.

$$Cellulose\ accessibility = \frac{Cellulose_{reducing\ sugar\ form}}{Cellulose_{total}} = \frac{229}{230} = 99.4\%$$

Equation 9-4

The values reported by Chandra Rajak and Banerjee (2015) are a result of an 85.4% delignification. Given the lower solids loading of the kraft pulp wash stream, it is expected that a lower delignification percentage will be obtained (assumed 60%), consequently reducing the accessibility of cellulose. Hence the accessibility calculated in Equation 9-4 was adjusted using Equation 9-5.

$$Cellulose\ accessibility = \frac{Cellulose_{reducing\ sugar\ form}}{Cellulose_{total}} \cdot \frac{0.6}{0.854} = 69.8\%$$

Equation 9-5

9.3.3 Investigating product cluster

The same processing routes and associated yield assumptions evaluated for Stream 1 were used for Stream 2 (see Table 9-15). In contrast to Stream 1, Stream 2 does not contain lignin in a lignosulphonate form. There is the potential to produce a further side product, bio-oil, through further processing of the lignin contained in this stream. Table 9-25 provides the processing information for this. By-products of depolymerisation include flue gas and char, which have conversions of 33% and 2%, respectively, using the catalytic hydro pyrolysis pathway (Azadi et al. 2013). Alternatively, with the use of a sub and supercritical solvent, a 45% conversion of lignin to bio-oil and a 52% and 4% conversion to flue gas and char can be achieved, respectively (Azadi et al. 2013). It was assumed that the accessibility of cellulose and hemicellulose were 69.8% and 100%, respectively, as described in Section 9.3.2. It was also assumed that all the hemicellulose from the initial waste water stream was converted to xylose, and only 43% of cellulose was converted to glucose (Moritz and Du, 1996). Table 9-26 summaries the product flowrates resulting from the different pretreatment methods and conversion processes.

Table 9-39 Depolymerisation of lignin

Process	Mechanism	Product	Yield
Lignin Products			
Depolymerisation	Catalytic Hydro pyrolysis using Hydrogen and a Ni-Mo-Cr2O3 catalyst	Bio-oil	65% conversion of lignin to bio-oil (balance forms char and gas)[1]
	Sub and supercritical water solvent	Bio-oil	45% conversion of lignin to bio-oil (balance forms char and gas)[1]

Key: [1](Azadi et al. 2013)

Key: DL: Enzymatic delignification, C2: coagulation using polyaluminium chloride, C3: coagulation using copper sulphate, E1: electrocoagulation using iron anode, aluminium cathode; E2: electrocoagulation using aluminium electrode; E3: electrocoagulation using the iron electrode.

Table 9-40 Product flowrates (kg/h) for the Kraft washing stream

	DL	C1	C2	E1	E2	E3
Ethanol (SSF)	2820	339	478	299	597	896
Ethanol (SHF)	7050	1200	1690	1060	2110	3170
Succinic Acid (SSF)	5680	681	961	601	1200	1800
Lactic Acid (SSF)	5370	789	1110	697	1390	2090
PHA (SHF)	1310	222	313	196	392	588
Furfural	6330	1080	1520	950	1900	2850
Bio-oil (catalytic hydropyrolysis)	3530	4890	4480	4620	4710	5420
Bio-oil (sub and supercritical water)	2420	3350	3070	3170	3230	3720

9.3.4 Evaluation of pretreatment methods

The evaluation of pretreatment methods considered the production rates of the various products from the different process pathways. Figure 9-4 shows the production of ethanol via the SSF using various pretreatment methods. A trend is observed across all product flow rates, which indicates that enzyme delignification pretreatment results in the highest generation of products. Bio-oil is a potential by-product produced from the processing of recovered lignin. The methods used to investigate the production of bio-oil from lignin were catalytic hydro pyrolysis and sub and supercritical water solvents. Figure 9-5 shows the results for catalytic hydro pyrolysis using various delignification methods, while the sub and supercritical production rates for bio-oil can be found in Table 9-26. Figure 9-5 shows that the highest production of bio-oil was achieved using E3. It was assumed that the value-added products produced with the cellulose and hemicellulose would take preference, so the techno-economic evaluation was then conducted for the DL, E3 and C2 pathways to make the selected value-added products. This was due to the assumption that value-added sugar products generate higher revenue in comparison to lignin-derived products. Maximising the production of targeted products is prioritised; thus, the methods which result in the highest target product flows (namely DL, E3 and C2) were used to evaluate the techno-economic viability of each process route.

