CRANFIELD UNIVERSITY

Cynthia Ediabai Adu

Designing a circular business model from industrial by-products: A case study on paper mill sludge

School of Aerospace, Transport and Manufacturing
EngD in Sustainable Materials and Manufacturing

EngD
Academic Year: 2015 - 2019

Supervisor: Prof Mark Jolly
Associate Supervisor: Prof Stephen Eichhorn
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This thesis is submitted in partial fulfilment of the requirements for the degree of EngD in Sustainable materials and manufacturing
(NB. This section can be removed if the award of the degree is based solely on examination of the thesis)

ABSTRACT

The circular economy (CE) emphasises the optimisation of resource yields by keeping products, components and materials at their highest utility and value. This recently popularised concept has created awareness within businesses, government and policymakers. However, there is a discourse that the concept lacks scientific rigour and has primarily been led by practitioners such as policy makers, social scientists and business consultants.

Resources in the CE concept are referred to as biological nutrients and technical nutrients. Based on the CE resource recovery model, biological nutrients such as organic waste/by-products are expected to return to the system. However, the current waste management sector is not equipped with how to innovate and/or create value from resources termed as waste/by-products. Whilst CE is a commendable strategy with insightful case studies, the philosophy currently lacks robust design guidance that can provide businesses with the tools and tactics required to meet the agenda.

Therefore, this EngD research applies design thinking innovation methodology to an existing business faced with the challenge of adopting a circular business model for resource recovery. The EngD research is based on Ecoganix, an organic waste treatment company. Ecoganix manages Paper Mill Sludge (PMS), a by-product derived from the waste-water treatment of paper mills. In the UK, a million tonnes of PMS is currently produced annually.

The management of PMS is an environmental challenge and the second highest cost for the sector after energy consumption. The PMS is collected by Ecoganix from 7 paper mills in the UK for use as soil improvement on farm land . The current management system of PMS is unsustainable and short-term. Moreover, the market is highly competitive due to increasing recycling rates and competitive pricing. Nonetheless, this material PMS is rich in organic cellulose fibres and inorganic minerals. Thus, a design thinking methodology is used to create new value streams of materials from this by-product.

The design thinking methodology is a four-stage process, namely; discover, define, develop and deliver. The ‘discover’ stage of the research is a convergent thinking

approach which employed techniques such as literature review, brainstorming, rapid prototyping and field study to gain insights on PMS. The ‘define’ stage focused on the characterization of PMS, which revealed possible applications of PMS. The 'develop' stage led to the innovation of a diverse product portfolio from PMS. These products are; production of cellulose nanofibres from PMS referred to as ‘Paper sludge nanofibres’ (PSNF), packaging foams from PSNF, PSNF spun into filaments and PMS composite panels.

The final stage of the methodology ‘deliver’ involved the proposal of a circular business model including an environmental an economic assessment. Ecoganix is now building a spin-out company Ecoprodux, which will be used to convert PMS into high valued products. Waste management companies can also adopt the methodology used in the research.

‘The key is simply to uncover value in waste.’

-Gunter Pauli, The Blue Economy 3.0: The Marriage of Science, Innovation and Entrepreneurship Creates a New Business Model That Transforms Society

Keywords:

Cellulose nanofibres; circular economy; design-thinking; paper mill sludge; upcycling

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I appreciate the 1st cohort of Sustainable Materials and Manufacturing CDT, it has been a pleasure supporting each other on this journey. Jake, Zoe and Ross; thank you for the pub quizzes, the lifts to campus and for immersing me into your creative personalities. I thank my remarkable parents who provided the resource and foundation for my education. I am grateful for my 5 amazing siblings who are always proud of me. Finally, to my fiancé Stuart, you are exceptional for the many roles you play as technical support, personal chauffer and my unfailing source of encouragement.

Cranfield, October 2019

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GLOSSARY

CE	Circular Economy	A proposed concept to move from the current resource intensive economic model to one that maximises the full potential of resources.
DT	Design thinking	A four-stage methodology for understanding problems and developing innovative compelling solutions.
DS	Deinking sludge	Sludge from mills using recycled paper, it contains minerals such calcium carbonate, silica and very low fibre content.
CNF	Cellulose Nanofibres	Fibres less than 100 nanometres in width extracted by mechanical or chemically treatment of pulp.
EMF	Ellen MacArthur foundation	UK registered charity promoting the circular economy.
IB	Internal bonding	Measure of materials ability to resist rupture in the direction perpendicular to the plane material surface.
MOE	Modulus of elasticity	Measure of the rate of change of stress to strain under uniaxial loading within elastic limits of a material. (N/mm2)
MOR	Modulus of rupture	Also known as flexural strength; it is the measure of the material strength in bending. (N/mm2)
PMS	Paper Mill Sludge	The by-product of paper manufacturing waste-water treatment process which contains cellulose fibres and inorganic minerals.
PS	Primary sludge	Sludge with high cellulose fibre content and lower mineral fillers.
PSNF	Paper Sludge Nanofibres	Nanofibres produced by mechanical fibrillation of paper mill sludge.
PVA	Poly Vinyl Alcohol	Water soluble synthetic polymer.
SS	Secondary sludge	Sludge obtained after biological treatment process, with high mineral content, microbial cell mass and less fibres.
TS	Thickness swelling	Measure of the increase in thickness of a material after immersion in water.
WWT	Waste-water treatment	Process for removing contaminant from wastewater to return it to the water cycle.

1 Introduction

> *'Our woods are the glory of the countryside and a vital record of our technological and artistic past. They have survived into our time not because they were treasured relics, but because they were useful. In the 20th century we almost forgot their value in our throw-away plastic culture. We began to believe that we did not need them. Now we know that we need to preserve woods it is time, perhaps to think about how we might still use them, to restore their biological, cultural and economic value in a new Wood Age. They are part of our heritage, and we of theirs'*- An excerpt from 'The age of Wood' *written by* Max Adams, Archaeologist and Author.

Paper is one of the most recycled products in the world. Its raw material wood is a renewable source that can be processed in many ways to replace fossil-based materials (Hagemann et al., 2016). Fundamentally, paper mills are biorefineries capable of converting renewable biological resources into value-added products that could otherwise be produced from fossil fuels. An example is the Äänekoski bio-product mill in Finland, which produces 1.3 million tonnes of pulp annually and utilises 100% of its by-product material. The mill transforms its by-products into biogas, textiles, chemicals and polymers whilst generating energy from biofuel and wood pellets. This is a quintessential exemplar of the biological cycle proposed in the circular economy. The Circular Economy (CE) has recently gained traction within Europe's political and academic landscape (EM Foundation, 2013). Bio-materials have been identified as an important element to deliver the strategy (Schoenmakere et al., 2018). A widely adopted definition of the circular economy by the Ellen McArthur foundation (EMF) is;

> 'A Circular Economy is one that is restorative by design, and aims to keep products, components and materials at their highest utility and value, at all times' (Webster, 2015).

In broad terms, the CE proposes a move from our current resource intensive economic model to one that manages our finite resources to its maximum potential. The CE concept groups resources into technical cycle and biological cycle. The technical cycle refers to synthetic materials which are expected to stay within the smallest loop of the system, by extending their product life, sharing and servitisation before considering

remanufacturing or recycling. Whilst the biological cycle refers to organic materials that can return to the systems as biochemical feedstock. The potential environmental and economic savings presented in the literature on the CE is attractive to businesses however, its scientific research content is unexplored (Korhonen, Honkasalo and Seppälä, 2018). Although the CE literature is growing, most studies focus on conceptual frameworks and the development of CE business models for the technical cycles. Design has been recognised as a catalyst for the circular economy. However, there is limited research on the application of design tools on the biological cycle of the circular economy.

1.1 Research question

There is a lack of evidence based research that informs businesses on how to use design to bring the CE concept into fruition (Moreno et al., 2016; Urbinati, Chiaroni and Chiesa, 2017). Therefore, this EngD research addresses the research question:

'How can waste management businesses uncover value from waste/by-product for the circular economy?'

This research question is addressed based on a case study of the EngD industrial sponsors; Ecoganix Ltd. This chapter details the background of the research, the research gaps and relevance in chapter 1.1 and 1.2. The research aim and objectives are outlined in chapter 1.3. The innovation statement and contribution to knowledge is presented in chapter 1.4. The structure of the innovation report in chapter 1.5 and the publication outcomes and dissemination of the research is illustrated in chapter 1.6.

1.2 Background

The pulp and paper industry is well-versed in recycling, with Europe boasting a 72% recycling rate and a set target of 74% in 2020. However, the manufacturing and recycling of paper requires large volumes of water, which generates waste-water requiring treatment. During this waste water treatment (WWT) process, a solid by-product known as paper mill sludge (PMS) is derived. Approximately 1 million tonnes of this by-product is produced annually in the UK and expected to increase because of high paper recycling targets. If disposed in landfill 1 tonne of paper mill sludge releases 2.69 tonnes of carbon dioxide, 0.24 tonnes of methane (Likon et al., 2011). The standard tax rate for landfill is currently £91.35 (Customs, 2019). The management of this by-product

poses a stringent environmental and economic challenge to the industry. Ecoganix Ltd manages the collection and utilisation of this paper mill sludge for seven mills in the UK. PMS comprises cellulose, a natural polymer, and minerals from chemical fillers used to enhance the properties of the paper. However, the primary waste management methods for PMS are agricultural land spreading, incineration and landfill (Confederation of paper industries, 2014; Monte et al., 2009; Phillips et al., 1997). These current waste management practices do not employ circular economy principles and lack viability long-term. The development of new value-added products from paper mill sludge is thus essential to increase the resource efficiency of the pulp and paper industry.

1.3 Industrial relevance

The world is in a digital age where the fundamental use of paper for storing and sharing information has been replaced by electronics. However, the pulp and paper industry continues to thrive, as global megatrends have accelerated the consumption of paper products (Berg and Lingqvist, 2017; Lingqvist and Berg, 2017). These megatrends such as the ageing population have increased consumption of hygiene paper products. The e-commerce industry is heavily reliant on paper products for packaging materials, urban lifestyles have created a high demand for food outlets which increase the consumption of food packaging materials. Hence, paper products remain a commodity. Paper can be recycled 4-6 times (Bureau of International Recycling, 2016) and it is typically recycled into products with very short lifespan (days). Which implies that the amount of resources consumed during its recycling may not be justifiable. There are global expectations set for paper recycling rates to increase, thereby a steady supply of recycled fibres is required to achieve quality grade paper. However, reused fibres have reduced properties which do not meet all product standards (Kinsella et al., 2018). Consequently, the increasing demand for paper products with high recycled fibres content leads to an increasing use of chemical additives and fillers to satisfy product quality. As a result, environmental regulations are required for managing paper mill waste-water. The management of the sludge separated from the waste-water prior to discharge is the second highest cost for mills. Therefore, the industry will benefit from environmental and economic savings if these by-products can be used to create new value streams.

1.4 Research aim and objectives

1.4.1 Aim

This research aims to use design-thinking methodology to transcend the current short-term management of industrial by-products of paper manufacturing into a circular business model.

1.4.2 Objectives

The objectives of this innovation report are to:

1. Discover applications for the utilisation of paper mill sludge as a value adding material.

2. Define the properties of paper mill sludge by the characterisation of its organic and inorganic fractions.

3. Develop paper mill sludge material applications and assess their technical feasibility.

4. Deliver a circular business case for paper mill sludge based on economic and environmental justifications.

1.5 Innovation statement

This research addresses the management of paper mill sludge towards a circular economy landscape by applying design-thinking methodology. This innovation report presents the conversion of paper mill sludge into the following products;

- Cellulose nanofibres (CNF) produced from PMS without chemical treatments. Henceforth, this material will be referred to as ‘paper sludge nanofibres (PSNF).
- Cellulose fibres/filaments spun from the dissolution PSNFs in ionic solvents.
- Foams produced from PSNFs and Poly-vinyl alcohol as a possible replacement of expanded polystyrene/polyurethane foams.
- PMS composite panels bonded with bio-resin as a proposed substitute for panels in dry conditions and floor tiling.
- The research proposes a new business model based on products derived from mill sludge.

- Finally, the methodology used in the research is proposed as a guideline for other waste management companies.

1.6 Innovation report structure

The EngD portfolio is made up of six individual reports and this innovation report/thesis is the final piece of written work that synthesises the portfolio submissions to tell a coherent story.

Chapter 1 discusses the industrial relevance, the research question, research aim, objectives and outlines the innovation statement and the innovation report structure.

Chapter 2 proposes design thinking as an innovation methodology to address the research gap and question. The methodology involves 4 stages known as discover, define, develop and deliver which are applied to the case study of PMS.

Chapter 3 is the 'discover' stage whereby a series of divergent design methods such as field study, brainstorming, literature review and rapid prototyping were used to gain insights on the properties and applications of PMS. *This chapter makes up submission 1 of the EngD portfolio.*

Chapter 4 is the 'define' stage, this chapter applies various material characterisation methods to identify the organic and inorganic content of PMS. *This chapter makes up submission 2 of the EngD portfolio.*

Chapter 5 is the 'develop' stage, whereby 4 main materials are prepared from PMS. The preparation and technical feasibility of each material is described in chapter 5.1-5.4.

Chapter 5.1 discusses the production of cellulose nanofibres from PMS which is referred to as paper sludge nanofibres (PSNF). *This chapter makes up submission 3 of the EngD portfolio.*

Chapter 5.2 discusses the spinning of PSNF into long filaments proposed for textile and composite materials. *This chapter makes up submission 4 of the EngD portfolio.*

Chapter 5.3 discusses the production of foams from PSNF. These foams are proposed as possible replacement of fossil fuel foams such as expanded

polystyrene and polyurethane products. *This chapter makes up for submission 5 of the EngD portfolio.*

Chapter 5.4 discusses the production of composite panels from PMS. *This chapter makes up for the final submission to the EngD portfolio, submission 6.*

Chapter 6 is the 'deliver' stage whereby the materials developed from PMS are proposed as a product portfolio in a circular business model. An economic and environmental assessment of the business model is also conducted.

Chapter 7 refers to the research question *'How can waste management businesses uncover value from waste/by-products for the circular economy?'*, by providing guidelines based on the design thinking methodology and insights from the case study.

The full innovation report structure is illustrated in figure 1 below. The portfolio submissions are coloured in blue. It is highly recommended to refer to the portfolio submissions as it expands on the research undertaken.

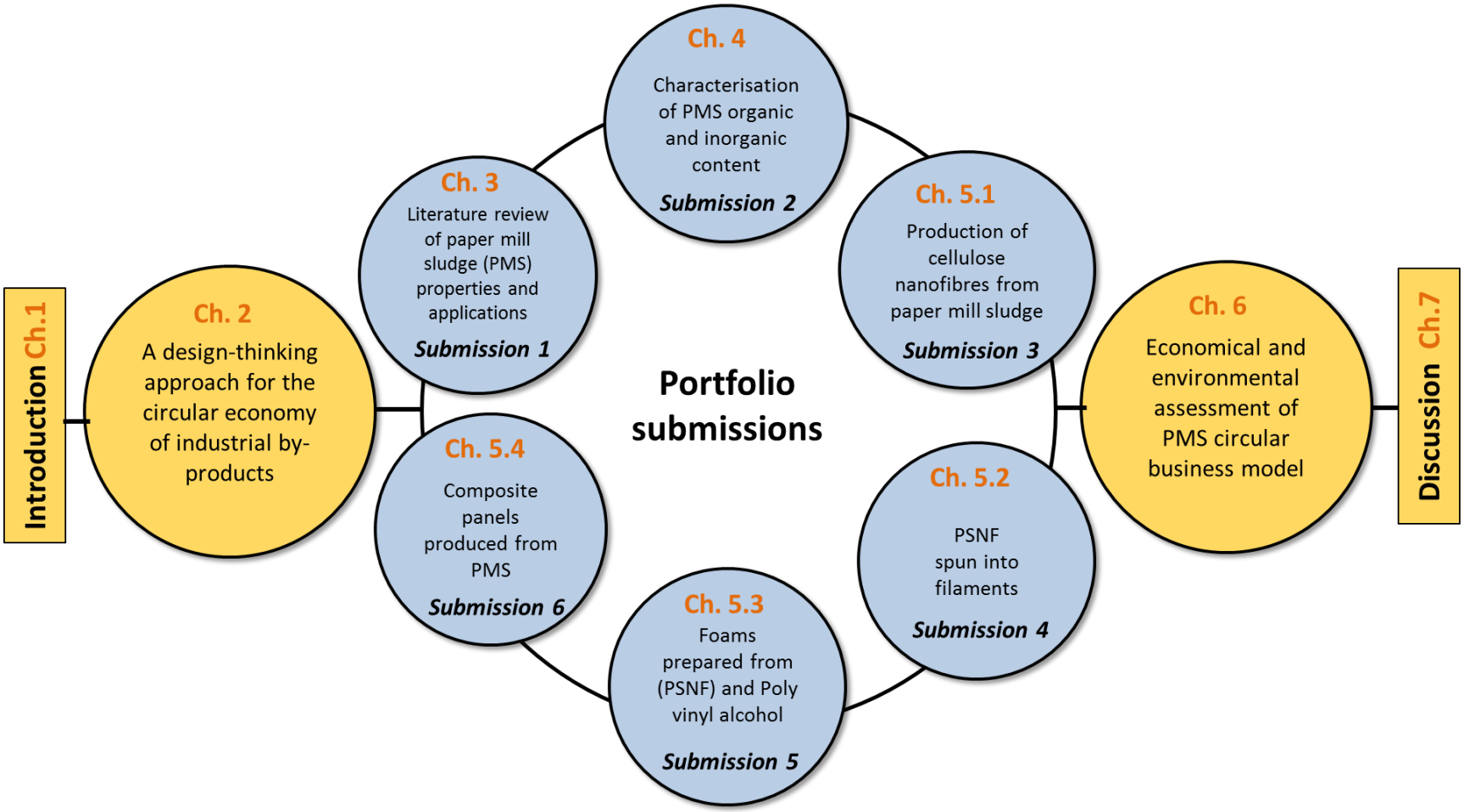


Figure 1: Innovation report structure showing portfolio submissions in blue.