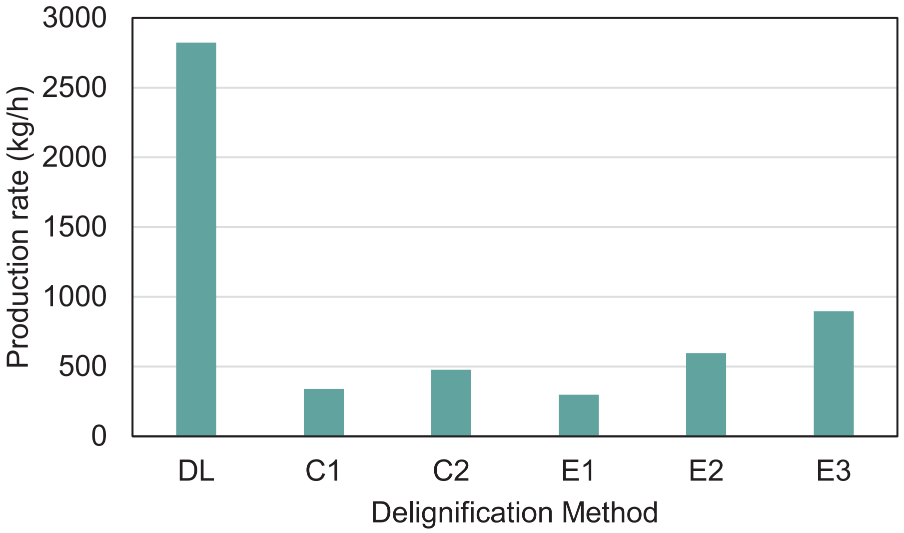

Figure 9-41 Ethanol production using SSF with various delignification methods

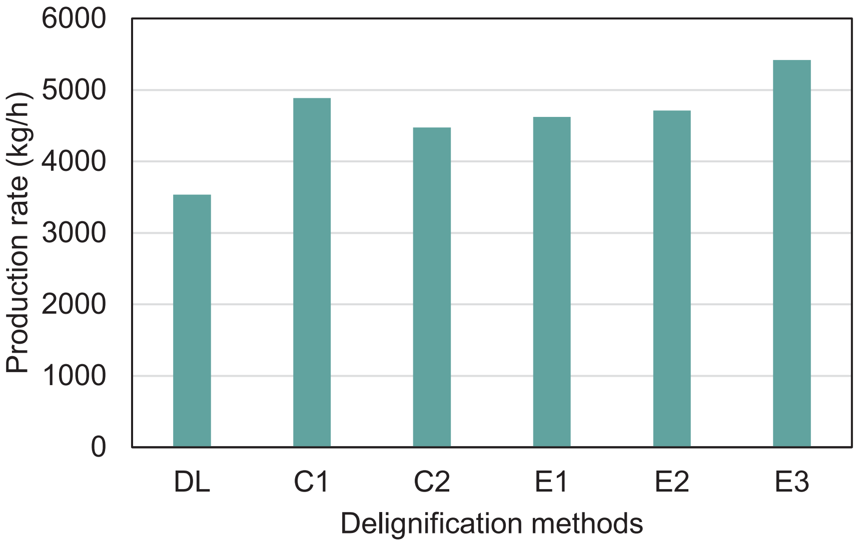

Figure 9-42 Bio-oil production via catalytic hydro pyrolysis

9.3.5 Evaluation of potential pathways

Electrocoagulation and chemical coagulation methods resulted in large operating and capital expenditures, which in turn were found to be impractical from a techno-economic standpoint. Hence, enzymatic delignification was implemented for all pathways considered as an alternative approach to delignification. Table 9-27 summarises the potential pathways evaluated for Stream 2 and the key process areas they utilise to produce various bioproducts.

Table 9-41 Potential pathways and key processing methods (Stream 2)

Pathway Number	Delignification Method	Bioproduct Processing Method	Target Product
1	Enzymatic Delignification	SSF	Ethanol, Bio-oil, Biochar
2		SHF	Ethanol, Bio-oil, Biochar
3		SSF	Lactic Acid, Bio-oil, Biochar
4		SSF	Succinic Acid, Bio-oil, Biochar
5		Fermentation	PHA, Bio-oil, Biochar
6		Thermal Conversion	Furfural, Bio-oil, Biochar

The accessibility of the cellulose prior to pretreatment was found to be lower than the accessibility in Stream 1. Owing to this, the capital and operating expenditure for these more intensive pretreatment methods were more significant for Stream 2 than for Stream 1.

The techno-economic analysis (Table 9-28) performed for Stream 2 assumed ideal separation and did not include capital nor operating expenditure related to DSP. The techno-economic analysis performed found pathways 1,3, and 6 unfeasible owing to their low rates of return and large pay back periods. This was largely attributed to the high operating costs associated with their respective processing routes. Table 9-27 provides the findings of the techno-economic analyses for pathways 2,4, and 5. To account for the water savings attributed to this processing, the quantity of water produced for recycling to the process was included in the revenue generation; this provided a more realistic perspective of the expected return from the processing of this nature. When compared to legacy practices of water usage, processing effluent from the pulp washing discharge results in a water savings of 0.2 million m^3/yr of water, which amounts to a cost savings of approximately R 6.28 million per year.

Table 9-42 Results of techno-economic analysis for potential pathways (Stream 2)

Pathway No.	OPEX (MR)	CAPEX (MR)	ROI	Payback Period	NPV (MR)	IRR (%)
2	706	5 450	2.55	15.0	-1510	6.03
4	1 600	443	4.31	12.1	-78.8	8.70
5	266	2 520	18.2	4,79	1730	20.2

9.4 Stream 3 (ECF Bleaching)

The decision pathway diagram for Stream 3 is provided in Figure 9-6.

9.4.1 Potential for remediation

From Chapter 4 (Section 4.3), it can be observed that there is a significantly smaller amount of carbohydrates in the ECF bleaching stream in comparison to the other two streams. This, coupled with the low accessibility of cellulose, indicates that remediation should be considered rather than valorisation. This would produce clean water that would aid in creating closed-loop cycles as well as energy from biomass that could be isolated.

9.4.2 Remediated Water Requirements

To be safely discharged to the environment or reused in the P&P industry, the effluent water needs to meet certain requirements. These limits are put in place to protect the environment and biological communities surrounding the discharge site. These specifications can be found in Table 9-29.

Table 9-43 Effluent discharge specifications according to Cloete et al. (2010)[1] and City of Cape Town (2020)[2]

Parameter	Value
COD[1]	1000
BOD/COD[1]	<0.5
pH[1]	6-7
TSS[2]	1000
Phenols[2]	25
Chloride[2]	1500
Carbohydrates[2]	1500
Sulphides[2]	50
Phosphorus[2]	25
AOX[2]	400

Key: 1: (Uǧurlu et al. 2008); 2: (Fernández-Rodríguez et al. 2015); 3: (Vinder and Simonič, 2012); 4: (Charles et al. 2013)

9.4.3 Remediation Methods

Four remediation methods were considered for the ECF bleaching stream; these included: electrocoagulation (EC), ultrafiltration (UF) membranes, ion exchange and adsorption using activated carbon. While EC was initially included as a method to consider, this method proved to have very large operating costs when implemented in Stream 2. Given that the throughput for Stream 3 is significantly greater than Stream 2, it is anticipated that the operating costs for EC would be exceedingly high; hence EC was excluded from further evaluation. Table 9-30 shows the pollutant removal efficiencies achievable for the various processes. The results for different removal methods can be found in Appendix A. It was assumed that the membrane and ion exchange process had the same chloride and AOX removal due to a lack of information in the literature. The removal of COD was assumed equivalent to the removal of phenols for UF due to the absence of available information in this regard.

Table 9-44 Remediation method removal efficiencies

Process Type	Lignin Removal (%)	COD Removal (%)	Chloride Removal (%)	AOX Removal (%)	Phenol Removal (%)
Membrane (UF 5 kDa)	65.6[2]	85.2[3]	87.5[3]	87.5[3]	85.2[2]
Ion Exchange: Amberlite IRA-96[4]	96.1	17.3	43.7	43.7	98.1
Adsorption: AC4	60.0	70.0	95.0	88.0	59.0

This data was used to generate flowrates and compositions for the treated water streams arising from them (Table 9-30 and Table 9-31). The compositions of these streams were compared with effluent specification standards to ascertain which methods of remediation were feasible.

Table 9-45 Flowrates for treated water from various remediation methods (in kg/hr)

Flowrates	Feed	EC	Membrane	Ion Exchange	AC
Hemicellulose	223	67.1	195	78.3	89.5
Cellulose	582	175	508	204	233
Lignin	25.8	5.20	8.90	1.00	10.3
Chloride	286	169	35.9	162	14.3
AOXs	9.80	3.30	1.20	5.50	1.20
Phenols	217	4.30	32.2	4.10	89.7
Water	514000	514000	509000	514000	514000
Total	515000	514000	510000	514000	514000

Table 9-46 Treated effluent compositions for various remediation methods (in mg/L)

Composition	Feed	EC	Membrane	Ion Exchange	AC
COD	2390	717	354	1980	717
TSS	55.5	55.5	55.5	55.5	55.5
Hemicellulose	434	130	382	152	174
Cellulose	1130	340	996	396	453
Lignin	50	10	17.4	1.95	20
Chloride	557	329	70.3	314	27.9
AOX	19	6.47	2.4	10.7	2.28
Phenols	422	8.45	63.1	8.02	174

9.4.4 Evaluation of potential pathways

Three key processes were considered for the remediation of the ECF bleaching effluent, namely: ultrafiltration membrane technology, adsorption using activated carbon and ion exchange. The COD (2.39g/L) reported for this stream was not sufficiently removed by ion exchange methods. Similarly, the phenol content (422 mg/L) could not be reduced to an acceptable standard using activated carbon. An analysis of combining these two methods was assessed; however, the cost of this combination made this process option unfeasible.