1.7 Research dissemination

This research has been disseminated through journal publications, conferences and public speaking events, as detailed below.

Academic journal papers

- Adu, C., Jolly, M. and Thakur, V.K. (2018) 'Exploring new horizons for paper recycling: A review of biomaterials and biorefinery feedstocks derived from wastepaper', Current Opinion in Green and Sustainable Chemistry, 13 pp. 21-26.

- Adu, C., Berglund, L., Oksman, K., Eichhorn, S.J., Jolly, M. and Zhu, C. (2018) 'Properties of cellulose nanofibre networks prepared from never-dried and dried paper mill sludge', Journal of Cleaner Production, 197 pp. 765–771.

- Adu, C., Rahatekar, S., Filby, J., Ayre, D. and Jolly, M. (2019) 'Structural packaging foams prepared by uni-directional freezing of paper sludge cellulose nanofibres and poly (vinyl alcohol)', Materials letters., 253 pp.242-245.

Conference publication

- Adu, C and Jolly, M. (Conference paper and oral presentation) 'Developing Fiber and Mineral Based Composite Materials from Paper Manufacturing By-Products' pp. 435-444. *Sustainable Design and Manufacturing International Conference (2017). Bologna, Italy.*

Conference presentations

- C. Adu 'Developing sustainable materials from paper mill wastewater sludge' *Clean Tech East 2018: Driving clean growth. 3rd September 2018. UEA enterprise centre, Norwich.* ***(Keynote speaker)***

- C. Adu and M. Jolly. 'Structural Polymer Foams Prepared from Paper Mill Sludge Cellulose Nanofibres and Poly Vinyl Alcohol by Crosslinking Using Directional Freezing'. *2019 TMS Annual Meeting & Exhibition. REWAS: Secondary and By-*

product Sources of Materials. 10th March-14th March 2019, San Antonio, Texas. ***(Poster presentation)***

- C. Adu, C. Zhu, A. Koutsomitopoulou, S.J. Eichhorn, M. Jolly. and K. Potter. 'Upcycling of paper mill sludge into cellulose fibres by ionic liquid dissolution and dry-jet wet spinning'. *ACS National Meeting & Exposition, 31th March- 4th April 2019, Orlando, Florida, USA.* ***(Oral presentation delivered by C. Zhu)***

Public engagement and outreach

- "What?! Your car is made from paper?" Soapbox Science Milton Keynes 2019

2 Methodology: A design thinking approach for the circular economy of industrial by-products.

> *'There are known knowns; there are things we know we know. We also know there are known unknowns; we know there are some things we do not know. But there are also unknown unknowns; the ones we don't know we don't know.'-Donald Rumsfeld, Former US secretary of Defence.*

This chapter addresses the rationale behind the researcher's choice of using design thinking as a methodology. The chapter also outlines the methods used in the four design thinking stages to collect data.

2.1 Research Design

This research addresses a real-world problem posed to a business with the aim of transitioning towards a circular economy. Researchers have acknowledged that business transition to a circular economy is a complex problem (Bocken et al., 2016; Yang, 2016). The appropriate response for resolving a problem is dependent on the nature of the problem. The Cynefin framework illustrated in figure 2 is a decision-making tool to aid problem understanding and to provide an appropriate response to a problem (Rubin, 2013).

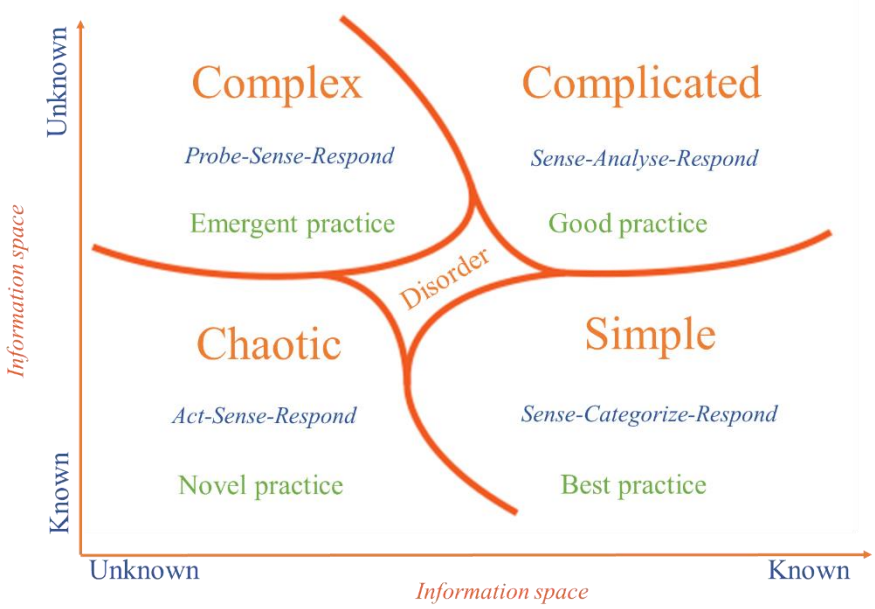


Figure 2: The Cynefin framework showing the four domains of problems.

The Cynefin framework is used to contextualise problems by bringing together ontology (what is out there to be known) and epistemology (what and how we can know about it) to aid decision making. The framework has been applied in engineering consultancy, policy making, action research and product development (Van Beurden et al., 2013; Hasan and Kazlauskas, 2009). It is based on the cause and effect relationship allowing problems to be placed in the domain of; simple, complex, complicated and chaotic (Snowden and Boone, 2007; Snowden and Kurtz, 2003).

Table 1: Understanding the 4 problem domains of the Cynefin framework

Problem domain	**Response**
Simple domain-(Known-known) *(Examples: Installation of smart meters in UK homes)* Cause and effect relationship is mostly linear. The outcomes of this domain are predictable.	***Sense-Categorise-Respond*** It can be resolved by drawing on best practices and following clear standards of procedures.
Complicated domain (Known-unknown) *(Example: Resolution of product defects)* A relationship exists between cause and effect. It is predictable however separated between time and space. Therefore, it becomes difficult to propose a solution.	***Sense-Analyse-Respond*** Problems in this domain require analysis and expert knowledge to apply good practice. Good practice is applied here because there may be several acceptable solutions to the problem.
Complex domain (unknown) *(Example: Reduction of food waste in UK household)* The cause-and-effect relationship are non-linear and multidisciplinary. Understanding the problem alone requires experimentation	***Probe-Sense-Respond*** The approach to problems in this domain is to develop 'probes' that reveal emergent patterns. The decision-making style in this domain is based on emergent practice because best practice or good practice copied and pasted form another system will

There are no right answers but mainly trial and error. There are competing ideas of solutions. It is difficult to predict how the system will react after intervention.	not work here. Hence the problem relies mainly on creativity and innovation.
Chaos domain (Unknown known) ('WannaCry' ransomware on the National Health Services NHS, natural disaster) There is no relationship between cause and effect at the system level. The system is turbulent and manageable patterns do not exist. This is typically a crisis with no time to think or consult people.	***Act-Sense-Respond*** A direct intervention is necessary here to bring the problem to one of the other domains. The suitable decision model is to act first then sense the influence of the action before making responses.

The framework should however not be interpreted as a 2 by 2 matrix as problems can be resolved allowing them to move from the complex domain to the complicated domain. Circular economy challenges display the same characteristics of a complex problem defined in the Cynefin framework. The proposed approach for solving complex problems requires probing, sensing and responding. Probing allows to develop open-minded observation rather than fast answers based on preconceived ideas. As patterns emerge from probing it is possible to sense (evaluate relevant information) which ideas are useful before responding. The framework also emphasises the relevance of innovation and creativity in solving complex problems. This problem-solving approach is the fundamentals of design thinking methodology, a divergent and convergent innovation process also known as the double diamond or 4D's of design (von Thienen, Meinel and Claudia, 2012; Waloszek, 2012).

2.2 Design thinking innovation process

Design thinking is a methodology for understanding problems and developing innovative compelling solutions. The concept originated from a design firm IDEO and Stanford university school of design. After which it gained attention in government projects, policy-making and businesses. It is a methodology proposed not only for designers but for decision-makers to tackle complex problems (Brown, 2009; von

Thienen, Meinel and Claudia, 2012). The design thinking stages have been proposed in in various formats. Stanford university design school format is a 5-stage process known as; empathise, define, ideate, prototype and test. Other formats include; understand, observe, define, ideate, prototype and test (Waloszek, 2012), Zurb design thinking model, Google design sprint process. Nonetheless all formats have a fundamental creative process of divergent thinking which stimulates idea generation and convergent thinking which is a more logical way of transforming ideas into solutions. Divergent thinking provides the ability to generate multiple solutions to a problem, it is a creative thinking process aided by applying tools such as brainstorming and mind mapping. Whereas convergent thinking is analytical and judgemental process similar to how the brain works (Hassan, 2016). The double diamond design-thinking thinking format from the Design Council which is known as the double-diamond is illustrated below in figure 3. The design thinking process starts out with a design brief, vision or intent. The aim of the 'discover' stage is to gain insight into the design brief. This is done by applying divergent thinking through ethnographic research, questionnaires, interviews, stakeholder engagement, field study, rapid prototyping. The next stage 'define', is a convergent thinking approach focused on defining the problem by identifying patterns, interpreting findings, mapping themes and causal inferences based on the insights from the discover stage.

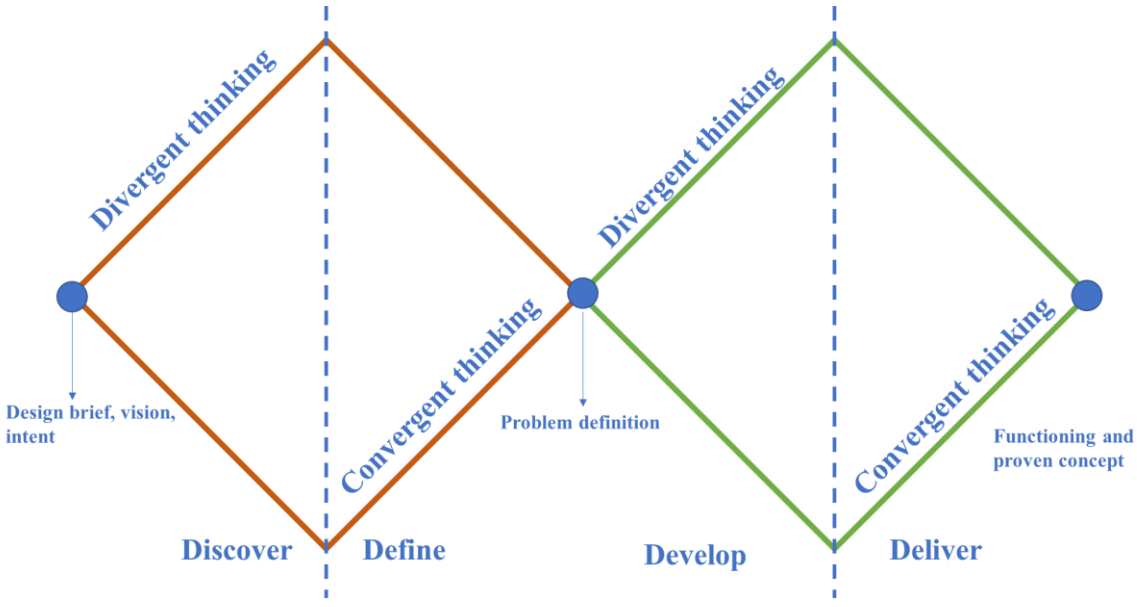


Figure 3: Design thinking innovation process showing the four stages.

After defining the problem, the ‘develop’ stage involves proposed ideas and concepts created by prototyping and experimentation. This stage also requires divergent thinking to explore different options, after which proposed concepts can be tested or benchmarked to deliver a proven concept. Other methodologies applicable for problem solving are; DMAIC (define, measure, analyse, improve, control); DMADV (define, measure, analyse, improve), agile and stage-gate process. However, DMAIC and DMADV heavily data driven six sigma methods which are more suitable for process improvements. These methods do not adopt the culture of creativity which required to design out waste. Design thinking methodology is suitable for developing concepts and lower Technological Readiness Level (TRL) 1-4 with lower risks whereas methods such as DMAIC and DMADV are more applicable to higher TRL level (5-9).

2.2.1 Limitations of design thinking methodology

Design thinking may be viewed as an ambiguous approach when strict project deadlines are important. There is a risk of not converging after the discover stage or the develop stage. The iterative process of the methodology may be difficult to adopt in a business environment as it is time consuming and the process requires multiple stakeholders (Liedtka, 2015). Design thinking is also linked with very high expectation that all leaders and innovators must be great design thinkers (Hassi and Laakso, 2011). Design thinking doesn’t have a performance measurement tool while the process is taking place. Its success can only be measured through the outcome. Thus, this makes it challenge when identifying if the process is going in the right direction.

2.3 Design and the Circular Economy (CE)

The commonly used definition of the CE by Webster 2015; ‘a Circular Economy is one that is restorative by design...’ signifies the importance of design to the concept. An overview of the growth of CE literature is shown in figure 4. The trend of the graph above shows a linear growth in CE literature as of 2001 based on the search key TITLE (‘circular economy’). The earliest document came from China which was also noted as the highest contributor to the CE literature. The early literature focused on the 3R’s (reduce, reuse and recycle) to promote the CE as a sustainable development strategy to

the Chinese government (Beijing Review, 2008; Lei and Yi, 2004; Yuan, Bi and Yuichi, 2006).

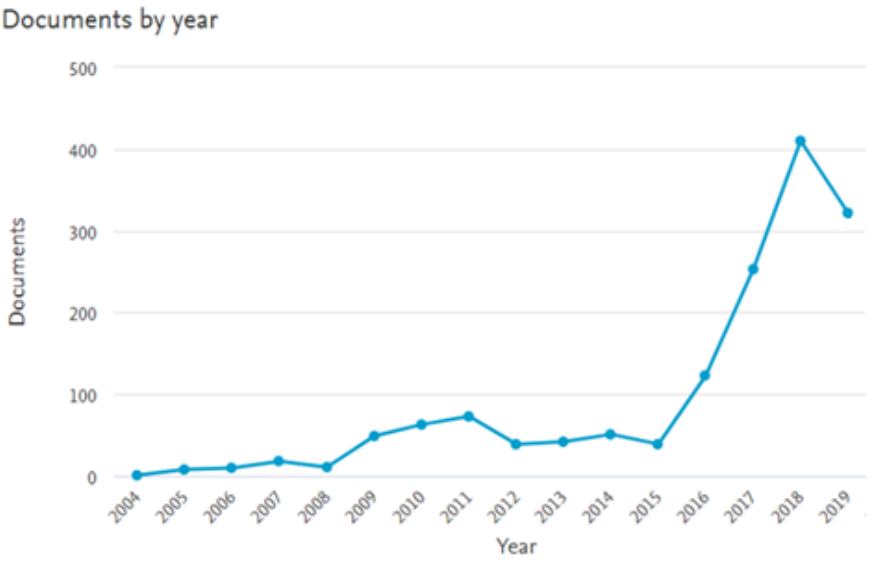


Figure 4: Growth in CE literature from Scopus database showing the huge acceleration since 2015

Yong and Doberstein (2010) noted that although the term 'Circular Economy' was coined by China, it was inspired by the close loop system adopted in Germany and Japan. This may explain why literature search with 'circular economy' is populated mainly from results from China as shown in the graph in figure 5 from 2004-2014.

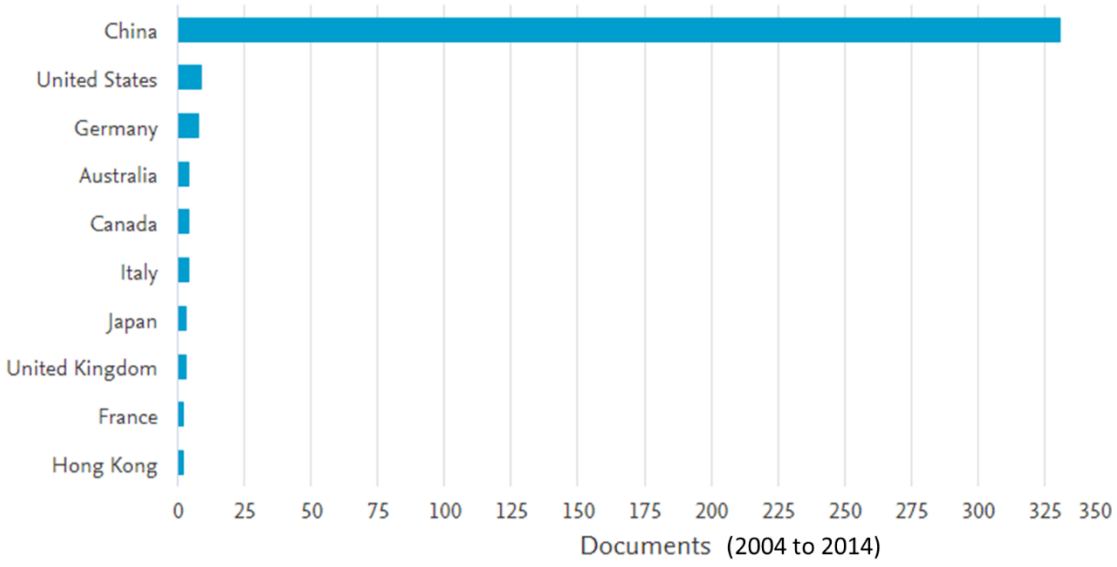


Figure 5: Circular economy literature by region from 2004 to 2014.