The unit treatment cost for each process route was determined by adding the operating cost of processing to an annualised capital cost and dividing this by the effluent flowrate. This unit treatment cost was compared to the unit treatment cost using traditional AS systems. Table 9-32 present the unit treatment costs associated with different remediation methods. It becomes apparent from these that membrane technology does offer an alternative to remediation that may be more cost-effective than traditional methods.

Table 9-47 CAPEX and OPEX for proposed and traditional remediation

	OPEX (RM)	CAPEX (MR)	Unit treatment cost (R/m^3)
Proposed Remediation			
Membrane (5kDa)	0.0996	4.88	0.492
AC + IR	625	358	1 050
AC	268	235	463
IR	626	123	1052
Traditional Remediation			
Activated Sludge	3.77	5.87	6,67

Since the bleaching effluent has the highest volumetric flowrate, this stream presents an attractive opportunity to recover a large quantity of water for reuse in the system, closing the loop and reducing the operating expenditure associated with makeup water. If 100% recovery of water is assumed, this process will recover 4.11 million m^3 of water per year; this has an estimate savings of R 144 million per year.

9.5 Observations and insights on complex streams preliminary techno-economics assessment

9.5.1 Stream 1 (Calcium spent liquor)

The calcium spent liquor stream (Stream 1) has the potential for valorisation into value-added bioproducts using a biorefinery approach. The most effective combination of pretreatment methods for this stream was found to be overliming, which serves as a detoxification method, and ultrafiltration using a 5 kDa membrane, which serves as a delignification method. The dissolving pulping method from which this stream arises ensures the highest accessibility of cellulose. This facilitates less intensive pretreatment methods, which in turn incur lower operational and capital expenditures. The most economically viable processing routes were found to be Pathways 2, 3 and 6.

Pathway 2 involves the production of ethanol via a simultaneous saccharification and fermentation process. To breakeven this process route has a minimum product recovery of 14% with an NPV of R 634 million. Pathway 3 involves the production of ethanol via an SHF process. The processing route was found to have a minimum product recovery of 39% with an NPV of R 3.2 billion. Pathway 6 involves the production of lactic acid via SSF. This process route was determined to have the highest NPV value of R 3.75 billion with a minimum product recovery of 38%. If ideal separation is assumed and all the water contained in this effluent can be recovered for reuse, processing of stream 1 could result in water savings of 0.5 million m^3 per year. This amounts to an approximate cost saving of R 16.3 million per year.

It is recommended that a further evaluation of the product-specific downstream processing costs be performed to ascertain a better reflection of the profitability of the aforementioned processing pathways. Further to this, a sensitivity analysis pertaining to the composition variability of the stream should be undertaken. This would require more in-depth stream characteristic data for process-specific operations.

9.5.2 Stream 2 (Kraft pulping stream)

The kraft pulp washing streams hold some potential for valorisation into value-added bioproducts. Cellulose is not as accessible in this stream as in stream 1; thus, more intensive pretreatment is required.

This is a major contributor to the processing costs associated with the pathways evaluated. Enzymatic delignification should be used as the pretreatment method for all streams. The pathway found to hold the most economic potential was pathway five. This considered the production of PHA via a fermentation process. A techno-economic analysis of this process determined an ROI of 18% with an NPV of R1.7 billion and an IRR% of 20.2%. If ideal separation is assumed and all the water contained in this effluent can be recovered for reuse, processing of stream 2 could result in water savings of 179 000 m^3 per year. This amounts to an approximate cost saving of R 6.28 million per year. It is recommended that a further evaluation of the actual product recoveries be performed and the cost of downstream processing be incorporated into the techno-economic analyses for this process route.

9.5.3 Stream 3 (ECF bleaching)

The high volume, low pollutant load and low complexity make this stream a suitable contender for remediation. Remediation using membrane technology may offer a cheaper alternative to current WWT practices, such as activated sludge systems.