Whilst China's approach for the circular economy was a top-down governmental proposal through the circular economy promotion law, other regions such as Europe and the Americas adopted bottom-up approach. The UK joined the CE conversation in 2013 with literature from the Ellen MacArthur Foundation (Webster, 2013). Webster discussed the six temptations to avoid when talking about the circular economy, this further influence how EMF depicts the CE strategy today. In the past decade, the CE strategy evolved beyond the 3Rs with the Ellen MacArthur foundation championing and promoting the strategy.

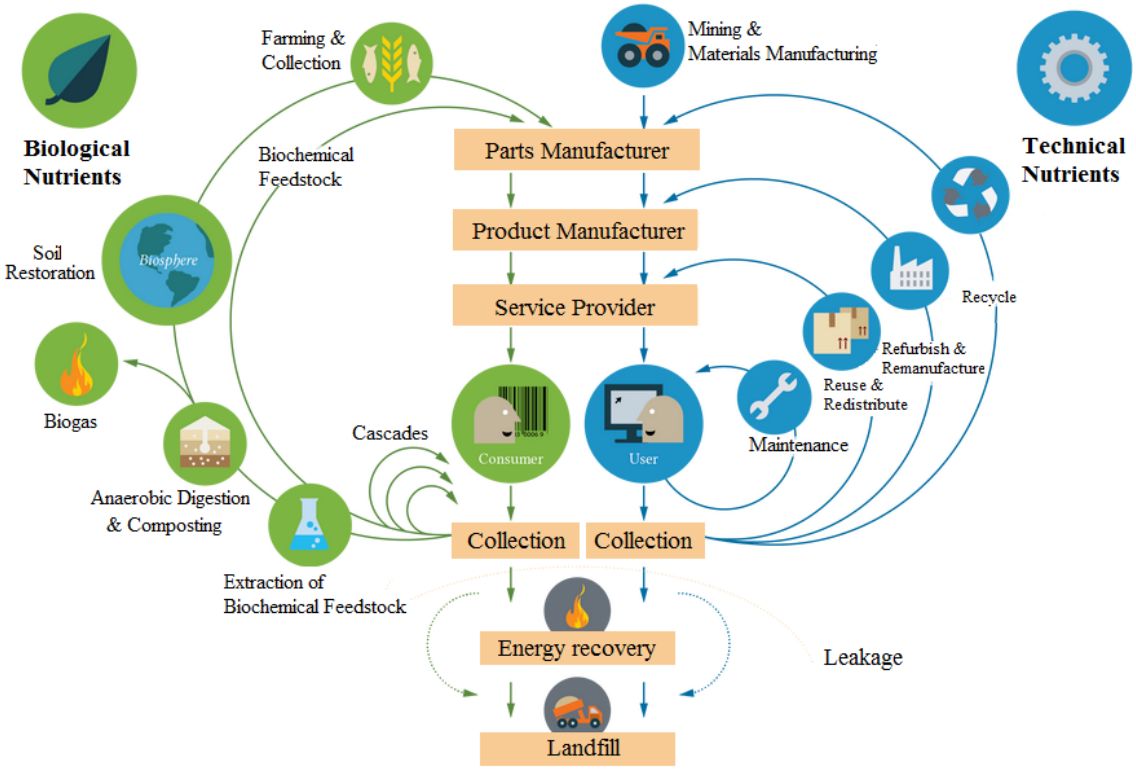


Figure 6: The butterfly diagram (EM Foundation, 2013).

The butterfly diagram from EMF shown in figure 6 was a key instrument in illustrating the CE concept and promoting understanding. Materials consumed in the system is referred to as biological nutrients and technical nutrients. The diagram is based on a close-loop system whereby the inner loops require less resources and serve higher value. Whereas, giving the second law of thermodynamics based on entropy, the outer loops will require more energy/resources to bring them back into the system and the quality of these materials will diminish. The term "Circular Economy" became popularly adopted amongst many countries in Europe and by the United States. The early academic

and grey literature on CE was primarily focused on conceptualising the CE; the literature typically discussed origins of CE, the principles, challenges and opportunities (Ghisellini, Cialana and Ulgiati, 2016; Su et al., 2013). As of 2015 a dramatic increase in CE literature occurred from 39 documents to 123 in 2016, this was after the EMF published two key reports

1) Growth within: A circular economy vision for a competitive Europe (25th June 2015)
2) Delivering the circular economy: A toolkit for policymakers (26th June 2015)

After the reports from EMF and interests from policy makers some, from 2015 onwards the literature became gradually populated by the UK, European countries and the United States as shown below in figure 6.

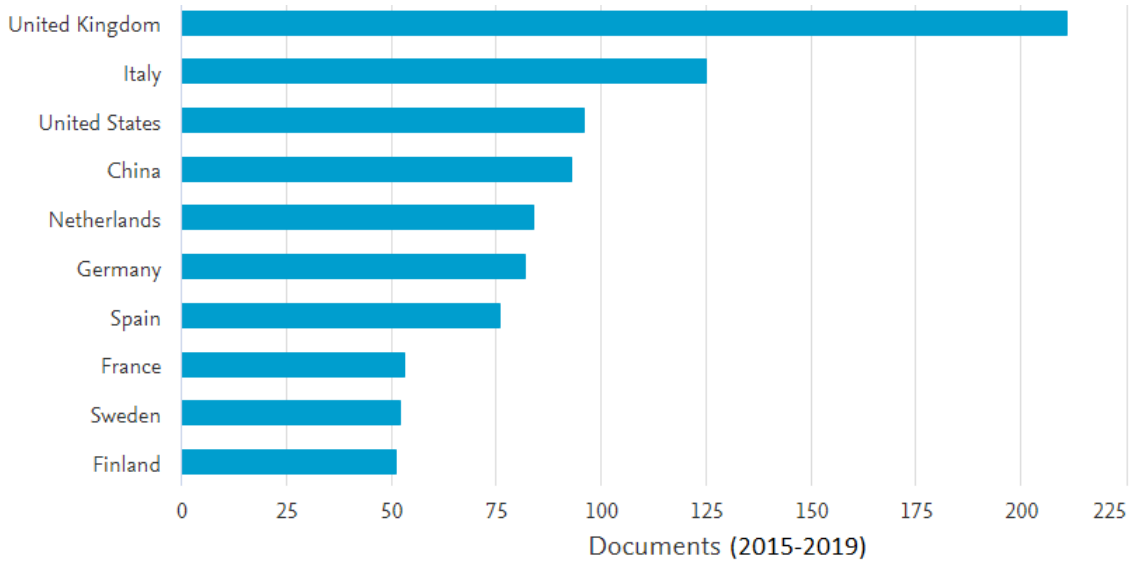


Figure 7: Circular economy literature by region from 2015 to 2019.

At the start of the EngD research, it was observed that the CE literature did not provide business with specific tools or tactics for designing a circular business model or product. To reveal this gap in the literature, a literature search on Scopus database was conducted to investigate if businesses have been provided with guidance for CE transition and if design thinking has been applied as a methodology for a CE business model. The search code; TITLE-ABS-KEY (‘circular economy’ AND ‘design’) was used which resulted in 182 articles as of 2016 when the research was conducted. These documents and their abstracts were reviewed to determine the following criteria:

- A: Articles discussing the CE concept directly/indirectly through various topics.
- B: Articles proposing CE business models, design strategies and providing businesses with the tools to apply CE principles.
- C: Articles actively applying design thinking or other innovation methodology to guide business innovations and transition towards circular economy.

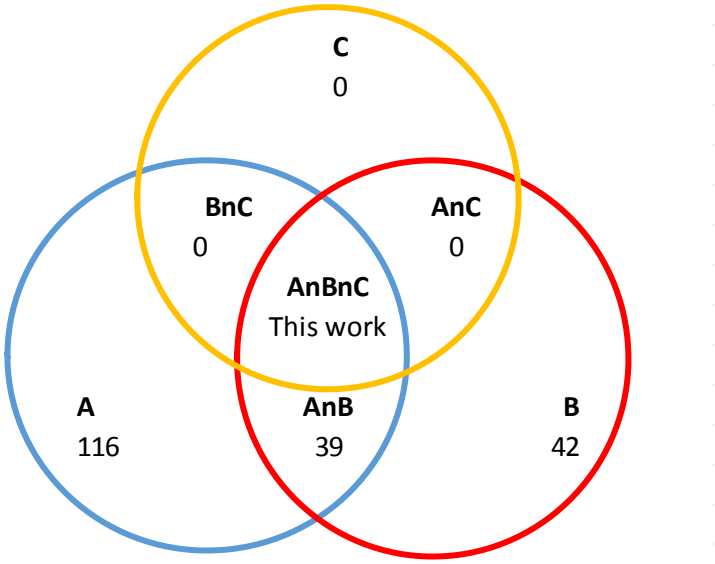


Figure 8: Venn diagram illustrating gaps in CE literature.

The Venn diagram in figure 7 illustrates the research gap in the CE literature. Out of the 182 articles, 116 met criteria A for discussing the CE concept directly/indirectly through various topics such as review of the circular economy (Ghisellini, Cialana and Ulgiati, 2016; Haas et al., 2015) collaborative systems of sharing in the circular economy (David, Chalon and Yin, 2016),biorefinery for waste processing (Mohan, 2016; Satchatippavarn et al., 2016), research on green packaging (Zhang et al., 2010a), circular economy and the automotive sector (Soo, Compston and Doolan, 2016; Zhang et al., 2010), studies on circular economy and the coal industry (Song et al., 2011; Xu, 2009), scarce metals/critical materials (André, Söderman and Tillman, 2016). Although, majority of the article were found to meet criteria A, 44 article met criteria B for proposing business models, design strategies and provide business with the tools to apply CE principles. Some well-cited literature includes articles on product-service systems for the circular economy(Bakker et al., 2014; Tukker, 2015), articles on strategies and frameworks for circular designs (Devadula and Chakrabarti, 2015; Moreno et al., 2016;

Yang, 2016), designing business models for the circular economy (Bocken et al., 2016; Lewandowski, 2016a). Authors identified the importance of the CE literature to move away from conceptualisation to transition. Authors such as (Bocken et al., 2016; Devadula and Chakrabarti, 2015; Moreno et al., 2016; Urbinati, Chiaroni and Chiesa, 2017) made their contributions on how to transition towards the CE by proposing business models and design strategies.

Particularly, the work from Bocken *et al*. (2016) which was cited 354 times addressed the question: 'What are the product design and business model strategies for companies that want to move to a circular economy model?'. The work introduced 3 key fundamental strategies to transform a linear business into a circular closed-loop model. These three fundamental strategies provided significant insight on what circular products and business models should follow, companies such as Accenture adopted these strategies to further conceptualise and understand the circular economy (Accenure Strategy, 2016). The strategies are as follows;

1. Slowing resource loops: the design of long-life products and product life extension that results slowing down or resources.
2. Closing resource loops: by recycling resources post-consumer use and during production.
3. Narrowing resource loops: also known as resource efficiency this is based on use of fewer resources per product.

Bocken *et al.* (2016) conceptualised the circular economy by reviewing product design strategies and business model strategies that businesses can adapt for; slowing, closing and narrowing resource loops. Whilst Bocken *et al.,* (2016) contributed to the fundamental understanding of designing circular business models and products, Moreno *et al*., (2016) later added that they had not considered the valuable literature on design for sustainability (DfX) and Moreno's research highlighted the need to provide designers and industrialist with how to apply specific design strategies to different circular business models. Thus, Moreno's work led to a comprehensive list of DfX methods/tools listed below in table 2.

Table 2: Design methods/tools for CE design strategies (Moreno *et al.*, 2016)

Circular Design Strategy	Design Focus	DfX Method/Tool
Design for circular supplies	Design for closing resource loops	Design for biodegradability
		Design with healthy/smart processes/materials
Design for resource conservation	Design for reduce resource consumption	Design for production quality control
		Design for reduction of production steps
		Design for light weighting, miniaturizing
		Design for eliminating yield loses/material/resources/parts/packkaging
		Design for reducing materials/resource use
Design for long life use of products	Design for reliability and durability	Design on demand or on availability
		Design the appropppriate lifespan of products/components
	Design for product attachment and trust	Create timeless aesthetics
		Design for pleasurable experiences
		Meaningful design
	Design for extending product life	Design for repair/refurbishment
		Design for easy maintenance, reuse and repair
		Design for upgradability and flexibility
	Design for dematerialising products	Design for product-service systems
		Design for swapping, renting and sharing
Design for multiple cycles	Design for resource recovery	Design for easy end-of-life cleaning, collection and transportation of recovered materials/resources
		Design for cascade use
		Design for (re)manufacturing and dis and re-assembly
		Design for upcycling/recycling
Design for system change	Design to reduce environmental backpacks	Design for the entire value chain
		Design for local value chains
	Design for Regenerative Systems	Design for biomimicry
		Design for biological and technical cycles

Whilst the extensive list of DfX method/tool presented in table 2 provides several options for designing circular products or materials, it is challenging for businesses that do not have product design as a skill or key competency to adapt these tools. Moreover, as CE emphasises on the flow of technical and biological nutrients; the current waste management sector is also responsible for the transformation of nutrients at their end of life, into new products. For example, in the waste management of paper mill sludge where the traditional practice is to use the by-product for land spreading, such businesses will require an innovation process that aids value creation from materials that have reached their end of life. Andrews (2015) was the researcher found to discuss the use of design thinking for the circular economy, the article explains how designers can lead a paradigm shift and have the potential to influence consumer behaviour and increase the perception

of product value through design thinking. Nonetheless, Andrews did not provide a tool to express how businesses can use design thinking to transition towards the circular economy. Additionally, the majority of the literature fulfilling criteria B on design strategies focused on the technical nutrients and design strategies on biological nutrients were not prevalent in the literature.

Moreover, since the circular economy has been criticised as being based on theoretical foundation rather than scientific rigour (Korhonen, Honkasalo and Seppälä, 2018), it should be analysed based on its theoretical rigour as the scientific literature is in its infancy. An approach by Whetten (1989) explains that, theoretical concepts should be based on the fundamental building blocks of 'Why? What? and How? and these logical factors should be considered when developing theories. Similarly, Sinek (2011) applies the same principle on how systems change should be based on the foundations of 'Why? What? And How?', also known as 'the golden circle' shown below in figure 9.

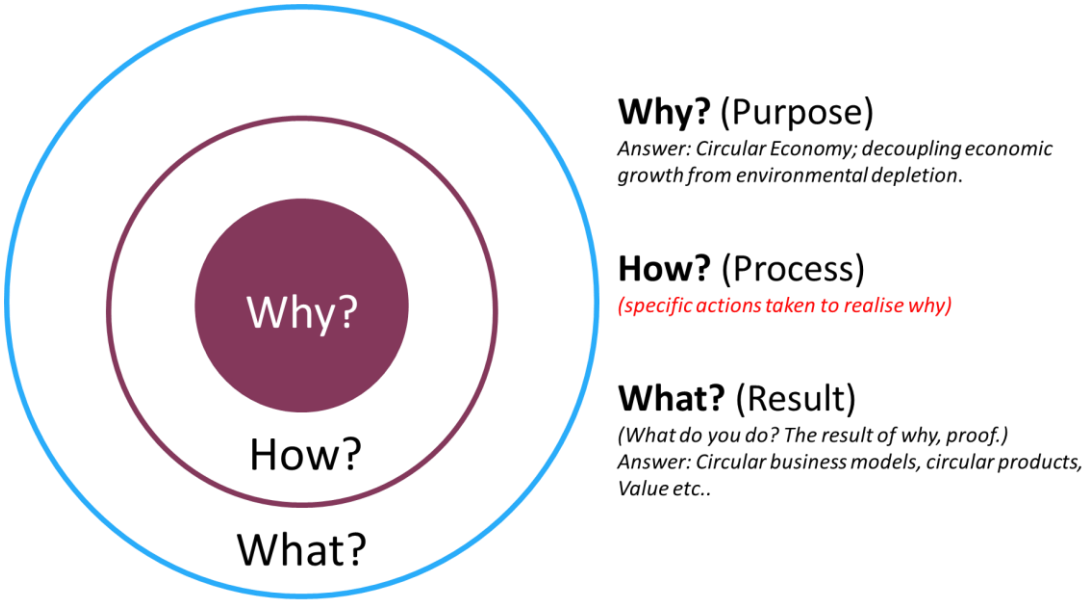


Figure 9: Addressing the circular economy with Sinek's Golden Circle showing…..

Sinek further explains that it is easier for organisations to drive change and communicate their business strategy efficiently when they start with 'Why?'. The golden circle here is used to understand the theoretical foundations of the CE from an organisation's perspective.

'Why?'-describes the purpose, of what the organisation is trying to achieve; circular economy, to decouple economic growth from environmental depletion.

'How'- is the process and specifications required to achieve **'Why'**.

'What'- is the result of **'Why'**, i.e proof (circular business model and products).

Since **'How'** depends on process and specifications required to achieve **'Why'**, is not clear, this makes it more challenging for organisations to reach **'What'**. **'What'** corresponds with the neocortex brain which allows us to rationalise and make decisions. Hence, this makes it challenging for an organisation to transition to a circular economy model. Thus, to answer the research question below;

'How can waste management businesses uncover value from waste/by-product for the circular economy?'