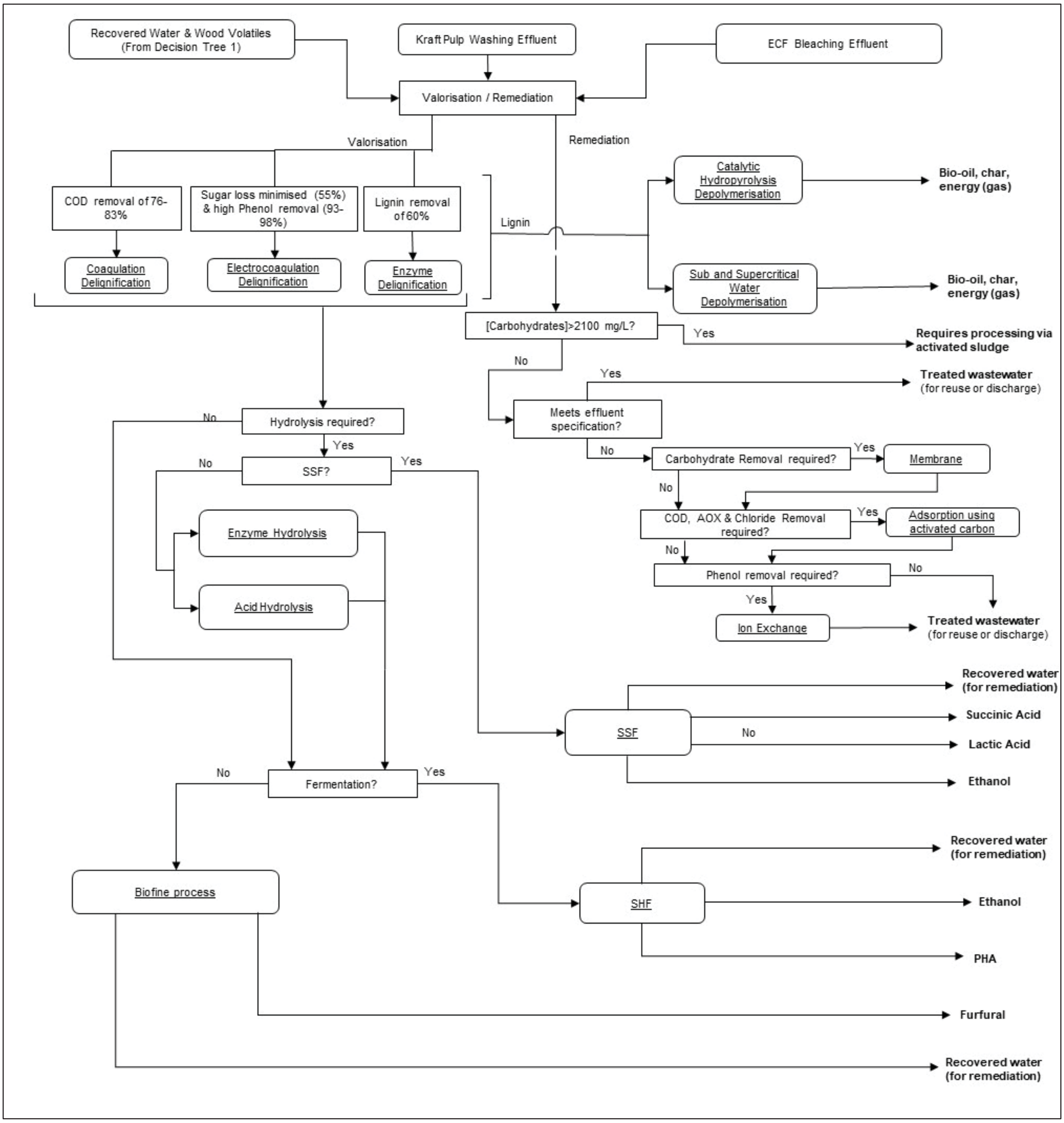

Figure 9-43 Decision pathways for streams 2 and 3

10 Conclusions

Increasingly, the need to maximise resource productivity and minimise environmental burden within the process industries is recognised. A core resource to contribute to both these goals is contained within wastewater. Through the concept of the wastewater biorefinery, in which the wastewater streams of major industries or domestic wastewater streams form the raw material, we seek to valorise waste components into products of value to society while, at the same time, upgrading the water quality to fit-for-purpose for use, allowing its reuse in place of virgin water resources. As such, wastewater biorefinery is based on the principles of industrial ecology and has the potential to contribute to the circular economy. Implementation of such technology has the potential for benefit in terms of resource efficiency, environmental protection and societal contribution.

On reviewing wastewater streams in South Africa and their potential to be considered as sources of raw materials for product generation or recovery or both to enhance efficiency in the use of natural resources, the pulp and paper industry has been recognised as a large consumer of water and hence generator of wastewater streams. Indeed, this holds both within South Africa and globally. With the success of concerted efforts to reduce the water footprint, these streams are increasingly concentrated and have been identified as having the potential for beneficiation through wastewater biorefineries, yielding both bioproducts and fit-for-purpose water.