This EngD research uses design thinking as an innovation tool to uncover value from industrial by-products from paper manufacturing.

2.4 Design thinking applied to PMS case study

The case study investigated, is based on the project proposal delivered at the start of the EngD research as follows;

Project title: Development of sustainable manufacturing materials from cellulose-based by-products.

Project description: Cellulose-based materials manufacturing processes often produce significant quantities of by-products. The large volume by-products produced are typically consistent in nature. A number of these products are currently successfully recycled however great potential remains for the development of added value manufacturing materials. There is an opportunity to up-cycle these by-products to ensure that the inherent material value is kept rather than down-cycling them as a farm humus for soil improvement. The business challenges cover developing plans for the whole process from collection, manufacture and market research to identifying opportunities as either raw materials or products to improve margins on these materials.

Material: Paper mill sludge; cellulose based by-product derived from waste-water treatment process of paper manufacturing.

Industrial sponsors: Ecoganix Ltd; organic waste management company.

Customer: 7 UK based paper mills; customers of Ecoganix LTD

Other stakeholders: Farmers

The project description highlights the challenge for a waste management business in contract with a client base of 7 paper mills. The relationship and current business model of the waste management company is illustrated below in figure 10. The waste management company collects the by-products from the paper mills and recycles them for soil improvement in the agricultural industry.

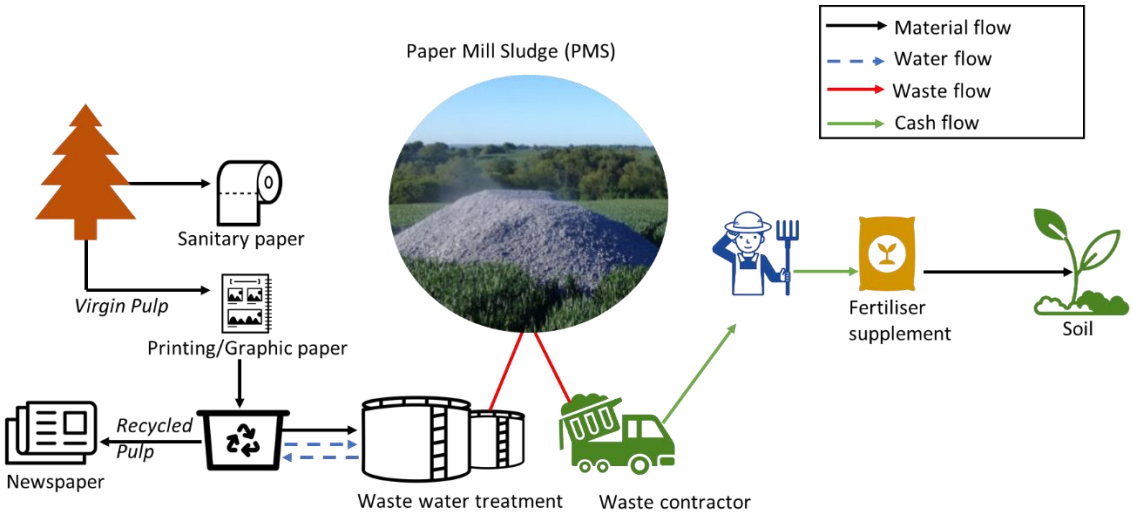


Figure 10: Relationships and current business model of Ecoganix.

PMS lacks sufficient macro-nutrient for soil enhancement (nitrogen, potassium, phosphorus). Thus, the waste management company pays the farmer for nitrogen supplements to encourage the use of PMS on the soil. Whilst the current process generates revenue the following challenges for the business and customer are highlighted below.

- Current waste management process is short-term.
- 1 million tonnes of PMS generated annually in the UK.
- Economic and environmental challenge to the paper mills.
- The current business model revenue growth.
- PMS management is a competitive market due to pricing.
- The lack of innovation in PMS management influences market competitiveness.

The following challenges have been taken into consideration and design thinking methodology illustrated in figure 11. The objectives of the research are achieved by following the 4 stages of the design thinking methodology; discover, define, develop, deliver.

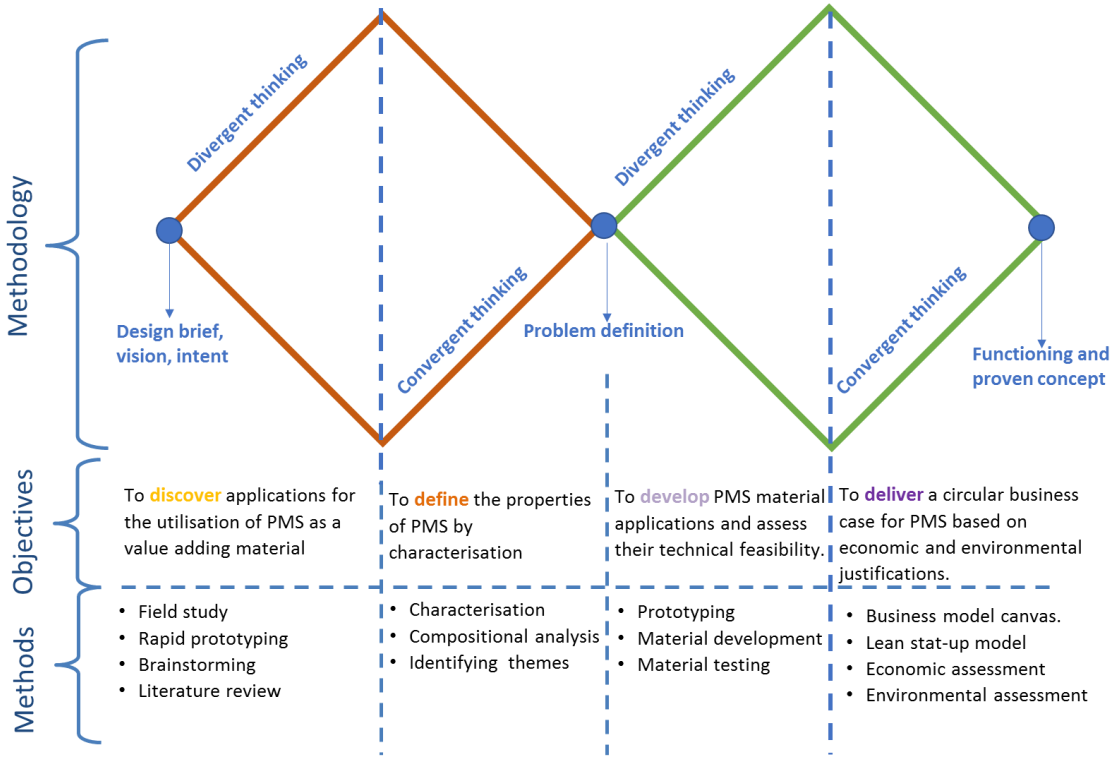


Figure 11: Design thinking methodology applied to PMS case study.

The methodology involves both quantitative and qualitative methods. In the discover stage qualitative methods such as field study, brainstorming, rapid prototyping and literature review are used to generate ideas and gain insights. The define stage uses quantitative methods such as material characterisation and compositional analysis which help with identifying themes i.e. which ideas generated from the discover stage should be explored further as a concept. These concepts are used in the develop stage and their technical feasibility is assessed. The developed concepts are proposed as a business model with economic and environmental assessments. Although the methods used here are relevant to this research there are other design methods that can be applied. For example, a consumer facing, or service problem can apply methods such as ethnography, survey, in the discover stage whilst in the develop stage methods such as user trial and ergonomic analysis (Martin and Hanington, 2012).

3 Discover: A literature review of paper mill sludge properties and applications.

This chapter address the first objective; To discover applications for the utilisation of paper mill sludge as a value adding material. In this chapter, divergent design methods such as field study, brainstorming, rapid prototyping and literature review were used to gain insights on the possible utilisation of PMS. *Refer to submission 1 of the EngD portfolio for more details on this chapter.*

Paper is a highly utilised commodity produced from forestry, according to the circular economy it is a biological nutrient as it can be returned to the system without causing environmental detriment. Paper is recycled widely, in the UK the recycling rate for paper and cardboard is 79% in 2017 (Defra & Government Statistical Service, 2019). During paper production large amounts of water are consumed leading to a global average water footprint of 5.1litres per A4 80 g printing/writing sheet. This average ranges from 1.01 litres/sheet in subtropical regions to 12.9 l/sheet in the temperate zone. 80% of this is attributed to blue water i.e. from rivers, lakes and groundwater. (Schyns, Booij and Hoekstra, 2017). Recycling and recovery of paper products drastically reduces water consumption by 40% (Oel and Hoekstra, 2010). During paper recycling water can be recycled in a waste-water treatment (WWT) process. However, paper products cannot be infinitely recycled as the fibres become shorter. These shorter fibres and mineral fillers obtained during the wastewater treatment process is known as paper mill sludge (PMS).

3.1 Paper mill sludge (PMS)

In the UK one million tonnes of PMS is produced yearly as the by-product of paper manufacturing waste-water treatment process. It was theoretically estimated by Likon *et al.*, (2011) that disposal of one tonne of PMS to landfill will contribute to 240 kg of methane emissions and 2.7 t of carbon dioxide emissions. Additionally, the cost of landfill tax in the UK is £91.35 per tonne by 2019 and is set to increase annually. Hence, with the proposed circular economy theory there is an opportunity to investigate if value from this by-product can be discovered. Paper mill sludge Can be described as primary sludge, secondary sludge and de-inking sludge (Bajpai, 2015).

Primary sludge (PS): This sludge is containing high cellulose fibre content and lower mineral fillers. Primary sludge is collected with filters and screens during the water the clarification process in the mill.

Secondary sludge (SS): This sludge is obtained after the biological treatment process it has high mineral content (>30%), microbial cell mass and less cellulose fibre.

De-inking sludge (DS): Paper mills using recovered paper products have deinking sludge from the paper recycling process. De-inking sludge contains high mineral content such as silica (SiO_2) and calcium carbonate ($CaCO_3$).

The quantity of sludge generated at the paper mill depends on the pulping process and raw materials used. An estimate of PMS generated per tonne of product depending on the pulping process is shown below in table 3 below (Dahl, 2008).

Table 3: Sludge generated per tonne of product for different pulping methods

Manufacture process and product	**Kg of Dry PMS /tonne of product**
Chemical pulping	20-25
Mechanical Pulping	15-20
Semi-chemical Pulping	25-30
Recycled fibre	50-120

The use of recycled fibres tends to generate larger volumes of sludge because of shorter fibres, ink and coatings on the recycled fibre source. A field study of the mills was carried out to understand the mill operations and type of sludge generated.

3.2 Field study

The field study enables the collection of data that is not available in literature and to gain practical insight that can complement theoretical knowledge. The field study research was undertaken at the paper mills who were suppliers of the industrial sponsor. During field study a tour of the paper mill was provided by the plant manager or senior member of the company with an understanding of the facility and business challenges. The competitive nature of the industry required this methodology for data collection as opposed to a formal interview/questionnaire style. This allowed the paper mills who are

all customers of Ecoganix to feel comfortable when asked about the mill operations. Moreover, this method allows for a deeper engagement with the customers. During the tour of the mill open ended questions were posed. The following pseudonyms have been used for the mills and their geographical location is illustrated below in figure 12.

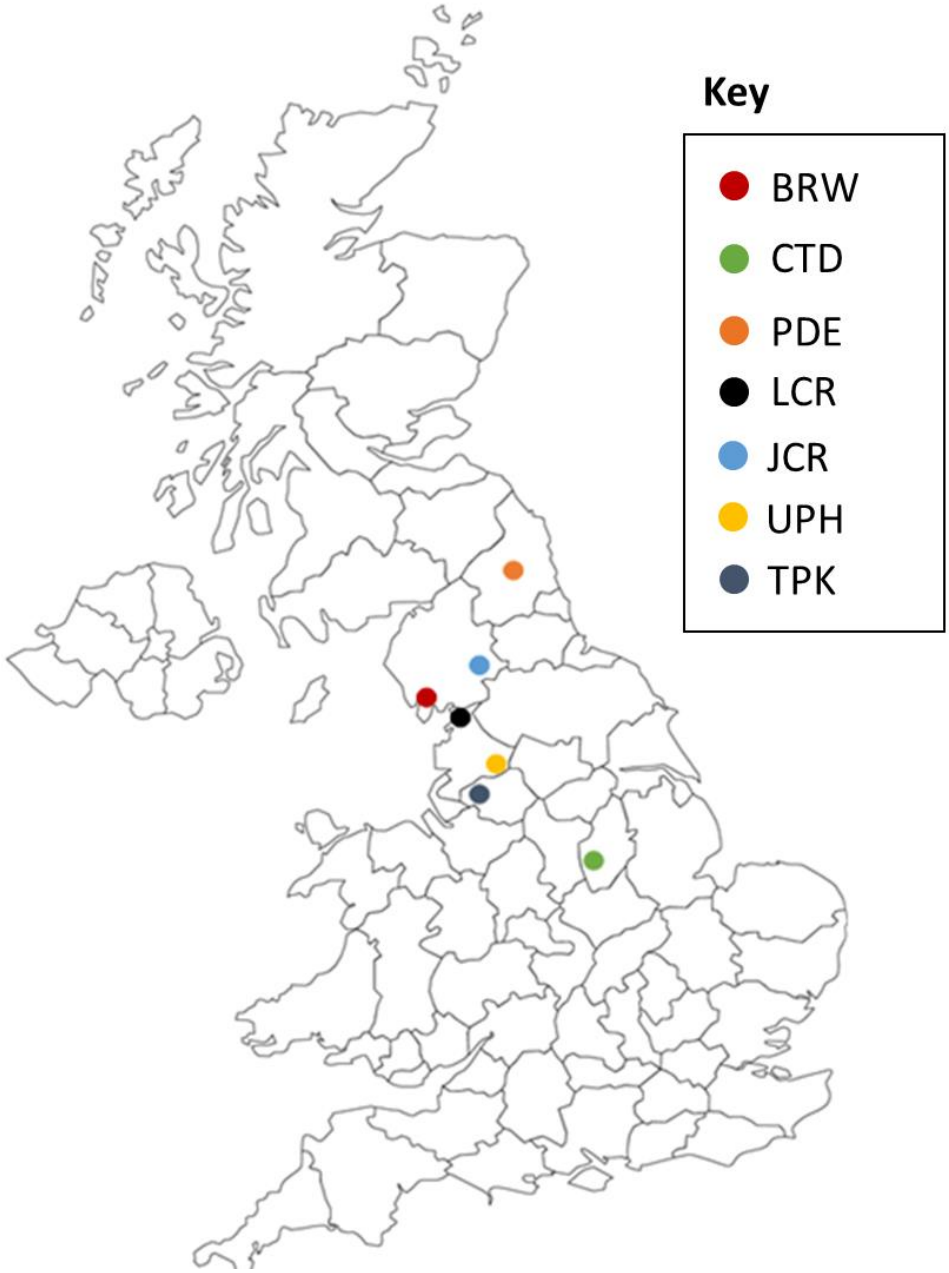


Figure 12: Map of United Kingdom showing geographical location of the 7 paper mills involved in the research.

Mill BRW: This paper mill located in Cumbria produces quality hygiene products. These products are sold under popular brand names such as Andrex^{TM} toilet roll and Kleenex facial tissue. The mill uses a mixture of virgin pulp and recycled paper as feedstock which leads to annual PMS production of 40,000 t.

Mill CTD: This paper mill produces 30,000 tonnes of hygiene products annually using recycled office paper. These products are specially supplied to the 'away from home' market as paper towels, toilet paper, napkins, used in a working environment, public restrooms etc. The sludge collected from this mill is mainly de-inking sludge of 40,000 t per year.

Figure 13: Away from home tissue products produced by Mill CTD (Upmarket Research, 2018).

Mill PDE: This mill has a capacity to produce around 100,000 t of paper products per year. The includes production of deinked secondary fibre pulp and recycling of office waste paper to produce hygiene products. The mill uses a combination of virgin wood pulp and secondary deinked fibre. The water used for papermaking is reused again for the deinking plant. The mill recycles all wastewater after which it is treated in a biological treatment plant before disposal into the River Tyne. The final product is marketed as well-known brands such as Velvet^{TM} toilet roll, Bodyform^{TM} female sanitary product and Plenty^{TM} kitchen towel roll.

Mill LCR: This mill has a capacity of 30,000 t per year to produce tissue and hygiene products. This mill used both virgin and recycled fibres to produce paper for hygiene products such as Kittensoft$^{TM.}$ The water used in the paper machine is recirculated. The water treatment plant uses dissolved air floatation (DAF) process to recover solids and the water is recycled back to the mill. The de-watered material is typically sludge produced at the mill, 16,000 t/year.

Mill JCR: This mill has a capacity of 50,000 t which produces luxury packaging materials and specialty paper with the use of virgin pulp, post-consumer waste and used coffee-cups as shown in figure 14.

Figure 14: A truck of post-consumer coffee-cups delivered to JCR mill.

The paper mill deals with 10 million paper coffee cups weekly. These cups are made up of 90% fibres and 10% polyethylene (PE). The PE is used as an inner coating to prevent leakage and to provide insulation. At JCR mill the plastic coating is separated from the paper using a method which was not disclosed. The plastic is also sent to a partner recycler to manufacture cable reels and the recovered fibres are used to produce luxury paper products and packaging for brands such as the distinctive yellow paper bags from Selfridges and moulded packing products soap manufacturer Lush. The mill supplies 80% of the paper used in hard books in the UK and are also the suppliers for the paper used in the signature red poppies for commemorating Remembrance Day. The mill produces very low amount of sludge at 7,600 t per annum which is collected. The paper

produced at the mill are usually in reels of different colours hence the sludge often appears in dark colours.

Mill UPH: This mill produces filtration paper products for the tea and coffee markets. The mill has a capacity of 6,000 t per year to manufacture filtration paper used in tea and coffee bags as shown in figure 15. Tea and coffee filter paper are produced using a mixture of Abaca fibres and wood pulp. Abaca fibre is a natural fibre derived from banana leaves indigenous to the Philippines. Abaca fibres have 15% lignin content, are up to 3m in length, possess high mechanical strength and resist damage from saltwater (Friedhelm and Werner, 2010). The Abaca fibre market is sometimes affected by pricing volatility or supply chain disruptions caused by adverse weather conditions in the Philippines. Thus, in these situations UPH mill can substitute Abaca fibres with Rayon fibres as it provides the desired mechanical properties.

Figure 15: Tea and coffee filter products.

Several tea and coffee bag products contain about 2% of polyethylene (PE) or polypropylene (PP) fibres used to seal the paper and to ensure it doesn't disintegrate when put in hot water. Although these bags are still compostable, they degrade and leave behind microplastics. Thus, consumers are becoming more aware of these issues and are requesting for 100% plastic free tea/coffee filter bags. Whilst UPH mill offers the tea/coffee filter bags containing PE/PP they also offer 100% biodegradable tea bags which use corn/starch bioplastics. This product is compatible with EN13432 composting standard. UPH also produces speciality filter paper for chef hats, boil-in-bags, descaling sachets and whitening bags used in laundry. The water used at UPH mill is treated onsite with a biological treatment process and a DAF to separate the solids which is up to 8000 t of PMS per year.

Mill TPK: This mill produces hygiene products with a capacity of 50,000 t per year. TPK is an integrated mill which converts paper into products that are manufactured and prepared to be sent directly to customers. The main brands produced at TPK mill are Cushelle^{TM} toilet rolls, Plenty^{TM} kitchen roll and supermarket own brand rolls. This mill uses virgin fibres from hardwood pulp of eucalyptus tree. Thus, the PMS at this mill is a primary sludge with low volumes of 4,000 t/year.

The composition of PMS obtained from a mill depends on the raw materials, pulping process, chemicals, final product and the wastewater treatment facility. The pulp used in the mills listed below in table are either imported from the paper mill headquarters, overseas suppliers or reclaimed paper products.

Table 4: Paper mills involved in the research.

Mill	**JCR**	**BRW**	**PDE**	**CTD**	**LCR**	**TPK**	**UPH**
Final Product	Luxury packaging	Hygiene product	Tissue	Tissue	Tissue	Tissue	Tea packaging
Capacity (t/yr.)	50,000	120,000	100,000	30,000	30,000	50,000	6,000
Sludge type	PS/DS	DS	DS	DS	DS	PS	PS
PMS (t/yr.)	7,600	40,000	80,000	40,000	16,000	4,000	8,000
Feedstock	Virgin pulp and recycled coffee cups	Pulp from recycled paper	Pulp from recycled paper	Recycled office paper	Recycled paper	Virgin fibres	Virgin fibres and 1% PE
Final Product	Luxury packaging	Hygiene product	Hygiene and feminine products	Hygiene product	Tissue	Tissue	Tea packaging

3.2.1 Waste-water treatment process at the mills

All 7 paper mills adopted a similar wastewater treatment process by applying a combination of various techniques such as clarification, stabilisation, coagulation and filtration as shown in figure 16. Large particles such as paper clips, staples, plastics found in the wastewater can be removed by clarification. After clarification, stabilisation is used to reduce the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) which is critical before water can be discharged into local rivers. Stabilization can be

obtained by using biological treatment methods such as aerobic/anaerobic treatment methods. Aerobic treatment method was common in all mill which employs the breakdown of organic matter in the presence of oxygen aided by enzymes and bacteria introduced into the system (Kamali et al., 2016). During aerobic treatment the removal of BOD and COD can be obtained by using fixed bed bioreactors (FBBR) or moving bed bioreactors (MBBR). After stabilisation, Dissolved Air Flotation (DAF) can be used as a filtration process to remove the total suspended solids (TSS) present in wastewater. These solid particles and colloids can be removed introducing micron air bubbles. Solids or colloids suspended in the waste-water attached to the air bubbles and float to the surface of the water treatment tank.

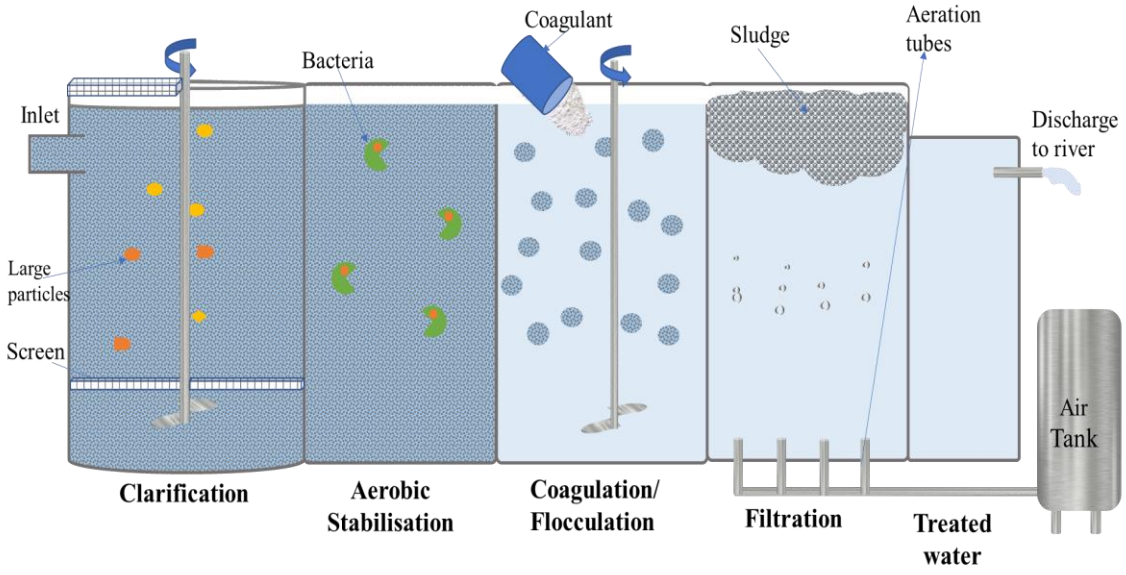


Figure 16: Illustration of wastewater treatment process.

Flocculators can also be used to improve the mixing and retention time in the DAF unit to provide adequate coagulation and flocculation. To enhance DAF process, coagulants such as aluminium sulphate ($Al_2(SO_4)_3$) is used to clump fine particles together (Pokhrel and Viraraghavan, 2004). Colour can also be removed during coagulation. The suspended solids are then collected from the surface of the wastewater tank after which it can be de-watered by centrifugation or belt pressing. The de-watered sludge still has high moisture content up to 60% thus the sludge can be dried further before land spreading.

3.3 Brainstorming

Brainstorming exercises are useful to companies as it helps to focus the efforts of a large group of employees, it creates excitement and interests that leads to some useful ideas (Birkinshaw, Bouquet and Barsoux, 2010). Brainstorming is as an effective tool for the "develop" stage in design thinking as it generates diverse ideas. Brainstorming was first proposed by Alex F. Osbourne known as 'organised ideation'. Osbourne suggested that groups of 5-10 yielded the best results based on claims that an average person will generate twice as many ideas when working in a group compared to working alone. However, an experiment by Taylor, Berry and Block (1958) disputed Osbourne's claim by showing that group participation during brainstorming inhibited creativity. They found that a group of 4 individuals brainstorming alone who later combined their best ideas (nominal), out-performed a group of 4 individuals who interacted through-out the brainstorming session. Additionally, Research by Furnham and Yazdanpanahi (1995) showed that an individual brainstorming alone has a higher creativity compared to two interacting individuals with the same personality trait, irrespective of how creative both individuals are. This was attributed to participant over/under-estimating as they have a reference to compare their thoughts with. The authors also added that creative production rate was higher for a group of four participants and creative production rate decreased as group size increased. Taking these studies into consideration the brainstorming activity was organised for 4 participants following the following brainstorming rules:

- **Criticism is avoided:** participants are told to avoid any form of evaluation or judgement.
- **Free-wheeling is welcomed:** there are no impractical solutions and participants are encouraged to generate wild ideas.
- **Quantity over Quality:** participants are encouraged to contribute as many ideas as possible.
- **Build on other ideas:** participant can combine ideas and expand their own ideas based on other participants contributions.

Two brainstorming sessions were held separately each with 4 participants. Session 1 was held at Cranfield university and session 2 was held at University of Warwick. Participants were volunteers with no incentive to participate in the task. Participants were provided

with marker pens, A4 plain sheets of paper, post-it notes and flipcharts. The participants were selected from diverse specialisations and levels of experience as listed below in table 5.

Table 5: List of participants from brainstorming session

Session 1 Cranfield university	**Session 2** University of Warwick
Researcher in sustainable materials and manufacturing.	Senior vice president at textile manufacturing company.
Product design researcher in water sanitation.	Engineering manager at global automotive parts manufacturer
Researcher in user centred design.	Product specialist electric car manufacturer.
Researcher in sustainable consumer behaviour.	Environmental manager for wastewater treatment company.

The brainstorming sessions were facilitated by the author. The duration of the entire session was for 45 minutes. 15 minutes were spent on explaining the rules and the brainstorming warm-up activity. The remaining 30 minutes were spent on the main brainstorming activity.

Brainstorming warm-up activity: The warm-up activity is recommended for participants to break out from pattern/logical thinking but allow imagination and freedom of thought. For the warm-up activity participants were each asked to draw a car on a plain sheet of A4 paper. After all participants finished drawing, the drawings were placed in the middle of the table. Participants were then told to take another A4 sheet of paper and design a way of moving from one location to another. After all participants finished this exercise the first and second results were compared to show participants how posing the same question differently can promote creative ideas

Brainstorming main activity: Participants were presented with various labelled samples of paper mill sludge collected from the field study. Participants were asked to generate ideas on how the materials could be used to manufacture new products or how they can be used in other industries. Participants were told to spend 15 minutes brainstorming ideas

on their own and then the ideas generated were discussed in the group to gather more ideas. Participants were also encouraged to relate ideas to their field of expertise. For example, paper mill sludge in electric cars. The ideas generated are listed below in table 6. There were 40 ideas generated during the brainstorming session with 18 ideas from session 1 and 22 ideas from session 2.

Table 6: Ideas generated during brainstorming session 1 and 2

	Session 1	**Session 2**
1	Medium Density Fibreboard (MDF)	Nitrocellulose
2	Craft book hardback	Pyrotechnics
3	Insulation	Wall insulation
4	Composting	Pelletise for biomass boiler
5	Plant pot filler	Road surfacing
6	Furniture	Natural composite
7	Anaerobic digestion	Composite reinforcement
8	Concrete filler	Paint binder
9	Packaging carboard	Cement filler
10	Mulch for soil moisture retention	Use in biomass boiler in the paper mill
11	Activated charcoal/carbon	On-site anaerobic digestion plant
12	Activated charcoal for water filtration	Substitute with wood fibres in furniture
13	Supercapacitor carbon	Door panels
14	Grow bag	Bricks
15	Loft insulation	Roofing tiles
16	Kraft carrier bag	Bean bag stuffing
17	Paper Mache flower pot	Building cement blocks
18	Paper Mache gift items	Substitution in cement mortar
19		Wall plaster
20		Foot mat
21		Fibre reinforced concrete
22		Fibre reinforced plastic

There are similarities between ideas generated and they were collated in themes as shown in figure 17.

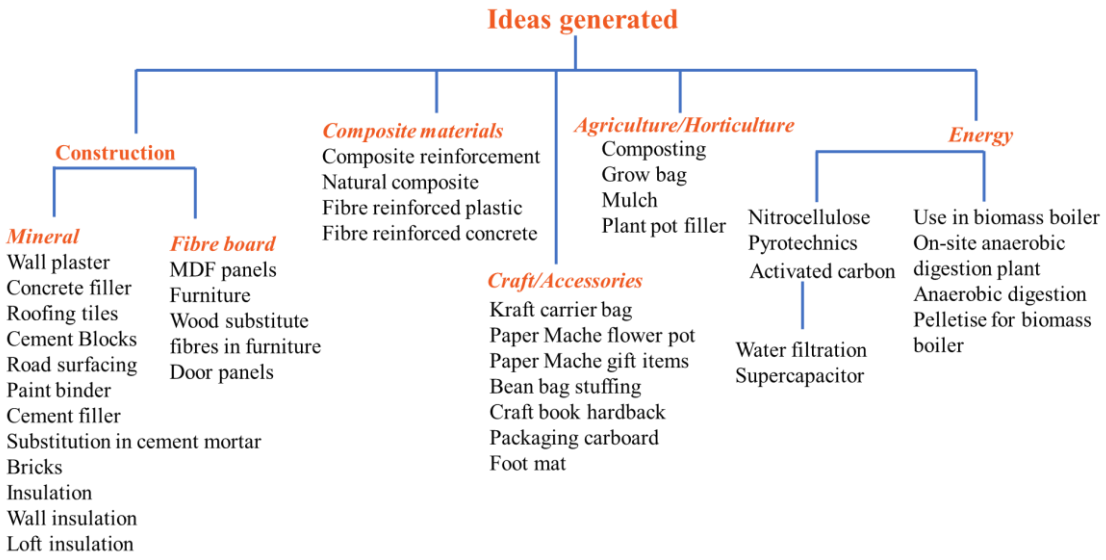


Figure 17: Ideas from brainstorming exercise collated in themes.

The ideas generated from the brainstorming session were arranged in the following themes; construction minerals, construction fibres, composite materials, agriculture, craft accessories and energy. The most populated theme was the use of PMS in construction material. This was separated under mineral and fibre construction. It was evident that participants proposed some ideas based on the appearance of the PMS, for example PMS with longer fibres were recommended for medium density fibreboard (MDF), furniture and substitution for wood fibres. PMS also seemed to be linked with agricultural and soil applications such as composting, grow bag used in gardening and mulch for retaining soil moisture. PMS was also recommended for reinforcement in composite materials.

Further discussions on the potential carbon content in the material during the brainstorming session led to PMS being proposed for use in energy generation through biomass pellets or anaerobic digestion. This broadened the brainstorming to potential applications related to high carbon content such as nitrocellulose and its application pyrotechnics. Participants in session 1 viewed the high carbon content as potential for producing activated carbon/charcoal which led to discussions amongst participants for its use in water filtration and supercapacitors. Although the brainstorming provided interesting ideas, there was no supporting scientific evidence. A literature review on the application of PMS was carried out in chapter 3.4 to provide more insights on the current developments on PMS management.

3.4 Rapid prototyping

Rapid prototyping involves building physical models with readily available resources to help in the expression of an idea or concept. Some of the ideas from the brainstorming sessions were used in rapid prototyping. Rapid prototyping was conducted with supervisors from the sponsor company. The session involved forming of board materials using PMS obtained from different mills and different binding agents.

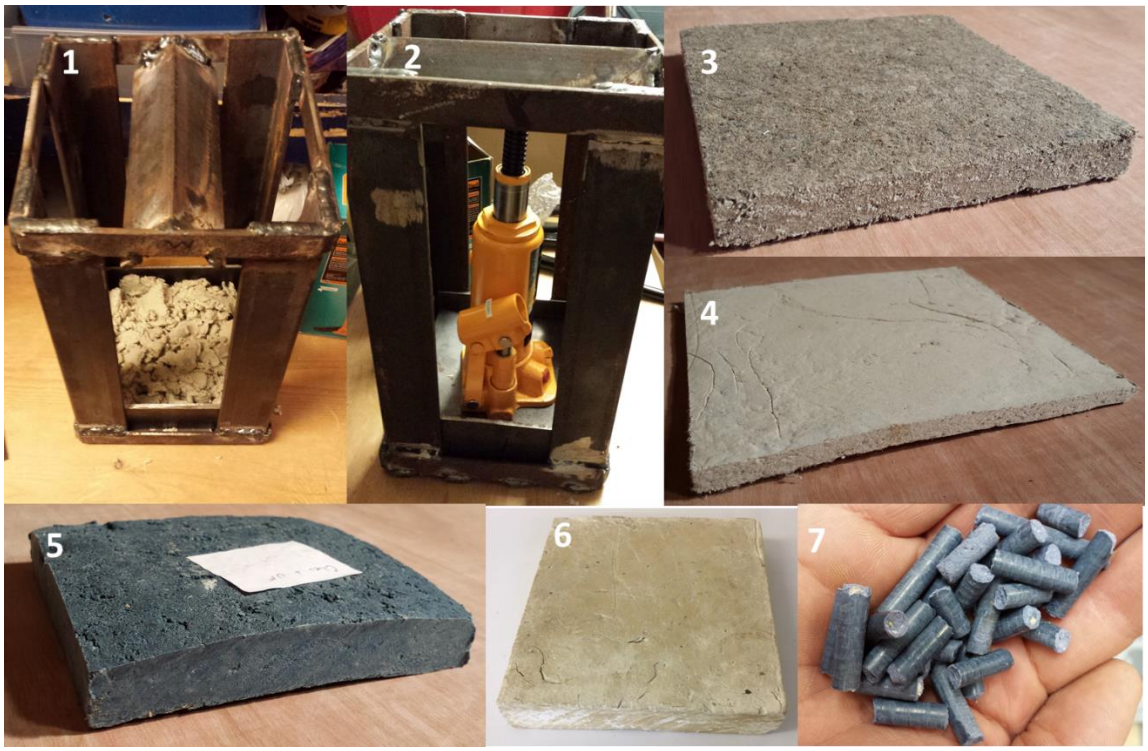


Figure 18: Images from rapid prototyping session and prototypes.