In addition to acknowledging the potential for re-thinking the handling and valorising of wastewater in the PPI, an increasing trend is observed globally to develop pulp and paper mills into 2nd generation biorefineries to maximise the use of all the constituents of woody biomass to create a diverse product range. This diversification further opens up the substantial opportunity, explored in this study, to extract value from the P and P wastewater while concomitantly upgrading it to fit-for-purpose use for, preferably, reuse or release through the development of the **P and P wastewater biorefinery**. We expand the approach of the 2nd generation biorefinery to the liquid streams rich in carbon, including sugars, lignocellulose, fibres and more, as feedstock for biofuels, bioproducts, and biochemicals to be produced in the **3rd generation wastewater biorefinery**. In the wastewater biorefinery, our focus is on both the remediation of the wastewater to provide fit-for-purpose water and the bioconversion of the carbonaceous materials to products.

In the initial phase of the study, reported as Part 1, we explore the wastewater generation in typical pulp and papermaking operations, their flows and composition, and the potential of individual or composite streams for conversion to the product of most interest, decreasing the environmental burden and increasing resource productivity. This part of the study defines the available resource for use within the WWBR. We also explore the global trends in such process plants, particularly in terms of the 2nd generation biorefinery and the move towards dissolving pulp and other products beyond paper. These trends in the diversification of products open up the range of products under consideration in the PPI; this facilitates the expansion of the product range associated with the WWBR and has the potential to be complementary.

Currently, in South Africa, the wastewater of most pulp and paper plants is treated through traditional wastewater treatment processes with associated sludge disposal. This represents both a cost and a wastage of potential resources. The resource content of P and P wastewater in South Africa is presented. These wastewater streams contain significant amounts of sugars, lignin, fibre and various other extracts that are available to be transformed into a range of products, including biofuels, bioproducts and biochemicals. By examining the individual wastewater streams on a P and P plant prior to their combination for WWT, less complex and more concentrated streams can be identified with improved potential for valorisation. Following the characterisation of individual and combined wastewater streams from the PPI in South Africa, we applied a scoring exercise based on the criteria of wastewaters suitable for conversion to high-value products, commodity products or energy in the wastewater biorefinery in terms of volume, complexity and concentration. Through this, we highlighted streams with the most potential for further valorisation and the potential nature of this valorisation. Streams for which remediation only is more appropriate are also identified. Preventing premature mixing of the latter with the former enhances the potential for both value generation and the quality of water likely to be achieved. This scoring system has the potential to identify the most favourable wastewater streams for the WWBR.

In considering valorisation routes, a product selection framework was adopted, addressing market compatibility, technical and economic feasibility, appropriate production path as well as environmental benefit. A qualitative screening method for product selection is presented, highlighting the interacting factors in selection. Such product selection was first applied to the selection of the major product of value to be generated through the conversion of the major organic carbon fraction present in the wastewater. Streams with high concentrations of organics with limited complexity have the most potential for biotransformation to platform chemicals. While lignocellulosic biomass can be processed directly to value-added products, its decomposition into its intermediates (cellulose, hemicellulose and lignin) offers greater valorisation potential through the production of high-value products such as platform chemicals, which can feed into various markets. Lignin is an under-utilised resource, and its potential exceeds far beyond traditional energy products. Lignin can be processed into a range of value-added products. Where complex, high-concentration streams require substantial pretreatment and detoxification for conversion, their conversion to bioenergy is typically preferred, particularly as the necessary pre-treatments for higher value addition are costly. Low-concentration complex streams are best treated through conventional remediation approaches. The scoring approach developed is applicable to implementation on P and P plants to identify the potential for valorisation as well as the best approaches to combined or separate processing of wastewater streams.

Noting these varied process routes, it is also important to recognise the need for a multi-product wastewater biorefinery for the concomitant realisation of product optimisation for improved resource efficiency and recovery of fit-for-purpose water as a non-negotiable product stream. This is an important feature of the wastewater biorefinery. Indeed, in the evaluation of process flowsheets in this study over a series of case studies, significant volume and value of water recovery are highlighted as key drivers, alongside valorisation and resource recovery, in the wastewater biorefinery approach.

The potential of the wastewater biorefinery, illustrated through this series of case studies, is further elucidated by consideration of each case study.

In Case Study 1, **an integrated multi-product wastewater biorefinery** was conceptualised to convert the carbon resource in a selected lignocellulosic wastewater stream into the platform chemical lactic acid for conversion to bioplastic, lignocellulolytic enzymes and a bioenergy product biogas while producing “fit-for-purpose” water. Preliminary laboratory scale experiments demonstrated the potential of producing lactic acid and biomethane from synthetic pulp and paper wastewater.