The equipment used during rapid prototyping and prototypes are shown in figure 18 and listed below:

1) A mould frame welded from mild steel sheets.
2) A 4-ton bottle jack.
3) UPH sludge bonded with polyvinyl alcohol (PVA) craft glue.
4) TPK sludge bonded with PVA craft glue.
5) Mixture of deinking sludges bonded urea formaldehyde and oven dried
6) TPK sludge bonded with cement.
7) Pelletised LCR sludge.

The mould frame was filled with a mixture of sludge and a metal sheet was placed on top, the bottle jack was used to supply hydraulic pressure and repeated for all prototype samples. The samples showed dimensional stability apart from the de-inking sludge which was very brittle until high amounts of urea-formaldehyde was used as a binding agent. Paper is a network of cellulosic fibres held together by inter and intra molecular bonding (Schmied et al., 2013). In paper making hand sheets are usually formed to test the mechanical properties of the pulp. PMS from the mills were used to prepare hand sheets by diluting 80 g of PMS in water, dispersion and vacuum filtration. The hand sheets were oven dried at 105 ℃ for 6 hrs.

Figure 19: Hand sheets prepared from different PMS (L to R: JCR, TPK and UPH).

Some of the PMS samples could form dimensionally stable sheets based on inter/intra fiber bonding as shown in figure 19. However, the de-inking sludges did not contain enough fibres to form sheets. This gave an indication of sludges that were most suitable for certain applications. Although not all the brainstormed ideas could be used in rapid prototyping, the exercise provided insights on the potential of the PMS, the differences between the various sludges and the importance of understanding their chemical composition. Particle size also played an important role in prototyped samples.

3.5 Literature review on PMS applications

A literature review of PMS utilisation will be discussed here. Previous literature studies from Bajpai (2015) and Faubert (2016) provided the state of the arts on PMS management and application. These were grouped into land application, energy recovery and materials recovery. This literature review will briefly discuss PMS in land application and energy recovery. However, material recovery of PMS is of greater interest based on circular economy principles and the waste hierarchy.

3.5.1 Land application of PMS

For over 20 years the spreading of PMS on agricultural land has been the most common method to utilise the sludge, it is commonly applied at the start and end of the growing season. A three-year experiment was conducted by Phillips et al. (1997) in the UK to understand the influence of PMS on agricultural land Different factors such as soil type, crop type, sludge type and spreading method were investigated. The most significant influence on crop yield was affected by the method of which the sludge was applied on the soil, surface spreading of underwatered sludge provided the highest yield. Additionally, spreading PMS over the 3-year period significantly improved the top soil. In the Phillips research the soil received a standard fertiliser dosage of Nitrogen, Phosphorus and Potassium (N, P, K) despite the application of PMS on the soil. Hence the effect of sludge with low nutrient on crop yield was not investigated. Other field studies showed that sludge with high Carbon: Nitrogen ratio (70-323:1) decreased crop yield (Aitken, Evans and Lewis, 2006; Legendre et al., 2004). This is because of nutrient immobilisation mainly nitrogen, to overcome nitrogen immobilisation the following is recommended;

- Allowing a fallow period for sludge C:N ratio before planting; 4 weeks for primary sludge and 2 weeks for de-inking sludge.
- Supplement with additional nitrogen fertiliser.
- Grow legumes as they are less reliant on nitrogen.
- Biologically treated PMS or composting PMS prior to spreading requires less nitrogen supplement due to increase N content.

Despite the compromises of nutrient immobilisation there are several other benefits of applying PMS on agricultural land as it provides organic matter in the soil, aids microbial growth, enzyme activity and promotes cation exchange (Camberato et al., 2006). PMS also improves soil condition in relation to porosity, moisture retention, bulk density and structural stability. Apart from spreading PMS on agricultural land it is also used in other land applications such as silviculture, compost and land reclamation (Feldkirchner et al., 2003; Larney and Angers, 2012). PMS has very low levels of heavy metals and pathogens compared to other organic materials such as animal slurry thus it was deemed to have no risks to the health of humans, animals or plants. A code of good practice for spreading PMS on agricultural land was also established to provide guidance for waste contactors, paper mills and farmers (Confederation of paper industries, 2014).

3.5.2 Energy recovery from PMS

PMS has been used in various types of energy recovery such as bioethanol production, anaerobic digestion and pyrolysis.

3.5.2.1 Bioethanol

Paper sludge was first investigated for ethanol production by Lark et al. (1997) yielding up to 35 g/l of ethanol by simultaneous saccharification and fermentation (SSF). A proposed ethanol production process from PMS was described by Gurram et al. (2015). The sludge was treated with hydrochloric acid (HCl) to remove the calcium carbonate. Chen et al. (2014) explained that $CaCO_3$ in PMS absorbs the enzymes which inhibits digestibility during fermentation. The de-ashed sludge is dosed with enzymes for hydrolysis at 50 °C for 72 hr. After enzymatic hydrolysis the material can be filtered to remove undissolved lignin fraction. The hydrolysed PMS solution containing glucose is fermented and distilled to produce ethanol. Mechanical grinding of the sludge was also found to improve the fermentation process. It was proven that paper mill sludge especially with high cellulose content can be used as feedstock in bio-ethanol production.

Gomes, Domingues and Gama (2016) showed that enzymes could also be recovered and reused 4 times. Although this leads to 15% reduction in glucose conversion, it could save 60% in enzyme cost. Nonetheless, the maximum concentration of ethanol produced was 50 g/l, which does not meet commercially feasible yields of

75 g/l (Öhgren et al., 2006). Additionally, ethanol recovery during distillation will be costlier for low yield. PMS feedstock in biorefinery is more applicable for a bio-ethanol process with mixed feedstock but not financially justified for the paper mills using recycled fibres. Biorefinery of PMS has been investigated for chemical production such as lactic acid (Romaní *et al.*, 2007) and Carboxymethylcellulose (Mastrantonio *et al.*, 2015). However, these processes also require several chemical pre-treatments which were not economically feasible on a large scale.

3.5.2.2 Anaerobic digestion

Anaerobic digestion is an advantageous biological treatment for paper mills wastewater as it reduces sludge volume and can destroy pathogens in the thermophilic process. The output of the process is methane for biogas and digestate for fertiliser. Methane yields from PMS anaerobic digestion vary in the literature from as low as 20 mL/g. VS to 429 mL/g. VS (Veluchamy and Kalamdhad, 2017). Methane yield is highly dependent on the pulping process, type of sludge, operating condition and nutrients in the sludge. Ekstrand et al. (2013) modelled the theoretical methane potential of 7 Swedish paper mills with different pulping processes such as Kraft pulping (KP), chemi-thermomechanical pulping (CTMP), thermo mechanical pulping (TMP) and Neutral sulphite semi-chemical pulping (NSSC). Paper sludge from the TMP process provided the highest yield for or anaerobic digestion as it was less toxic to methanogens. Wastewater from CTMP, NSSC and Kraft mills contain bleaching effluents, wood extractives, resin acids and sulphur will inhibit methanogens.

The recommended C:N ratio for anaerobic bacterial growth is between 20-30:1 as low C:N results in increase in total ammonia nitrogen or accumulation of volatile fatty acids (Li, Park and Zhu, 2011). PMS tends to have higher C:N ratio causing rapid nitrogen consumption by methanogens and low biogas yield. The challenges of achieving economically feasible biogas yields from anaerobic digestion of PMS are due to technology, long hydraulic retention times (HRT) from 20-30 days and cost of suitable pre-treatment infrastructure (Elliott and Mahmood, 2007; Kamali and Khodaparast, 2015). Several pre-treatment methods and modifications have been applied to increase methane yield and hydraulic reduce retention (HRT) time. Pre-treatment methods studied to improve PMS methane yield are ultrasound, chemical pre-treatment with nitric acid

(HNO_3) and sodium hydroxide (NaOH), mechanical pre-treatment, hydrothermal and enzymatic pre-treatment (Bayr, Kaparaju and Rintala, 2013). Gijzen, Derikx and Vogels (1990) found that rumen fluid as inoculum increased microorganism activity during digestion. PMS sludge pre-treated with high-pressure homogenization with 3 days HRT resulted in methane yield equivalent to 20 days HRT without pre-treatment (Elliott and Mahmood, 2012). Biological pre-treatment with a microbial consortium from spent mushroom substrate was used for anaerobic digestion of PMS. The PMS was co-digested with rice straw and waste from monosodium glutamate. The processes resulted in produced a cumulative methane yield of 429 mL/g. VS after 45 days retention time (Lin *et al*., 2017). Anaerobic digestion of PMS for biogas production is mostly suitable after pre-treatment and co-digestion with other types of feedstock. Pulping mills with mixed feedstock such as wood chips, barks and hemicellulose are environmentally and economically feasible for anaerobic digestion as they can achieve higher methane yields (Meyer and Edwards, 2014). However, paper mills with deinking sludge and low volumes of primary sludge cannot commercially justify AD investment or the resources required for pre-treatment to achieve considerable methane yields.

3.5.2.3 Pyrolysis of PMS

Pyrolysis can be used to thermally decompose PMS in an inert atmosphere to produce bio-oil fuels, charcoal and hydrocarbons. Lou *et al*., (2012) pyrolyzed deinking sludge from paper mill using old newsprint as feedstock at 800 ℃ at a heating rate of 10 ℃.ms^{-1}. The products obtained from the process were gaseous (30%), bio-oil (24%) and solid residues (46%) These products were mainly hydrocarbons; styrene, toluene, benzene, small amounts of acid; hexadecenoic acid, acetic acid, isocyanic acid and calcium carbonate that can be reused as filler in paper. Ouadi *et al.*, (2013) used deinking sludge (74% ash) in a pyrolysis reactor to produce bi-oil. The sludge was dried (< 3 wt%) and was pelletized to 6 mm by 15 mm in diameter and length prior to feeding into the reactor. The bio-oil produced had high heating value of 37 MJ/kg. It was also shown the pyrolysis oil from de-inking sludge could be used in diesel blends up to 20% in a CI engine without requiring ignition additives or surfactants (Hossain et al., 2013). High ash content in deinking sludge renders PMS a challenging feedstock for pyrolysis as it is made up of calcium carbonate with low calorific value of 6-7 MJ/kg (Méndez *et al.*, 2009; Ridout, Carrier and Görgens, 2015). The high moisture content in sludge affects the

overall energy efficiency of the process and high capital investment and annual operating costs < £1 million makes pyrolysis of PMS a challenging route (Shemfe, Gu and Ranganathan, 2015).

3.6 Material from PMS

Paper mill sludge comprises of cellulose, hemicellulose, lignin, inorganic minerals and ash which can be used to produce materials for other industries. Particularly, cellulose is an abundant natural and the principal structural component of plant cell wall. Wood is the most common source of cellulose as they contain 40-70% cellulose which can be mechanically or chemically process to manufacture paper (Roberts, 1996). Although, cellulose can also be found in non-woody sources such as cotton, wheat, straw, flax, hemp, tunicate, algae and some bacteria such as gluconacetobacter xylinus (Moon *et al.*, 2011). Cellulose is composed of linear polymer chains of betta D-glucose units as shown in figure 20. Its molecular formula is given by $(C_6H_{10}O_5)n$, with 'n' denoting the degree of polymerisation. Cellulose has high axial stiffness due to its inter and intra chain hydrogen bonding.

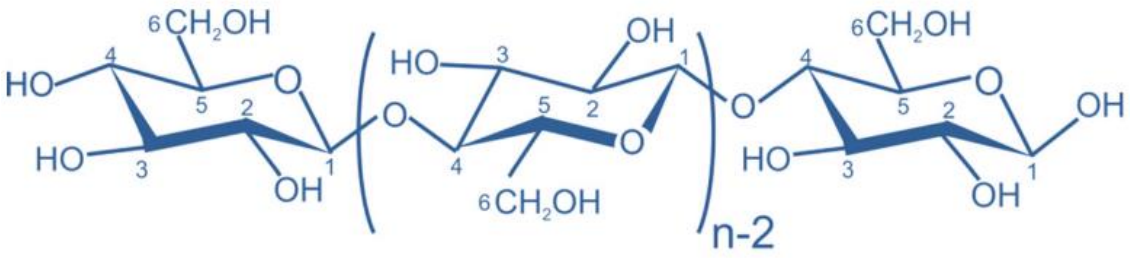


Figure 20: Repeating unit of cellulose (French, 2017).

Cellulose materials contain crystalline and amorphous regions. The elastic stiffness of the crystalline regions of cellulose from bleached ramie fibres were first analysed by Sakurada, Nukushina and Ito (1962) resulting in modulus (E) of 137 GPa. Values ranging from 100-140 GPa have been reported by other researcher (Northolt *et al.*, 2005; Sturcova, Davies and Eichhorn, 2005). Cellulose has density (ρ) of (~1500 kg/m^3) thus the specific modulus (E/ρ) of cellulose is comparable with that of aluminium, steel and glass. This renders it useful as an engineering material. The inorganic minerals found in PMS are from various enhancers used to improve the properties of the paper. Silica (SiO_2)

is used to enhance the frictional and printing properties of the paper. Calcium carbonate ($CaCO_3$), kaolin clay ($Al_2Si_2O_5(OH)_4$), and talc ($Mg_3Si_4O_{10}(OH)_2$) are used to coat paper which provides its smoothness, brightness and opacity (Hubbe and Gill, 2004). This chapter will discuss the literature on the use of PMS in material applications grouped under fiber based materials and mineral based materials.

3.6.1 Fibre based materials

PMS with low mineral content has been explored for various kinds of fibre boards; hardboard, medium density fibreboard (MDF), polymer reinforced composites and nanomaterials.

3.6.1.1 Boards from PMS

One of the earliest studies popularly cited for production of fibreboard from PMS was by Taramian *et al.*, (2007). PMS and wood chips (WC) were mixed at varying ratios of (PMS: WC at 0:100, 15:85, 30:70 and 45:55) to produce single layered boards and 3-layed boards with WC core and PMS surface. The sludge used contained 20% cellulose, 28% ash and 17% lignin. Two types of adhesives were used; Urea formaldehyde (UF) at 10% and 12%, and methylene diphenyl diisocyanate (MDI) at 3% and 4%. The boards were tested for their bending strength, water absorption, shear strength and thickness swelling. The 3-layer 12% UF board with 15:85 PMS:WC ratio satisfied the following standards; EN, ASTM D 1037-99 (standard Test Methods for Evaluating Properties of Wood-Base Fiber and Particle Panel Materials) and ANSI A208.1-2009 for general use of particle board. The mechanical properties reported for the 3-layer 12% UF board with 15:85 PMS:WC reached a bending strength of 16 MPa and shear strength 4.3 MPa. The single layer boards were generally weaker in bending strength and the UF bonded boards showed better mechanical properties compared to MDI. Increasing the PMS content reduced the bending strength.

Similarly, de-inking sludge (DS) and primary sludge (PS) were mixed separately with spruce pine fibre (SPF) with 12% UF resin (Geng, Zhang and Deng, 2007). The 70:30 PS: SPF and 30:70 DS: SPF boards met ANSI A208.1-2009 for interior applications. Increasing PS and DS content reduced the modulus of rupture (MOR) and modulus of elasticity (MOE) of the board. Generally, the DS had lower mechanical

properties due to its mineral content and shorter fibres. Another study from Geng, Deng and Zhang (2006) investigated the processing parameters on the mechanical properties of paper sludge fibreboards. The MOR was highly dependent on-board density; boards of 1100 kg/m^3 under the same temperature and pressing time reached a MOR of 13.5 MPa whereas the 750 kg/m^3 board reached 3.4 MPa. Increasing the pressing temperature from 180 to 210 ℃ increased the MOR by 40%. The values from 6mins and 8 mins pressing time showed no statically significant difference. Thickness swelling was up to 50% less when temperature increased from 180 to 210 ℃. The optimal parameters at 1100 kg/m^3, 210 ℃ and 8 mins resulted in internal bond strength, modulus of rupture, modulus of elasticity and thickness swelling of 1.25 MPa, 13.5 MPa, 2165 MPa and 24.3%.

Migneault *et al* (2011) adopted the same parameters from the study to prepare PMS fibreboards PMS without binders. The boards were made from a mixture of PS and secondary sludge (SS) at varying ratios of 1:9, 2:8, and 3:7 from different pulping processes (KP, CTMP and TMP). Secondary sludge was intended to serve as the binding agent as it contains microbes and protein that may act as binders. The IB increased by 90% at PS:SS ratio 3:7 for the CTMP pulp compared to the Kraft pulp with only 20% increase in IB at PS:SS ratio 3:7. It was found that there was a strong correlation between IB and lignin content in the sludge. The SS from the CTMP had a higher lignin content (50%) compared to the kraft pulp (36%). This is suspected to have improved the bond between lignin and cellulose fibres because of softening and crosslinking at the pressing temperature of 210 ℃.

In addition to fibreboards, hardboards have also been extruded from PMS. Hardboard is much denser and typically 3mm in thickness compared to MDF boards which are from 6mm-12mm. Scott et al (2000) showed that a water-soluble polymer such as sodium-carboxymethylcellulose (SCMC) improves the rheology of pulp to form a homogenous paste for extrusion. The rheological properties are important for extrusion because at high viscosity, shear forces increase and jam the extruder (Scott, Klingenberg and Zauscher, 1999). PMS from various mills and old news prints were pulped and extruded into hardboard sheets of 3 mm. 3% SCMC was added to the pulp and fed into a 32 mm twin screw extruder with a barrel temperature of 50℃. A second pass was made

to improve dispersion and sludge samples were pressed at 150℃ at 70 kPa and 350 kPa to be compared with commercial grade hardboard. Increasing pressure to 350 kPa increased the properties of the hardboards by up to 40%. The highest properties for MOR and MOE were found for 100% ONP at 25.2 MPa and 3.96 GPa. For sludge obtained from a recycling linerboard mill; at ratio 7:3 of PMS: ONP, the mechanical properties reduced to 24.4 MPa and 4.31 GPa for MOR and MOE respectively. The MOR and MOE reached as low as 10.4 MPa and 2.84 MOE for 7:3 PMS: ONP for de-inking sludge with 58% ash content. Although the 100% ONP and 7:3 PMS: ONP from the linerboard mill board met commercial hardboard properties further improvements were required for the other sludges from deinking mill and for higher additions of PMS. Extrusion of PMS resulted in higher mechanical properties in the boards compared to hot pressing.

Another study by Tikhonova, Lecourt and Irle (2014) prepared hardboards from a blend of TMP pulp and PMS fibres. The wet process was used whereby webs/sheets of fibres were formed in an automatic sheet former. The webs were placed on top each other and cold pressed to remove moisture after which it was hot pressed at 5 MPa into 2mm and 4mm thick panels at 190 ℃ for 7 mins and 180 ℃ for 6 mins respectively. Mechanical properties of the board increased with addition of primary sludge containing 17% ash content and fibres of >1.18 mm whereas for PMS with 71% ash containing fines < 0.105 mm mechanical properties reduced whilst thickness swelling was minimised due to minerals present. Highest properties were obtained for 50:50 PMS:TMP pulp for MOR, MOE and TS at 45 MPa, 6179 MPa and 65%. This wet sheet forming process employed by Tikhonova improved the mechanical properties of the board compared to the hot pressing in other studies.

PMS was also used to produce pallets. Pallets used in storing and handling goods during logistics operations are produced with wood fibres. Kim, Kim and Park (2009) substituted wood fibres to produce pallets. Small (1-3 cm) and big (3-5 cm) particle sizes of PMS were used. The PMS contained cellulose and ash content of 21% and 28% respectively. All pallets with addition of 10-30% small particles of PMS achieved a higher MOR compared to the control sample. However, the pallets were not tested in accordance with the appropriate standard BS EN ISO 8611-3:2012.

Learnings from previous studies preparing fibreboards show that there is scope for improvements if other parameters are considered such as increase in temperature, chemical composition and addition of binding agents.

3.6.1.2 PMS in polymer reinforcement and composites

PMS has been used a reinforcement in wood plastic composites (WPC) and in polymers such as polypropylene (PP), high density polyethylene (HDPE) and reinforced rubber. WPC are prepared by extrusion and injection moulding of wood fibres and polymers. The polymer reduces thickness swelling and water absorption thus it is suitable in external construction such as roofing tiles, fence, decks. Girones et al (2010) extruded blends of PP with varying PMS content of (25%, 37.5% and 50%) using Maleic anhydride grafted polypropylene (MAPP) as a coupling agent at concentrations of 4 wt%. The sludge contained up to 70% ash, the mineral content of the ash mainly $CaCO_3$ acted as a filler in the PP matrix which increased the modulus of the material. Nevertheless, this resulted in reduction in tensile strength. The mechanical properties of the PP reinforced with 50% PMS was superior to that of a commercial WPC fence.

A similar study from Hamzeh, Ashori and Mirzaei (2011) also showed that up to 60 wt.% of de-inking sludge can be used to produce WPC from coupling PMS and HDPE with Maleic anhydride grafted polyethylene. Both studies agree that a crucial factor affecting mechanic properties is the interfacial adhesion of the fibre matrix which is improved by the coupling agent. Other coupling agents such as polyamideamine-epichlorohydrin (PAE) have been shown to improve stiffness of de-inking sludge and recycled HDPE for wood plastic composites (Elloumi *et al.,* 2018). The studies showed that the WPC with PMS content is suitable for non-load bearing applications such as decking and fencing. Similar studies have also been conducted by Huang *et al.,* (2012) and Soucy *et al.,* (2014) showing the correlation between sludge composition (cellulose, ash, nitrate, lignin and extractives) on the WPC mechanical properties. Ash contents positively correlates to MOR which contradicts the fibreboards ash reduced MOR. High cellulose content increases MOE and MOR due to improved affinity with the coupling agent and polymer.

Since PMS has reinforcing ability, Ismail *et al.*, (2008; 2007; 2005, 2006) studied the effect of PMS as a filler in rubber composites. Natural rubber was grafted with maleic anhydride and other rubber fillers such as zinc oxide, stearic acid, sulphur was added for compounding. The mixture was compounded in a two-roll mill and compression moulded in a moving die rheometer. Increasing the PMS content enhanced the curing time and modulus but reduced strength and elongation at break. A follow up study on the fatigue life of the rubber showed that it reduced at higher PMS loading (Ismail, Rusli and Azura, 2007).

3.6.1.3 Nanomaterials from PMS

Primary sludge has been chemically and mechanically treated to remove its lignin and extractive content during pulping which highlight the potential to produce nanocellulose. Cellulose is contained in the cell wall of woody plant as shown in figure 21, it can be obtained to produce cellulose nanofibres (CNF) or cellulose crystals (CNC) by mechanical grinding and or acid hydrolysis (Eichhorn *et al*., 2010; Hsieh *et al*., 2008; Moon *et al*., 2011).

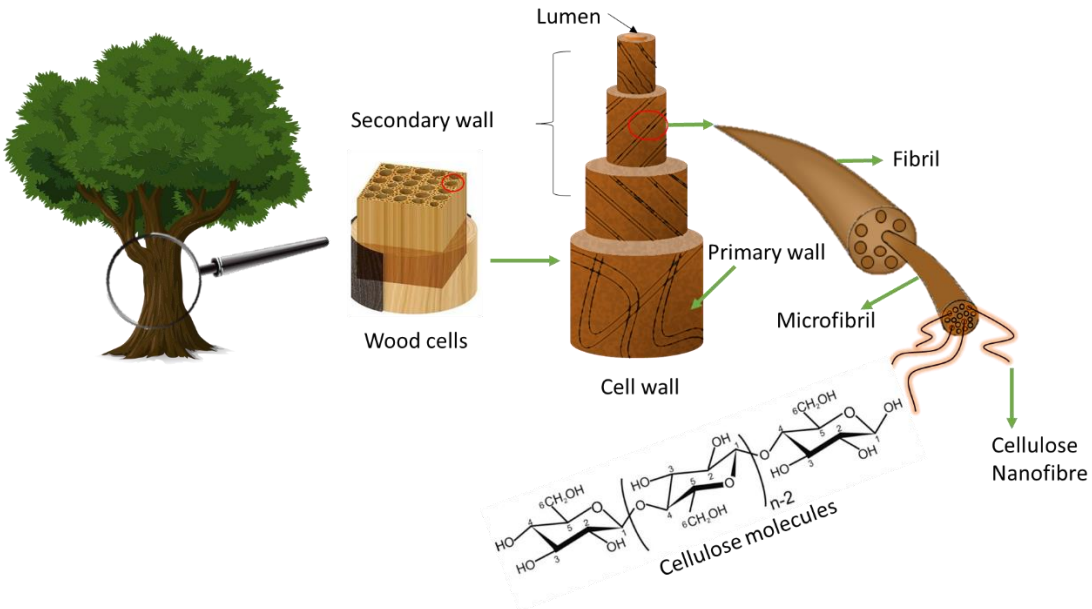


Figure 21: Schematic of the hierarchical structure of wood from macro- to nano-scales.

CNFs range from 10-100 nm in width and up to 10µm in length, whilst CNCs are shaped like rods or whiskers 3-5 nm in width and 50-500 nm in length with which provides them with high aspect ratio. In addition to their high aspect ratio nanocellulose materials are

renewable, bio-compatible, have high specific surface area and mechanical properties. These characteristic render CNF/CNCs favourable in material applications for composites, packaging, bio-engineering, electronics, sensors and membranes (Galotto and Ulloa, 2015; Mathew et al., 2012; Reddy et al., 2013; Trache et al., 2017; Wasim et al., 2018). Owing to its biocompatibility and aspect ratio nanocellulose has reinforcing potential, Favier *et al.,* (1995) was one of the earliest studies to report the use of CNC as reinforcement in synthetic polymer which was referred to as a nanocomposite, following from this research several others nanocellulose as a reinforcing additive in thermoplastics. Nonetheless, the application of cellulose nanomaterials is limited by high processing costs which renders it unsuitable for mass production. Thus, it is primarily used in high value niche markets (Delgado-Aguilar *et al*., 2015; Oksman *et al.*, 2016).

Leão *et al.,* (2012) was the only research found to have prepared nanocellulose from PMS. Primary sludge was treated with sodium hydroxide (NaOH) and autoclaved at 138kPa for 60 minutes. The bleached 6 times using NaOH and acetic acid. After bleaching they were washed with distilled water until pH was brought down to 7. The fibres obtained from the PMS was then oven dried autoclaved in an oxalic acid bath at 138 kPa for 60 minutes with pressure release the repeated for 8 times. Finally, the acid was washed off and the fibres were suspended in distilled water under stirring for 4hrs to prevent agglomeration. The fibres obtained from the sludge were in < 20 nm in width and used as reinforcement in polyurethane. At 4 wt% addition of the PMS nanofibres the PU increased in tensile strength and modulus from 16 MPa to 46 MPa and 38 MPa to 153 MPa. Whilst the research showed interesting potential to reuse PMS the method applied by Leão *et al.,* is highly energy and chemically intensive. Thus, research into more feasible methods of converting primary sludge PMS into nanocellulose is required to address the knowledge gap.

3.6.2 Mineral based materials

Mineral based materials from PMS refer to material application that take advantage of the inorganic contents in deinking sludge. The substitution of cement industry materials can deliver substantial environmental impacts to reduce greenhouse gas emission (Kajaste and Hurme, 2016). The most widely research on material

application for PMS is for feedstock in mineral based building materials (Wiegand and Unwin, 1994). This is because deinking PMS contains minerals such as kaolin clay, Talc, Quartz (Bundy and Ishley, 1991). Kaolin clay for example is chemically composed of elemental oxides such as SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, TiO_2 and K_2O (Yahaya *et al.*, 2017) that can be found in Portland cement. De-inking sludge has been used as substitution in cement mortar aggregates, clay bricks, mineral boards, plaster boards and tiles (Frías, Rodríguez and Sánchez de Rojas, 2015).

3.6.2.1 Cement mortar from PMS

De-inking sludge has been added to cement mortar at 5,10,15 and 20 wt.% to test its compression strength and curing time (Yan, Sagoe-Crentsil and Shapiro, 2011). The setting time of the samples showed a linear increase as sludge content. Setting time of the mortar without DS was 400 min and increased to (700, 1000, 1500 and 2000 mins) as sludge content increased. The compressive strength of the reference mortar samples sample was 33.2 and samples decreased to 24, 22, 21, 20.5 MPa at increasing PMS content.

The increased setting time means deinking sludge can be used as a retarding admixture in cement. PMS also reduced mortar flow, as organic matter absorbed the water in the mixture. The results from this study correlate with other studies incorporating PMS in concrete mortar (Ahmadi and Al-Khaja, 2001; Nazar, Abas and Mydin, 2014). PMS was mixed with grounded expanded polystyrene (EPS) and cement to prepared lightweight insulation mortar (Ferrándiz-Mas *et al.*, 2014). The compressive strength and thermal conductivity of the of the mortar was still considerably lower than the control mortar.

The 20% PMS mortar was suitable for CSIII, CSII and M.25 in accordance with BS EN 998-1 *Specification for rendering and plastering mortar* and BS EN 998-2 *Specification for masonry mortar*. Wong *et al.*, (2015) ball-milled de-inking sludge to particle size between 2-5 μm as an hydrophobic surface coating on cement which decreased the water absorption and sorptivity by 85%. Heating de-inking sludge at high temperature (900 ℃) yields PMS ash with pozzolanic behaviour comparable to commercial metakaolin used in concrete. PMS, lime mud and fly ash was fired at 1390 ℃ and mixed with cement aggregates to prepare mortars. Although the mortar reached

compression strength above the technical standard, this cannot be attributed solely to PMS (Buruberri, Seabra and Labrincha, 2015).

3.6.2.2 Bricks and cement blocks from PMS

PMS has been moulded into cement blocks and fired for clay bricks (Shermale, Shermale and Varma, 2015; Sudarsan et al., 2017). Soos *et al.*, (2017) even designed a production line to mould blocks prepared from PMS and cement. Cusidó *et al.*, (2015) reported on the 10 years' experience of using PMS in Spanish clay brick production. PMS at different ratios (0, 5, 10, 15, 20 and 25 %) was mixed with crushed clay and extruded into rectangular bricks. The formed brick samples were sintered at a heating rate of 160 ℃/hr up to 980 ℃. The high calcite content in PMS aids the formation of the glass phase during sintering. The mineral phases identified in the samples were like that found in standard clay brick. At increasing sludge content, the samples showed a reduction in compression strength at 47, 49, 38, 42, 34 and 24 MPa respectively. Clay brick with 5% PMS showed improvement in compressive strength.

Overall the addition of PMS decreased the thermal conductivity of the samples indicating increase in thermal insulation, values of thermal conductivity recorded for (0, 5, 10, 15, 20 and 25 %) addition of PMS were (0.69, 0.72, 0.66, 0.58, 0.49 and 0.43 $Wm^{-1}K^{-1}$). Other studies confirmed similar properties for addition of PMS in clay brick formation. It was also noted that increase in PMS level lead to increased porosity in the bricks because of organic materials which burnt off during firing. Increase in porosity improves insulation capacity of the brick. However, excessive porosity leads to embrittlement (Kizinievič, Kizinievič and Malaiškienė, 2018; Singh *et al.*, 2018). Clay bricks have a range of compressive strength from 10 MPa to 100 MPa depending on application (Mineral Products association, 2013), the bricks produced with PMS meet EN 771-1 *Specification for clay masonry units-part 1: clay masonry units.*

3.7 Summary

This summary concludes the discovery stage of the research. The first objective; to discover applications for the utilisation of paper mill sludge as a value adding material was fulfilled with the following methods; field study, brainstorming, rapid prototyping and literature review. The field study provided an understanding of the paper mill process,

wastewater treatment methods and collection of sludge samples. The brainstorming exercise was used to generate ideas on utilisation for PMS. Some of the ideas were used in the rapid prototyping stage which revealed the different characteristics of PMS depending on the mill. The ideas proposed in the brainstorming session were used as keywords in Scopus database to highlight the research gap in PMS management as shown in figure 22. The abstracts of the literature were also screened to ensure they were attributed to the relevant application.

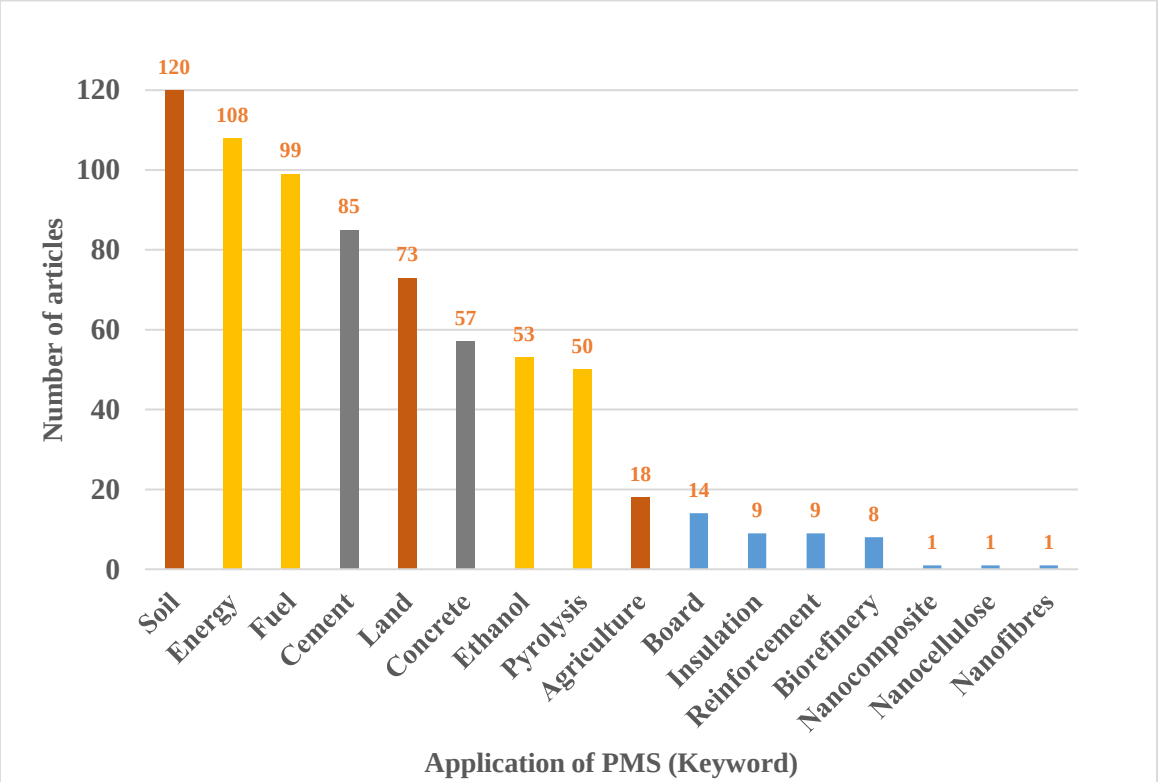


Figure 22: Number of articles found for PMS applications.