For the production of lactic acid using *Bacillus coagulans DSM2314*, simultaneous saccharification and fermentation was the selected approach, following de-ashing. Small-scale reactor studies were used to investigate the fermentation conditions (aerobic vs anaerobic), the type of the carbon source (glucose vs xylose), the impact of pH control and the effects of lactic acid as an inhibitor. While aerobic conditions demonstrated higher OD readings compared to anaerobic conditions, pH control was found to be necessary to sustain bacterial growth in the anaerobic system over long periods of time due to the accumulative effects of the lactic acid. While xylose was metabolised at a slower rate than glucose, the same final amount of biomass was achieved for both glucose and xylose, demonstrating that the carbon source was not the limiting factor in the overall biomass production. Lactic acid was shown to negatively impact the growth rate of *Bacillus coagulans DSM2314,* highlighting the need to remove lactic acid from the reactor as it is being produced. A preliminary material balance showed the lactic acid potential in the wastewater potential of a recycling mill, with the production of 0.25 kg of lactic/kg of primary sludge.

The experimental production of biomethane further demonstrated the efficiency of a UASB reactor in treating pulp and paper wastewater. Results obtained from this study showed that increasing the organic loading rate of pulp and paper wastewater results in high methane productivity, with organic loading rates of > 35 g/L/day being processed in a stable system. To avoid process instabilities, such as VFA accumulation, it is recommended that an increase in organic loading rate occurs in a gradual manner.

In the second set of case studies, three complex streams were considered to identify potential processing routes through a desktop study, assessing the processing train to produce maximum potential while reclaiming fit-for-purpose water. In two of the three cases (sulphite spent liquor and kraft pulp washing liquor), despite the complexity of the wastewater stream, the desktop analysis shows potential for the recovery of a substantial water stream, the achievement of improved resource efficiency and predicted cost savings. For sulphite spent liquor, the product spectrum for the wastewater biorefinery explored the following potential products: ethanol, PHA, furfural, as a cluster or ethanol, succinic acid and lactic acid as a cluster. Lactic acid showed the most favourable techno-economic analysis, with ethanol also showing promise, with the need for further interrogation of DSP being recognised. As indicated above, water recovery is a key component of the economic benefit.

For the kraft pulp washing liquor, recovery of bio-oil and PHA were explored. While these products showed promise, the accessibility of the substrate is highlighted, with pre-treatments forming a core cost component when required. On considering the low-concentration but complex ECF bleaching stream, value recovery is not feasible, and remediation is preferred.

The multi-product flexibility of a pulp and paper wastewater biorefinery presents significant opportunities to traditional pulp and paper mills by offering various pathways to jointly remediate their wastewater and fuel a multi-product value chain beyond traditional pulp and paper products.

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Appendix A: Chapter 9 - Techno-Economic Analysis Calculations

Appendix A-1 Revenue Calculations

The revenue generated for each process route was determined using the chemical market price shown in Table A-1, obtained from Rueda et al. (2014) and using Equation A-1

Table A- 1: Product market prices

Product	Price (R/ton)
Lignosulfonates	21864
Furfural	9110
PHA	75380
Succinic Acid	38025
Ethanol	13483
Lactic Acid	15305

$$Revenue = Market\ Price\ \left(\frac{R}{ton}\right) \cdot Product\ Flowrate\ \left(\frac{tons}{yr}\right) \qquad \text{A- 1}$$

Appendix A-2: OPEX Calculations

Overliming

Rueda et al. (2014) reports an operating cost of 0.11 M€ per year for the overliming of a stream with a feed flowrate of 616 000kg/hr. To determine the OPEX associated with the overliming method for detoxification Equation A-2 was used.

$$OPEX = \frac{Feed_{\ actual}}{Feed_{ref}} \cdot\ OPEX_{ref} \qquad \text{A- 2}$$

Ultrafiltration

Rueda et al. (2014) reports a cost of manufacturing using ultrafiltration of 420 000 €/yr, production has an average permeate flowrate of 39 100 tons/hr. The OPEX for ultrafiltration (both 5kDa and 1kDa) was calculated according to Equation A-3.

$$OPEX = \frac{Permeate_{actual}}{Permeate_{ref}} \cdot OPEX_{ref} \qquad \text{A-3}$$

SSF for ethanol production

The production of ethanol via SSF using olive tree pruning is reported to cost 1710000$/yr (Solarte-Toro *et al.*, 2019). This production cost is associated with the production of 5220000 litres of ethanol. The production cost to produce ethanol via SSF was calculated according to Equation A-4. The production costs associated with the production of ethanol via SHF were assumed to be over a similar magnitude and hence were calculated using the same approach.

$$OPEX = \frac{Ethanol_{actual}}{Ethanol_{ref}} \cdot OPEX_{ref} \qquad \text{A-4}$$

SSF for lactic acid production

A process which produces 100 000 tons/year of lactic acid is reported to have a production cost of 1180 $/ton (Manandhar and Shah, no date). The total production cost was calculated using Equation A-5.

$$OPEX = Lactic\ acid\ produced \cdot Production\ cost_{ref} \qquad \text{A-5}$$

SSF to produce succinic acid

Klein et al. (n.d.) reports a succinic acid (SA) production cost of 2.32 $/kg. This was used Equation A-6 to determine the OPEX for this process route.

$$OPEX = Production\ Cost\ _{SA} \cdot Production\ rate_{SA} \qquad \text{A-6}$$

Fermentation to produce PHA

Choi et al. (2010) reports an operating cost of $6 700 000 per year for a plant producing 12 tons of PHA per day. This operating cost was used to determine an estimate for the production costs associated with producing PHA in various processing routes using Equation A-7.

$$OPEX = \frac{PHA_{actual}}{PHA_{ref}} \cdot OPEX_{ref} \qquad \text{A-7}$$

Thermal conversion to produce furfural

A plant producing furfural with a feed flowrate of 33 000kg/hr has an associated operating expenditure of €90 000 000 per year (Giuliano *et al.*, 2018). This value was used to estimate the OPEX associated with process routes producing furfural according to Equation A-8.

$$OPEX = \frac{Feed_{actual}}{Feed_{ref}} \cdot OPEX_{ref} \qquad \text{A-8}$$

DSP Baseline Estimate

The baseline estimate for the associated OPEX of DSP was estimated using the costs attributed to the downstream processing of bioethanol. This is estimated to be \$0.16 per gallon of ethanol produced (Solarte-Toro *et al.*, 2019). The OPEX for the DSP in each process route was found by multiplying this production cost by the quantity of bioproduct being produced.

Appendix A-3: CAPEX Calculations

Overliming

Kazi et al., (2010) reports an overliming capital cost of \$47313 (in 2007), this is associated with a throughput flow of 616 000 kg/hr. The overliming CAPEX was calculating according to Equation A- 9 below.

$$CAPEX_{overliming} = \frac{Feed_{overliming}}{Feed_{ref}} \cdot \frac{CEPCI_{2019}}{CEPCI_{2007}} \cdot CAPEX_{ref} \tag{A- 9}$$

Ultrafiltration

Rueda et al. (2014) reports a capital cost of € 20 600 000, for an associated permeate flow of 39 100 tons/hr. The CAPEX for each ultrafiltration process within each pathway was determined using Equation A-10.

$$CAPEX = \frac{Permeate_{actual}}{Permeate_{ref}} \cdot\ CAPEX_{ref} \tag{A- 10}$$

SSF to produce ethanol

The production of ethanol via SSF using olive tree pruning is reported to have a CAPEX of \$ 24 530 000 (Manandhar and Shah, no date). This production cost is associated with the production of 5220000 litres of ethanol. The CAPEX for this processing route was determined using Equation A-11. The same assumption (mentioned in Appendix A-2) regarding the OPEX of SHF pertains to the CAPEX for SHF processing.

$$CAPEX = \frac{Ethanol_{actual}}{Ethanol_{ref}} \cdot\ CAPEX_{ref} \tag{A- 11}$$

SSF to produce lactic acid/succinic acid

The CAPEX for the SSF process route to produce lactic acid was reported to be \$130 000 000 for a process which produces 100 000 tons/yr lactic acid. To determine the CAPEX associated with the production of lactic acid for various pathways, this capital cost was scaled according to Equation A- 12. It was assumed that the capital cost associated with the production of succinic acid would be similar in magnitude, and hence the CAPEX of this route was calculated in the same manner.

$$CAPEX = \frac{Lactic\ Acid_{actual}}{Lactic\ Acid_{ref}} \cdot CAPEX_{ref} \tag{A- 12}$$

Fermentation to produce PHA

Choi et al. (2010) reports a capital expenditure of \$55 000 000 for a plant producing 12 tons of PHA per day. This CAPEX was scaled using Equation A-13 to determine the CAPEX for pathways producing PHA.

$$CAPEX = \frac{PHA_{actual}}{PHA_{ref}} \cdot CAPEX_{ref} \tag{A- 13}$$

Thermal conversion to produce furfural

A plant producing furfural with a feed flowrate of 33 000kg/hr has an associated capital cost of €64 400 000 (Giuliano *et al.*, 2018). This value was used to estimate the CAPEX associated with process routes producing furfural according to Equation A-14.

$$CAPEX = \frac{Feed_{actual}}{Feed_{ref}} \cdot CAPEX_{ref} \tag{A- 14}$$

DSP Baseline Estimate

The CAPEX for a DSP unit involved in the production of 25 000 gallons of bioethanol is estimated to be \$18 400 000 in 1999 (Solarte-Toro *et al.*, 2019). An estimate for the CAPEX of DSP for each pathway was calculated using Equation A- 15 and the respective bioproduct production.

$$CAPEX = \frac{Bioproduct\ produced_{actual}}{Ethanol\ produced_{ref}} \cdot CAPEX_{ref} \cdot \frac{CEPCI_{2019}}{CEPCI_{1999}} \tag{A- 15}$$

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