The literature search showed that utilisation of PMS focused mainly on soil applications (orange bar) and energy recovery (yellow bar). Another popular area was the use of PMS in mineral based construction materials (coloured in grey); cement and concrete. However, other areas such as boards, insulation, reinforcement, biorefinery for chemical production required further research as there was no reports of them being employed in a real case scenario. Meanwhile the use of PMS to produce nanomaterials showed a considerably large literature gap that required further investigation.

There is opportunity for utilisation of PMS in materials instead of use on soil and energy recovery. However, these applications must meet technical standards if they will be used in any commercial products.

The fibre board application of PMS was hindered by thickness swelling caused by porous fibres absorbing water which limited their tensile strength. There is still very high variability in how much PMS can be added into fibre board production despite efforts made by Xing *et al.*, (2012) to find the optimal percentage of PMS. On average 15% of PMS can be used to substitute wood chips in MDF to meet technical standards.

Alternative bonding agents that are more environmentally friendly compared to UF and MDI could be investigated for PMS board production. The wet process which uses layers of webs/sheets of fibres before hot pressing was found to increase mechanical properties (Tikhonova, Lecourt and Irle, 2014). Mechanical properties of extruded boards (Scott *et al.*, 2000) were also higher than hot pressed boards (Geng, Deng and Zhang, 2006; Geng, Zhang and Deng, 2007; Migneault *et al.*, 2011; Tikhonova, Lecourt and Irle, 2014).

PMS was successful prepared with thermoplastic polymers HDPE and PE for wood plastic composite. PMS based wood plastic composite met specification for use in decking and fencing. The only study found where PMS was prepared into nanocellulose required many chemical steps and was highly energy intensive. There is scope to identify alternative means of nanocellulose production from PMS which could be used as a raw material for a variety of applications.

The mineral applications from PMS include cement mortar, blocks and clay bricks. The compressive strength of cement mortar reduces as PMS is added. 10 wt.% of PMS added to cement mortar meets specification for outdoor plastering. Addition of PMS also leads to better insulated material. PMS was successful in clay brick application when fired at high temperature bricks with 5% of PMS showed improvement in compressive strength. Further addition of PMS also reduced compressive strength however the PMS clay bricks can still be sold for masonry application if the properties of the material is declared by the manufacturer.

The material applications proposed for PMS are shown below in figure 23. These applications were compiled from the insights gathered in the discover stage.

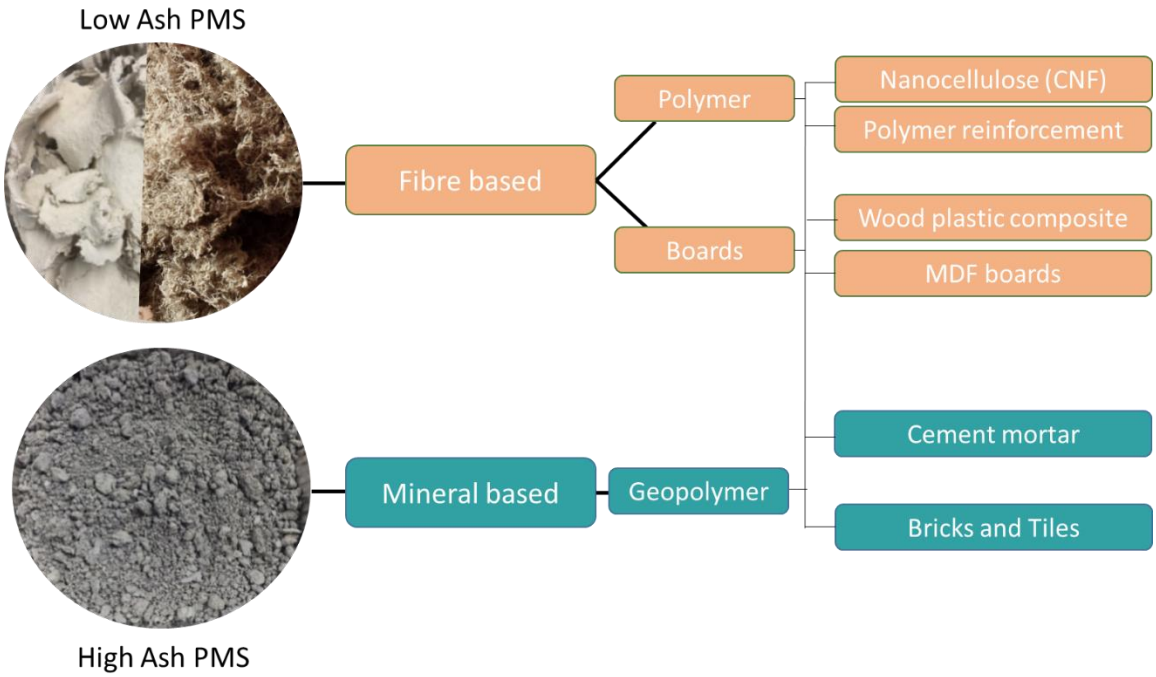


Figure 23: Illustration of material applications for PMS

PMS varied across the 7 mills depending on the pulping process, raw material used and final product. Even from the literature review it was clear that the composition of the PMS affected the materials' application. Hence the material utilisation of the PMS was grouped into fibre based and mineral based material.

Fibre based materials are those with low mineral content < 30% which will could be investigated for nanocellulose production, polymer reinforcement, wood plastic composite and medium density fibreboards.

The mineral based materials are for the PMS with high ash content > 30% can be used to prepare geopolymer by partial substitution with existing materials such as cement mortar, bricks and tiles. The next chapter will define the properties of PMS by characterisation of its organic and inorganic fractions.

4 Define: Characterisation of PMS organic and inorganic content.

This chapter address the second objective; To define the properties of paper mill sludge by the characterisation of its organic and inorganic fractions. *Refer to submission 2 of the EngD portfolio for further details on the characterisation methods and analysis.*

4.1 Overview of PMS characterisation methods

There is no technical standard for characterising PMS thus standards from the Technical Association of Pulp and Paper Industry (TAPPI) are adopted. Figure 24 shows the methods used for compositional analysis of PMS.

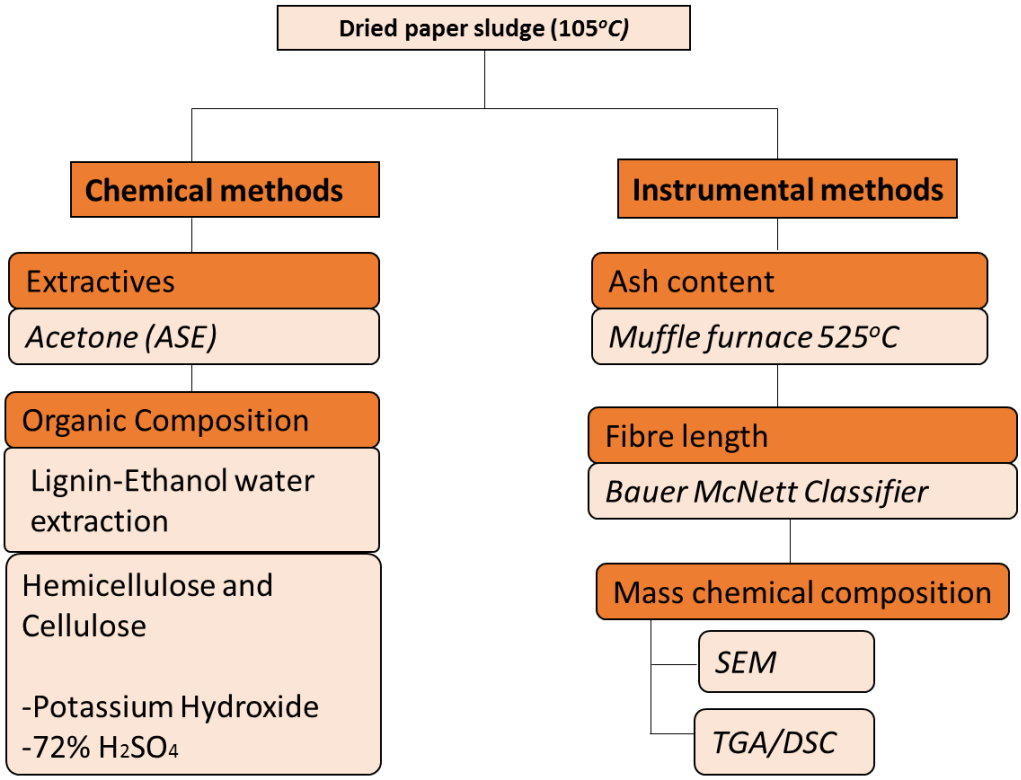


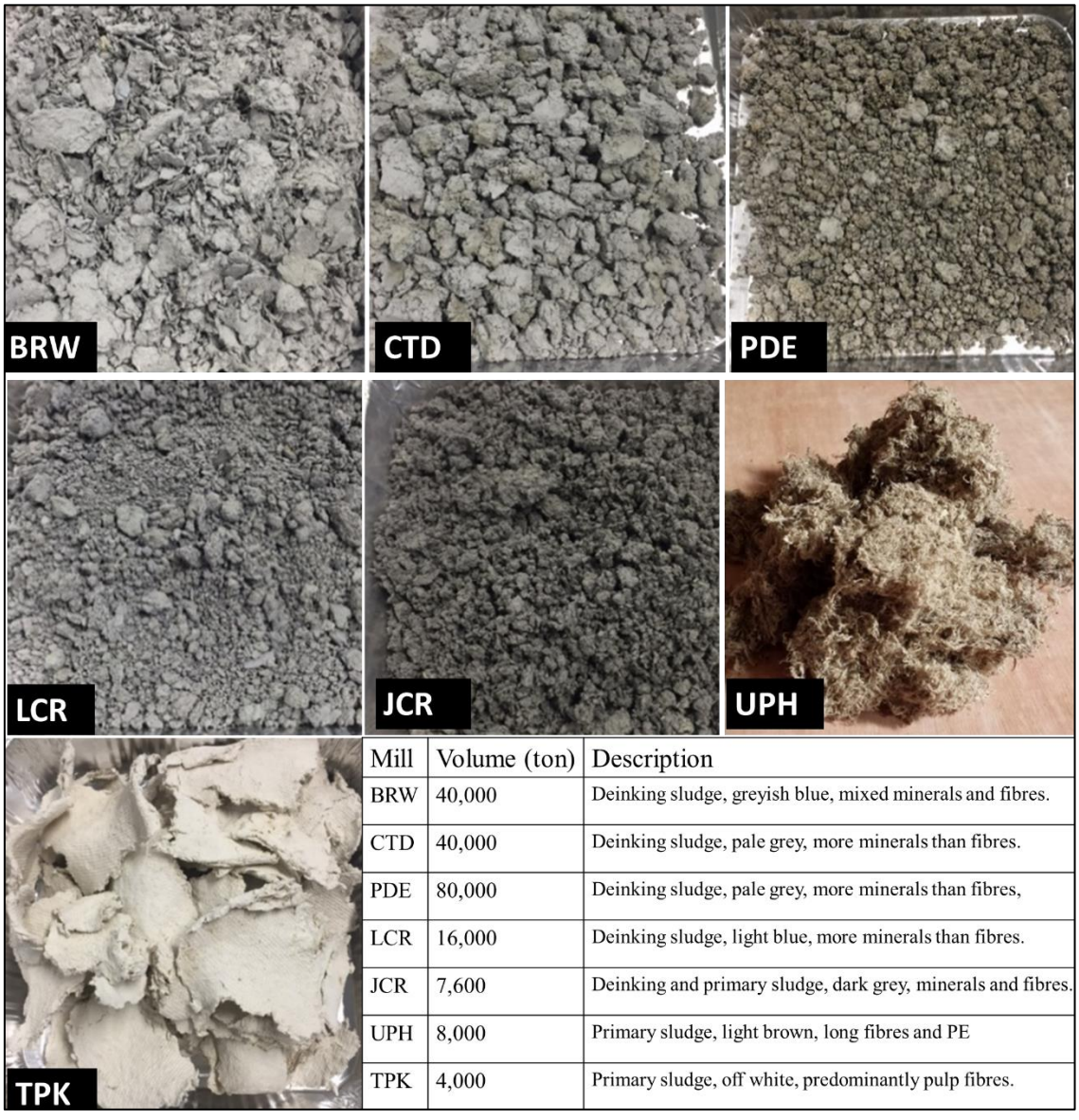
Figure 24: Methods used for characterisation of PMS.

PMS samples were oven dried at 105ºC for 24 hours prior to any test. First, the moisture content of the sludge shown in figure 7 was determined in accordance with TAPPI T 550 (Technical Association of Pulp and paper Industries, 2003).

Table 7: Moisture content of PMS

Mill	BRW	CTD	PDE	LCR	JCR	UPH	TPK
Moisture (%)	58	63	39	63	62	86	80
Standard deviation (%)	4	2	6	2	5	2	4

The appearance of sludge samples after drying is shown below in figure 25.



Mill	Volume (ton)	Description
BRW	40,000	Deinking sludge, greyish blue, mixed minerals and fibres.
CTD	40,000	Deinking sludge, pale grey, more minerals than fibres.
PDE	80,000	Deinking sludge, pale grey, more minerals than fibres,
LCR	16,000	Deinking sludge, light blue, more minerals than fibres.
JCR	7,600	Deinking and primary sludge, dark grey, minerals and fibres.
UPH	8,000	Primary sludge, light brown, long fibres and PE
TPK	4,000	Primary sludge, off white, predominantly pulp fibres.

Figure 25: Physical appearance of PMS samples obtained after drying.

De-inking sludges from BRW, CTD, PDE and LCR have similar appearance whilst the primary sludges from UPH and TPK have distinct appearance. Sludge from JCR appears darker as the mill operations uses colouring and recycled coffee cups which are also coloured. The UPH sludge is brown because of the high lignin content in abaca fibres. Whereas the TPK sludge is white because the mill uses virgin pulp which has already undergone pre-treatment.

4.2 Analysis of Inorganic content of PMS

The ash content is determined based on TAPPI 221 for any material left after igniting the sample in a muffle furnace at 525 ℃ (Technical Association of Pulp and paper Industries, 2004). Ash content is made up of inorganic matter consisting of chemicals and fillers found in the sludge. Three separate batches of PMS were tested for ash content. Each batch was tested in triplicates. The average ash content of PMS obtained from the 7 mills is shown below represented in figure 26.

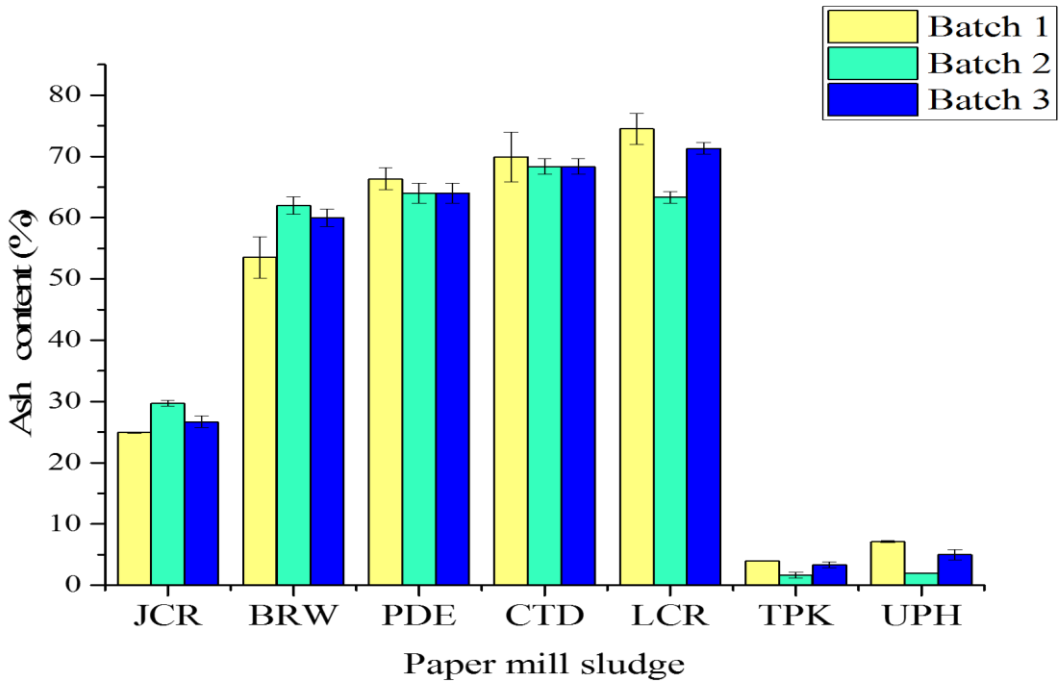


Figure 26: PMS ash content from 7 mills

The PMS ash content varied slightly across each batch, although this variability was observed mainly for mill BRW and LCR. As both mills use recovered waste fibres

as feedstock, it is expected that sludge composition will vary at different times collected. Sludges from BRW, PDE, CTD and LCR mill are high ash sludges (ash content > 30%), meanwhile sludges from mills JCR, TPK and UPH are low ash sludges (ash content < 30%).

Elemental analysis of the PMS in table 8 was provided by UKAS accredited laboratory SOCOTEC LTD (Burton upon Trent, United Kingdom) using inductively coupled plasma (ICP) mass spectroscopy.

Table 8: Composition of inorganic minerals and elemental oxides in PMS.

	Units	JCR	BRW	PDE	CTD	LCR	TPK	UPH
Arsenic	mg/kg	0.8	0.6	0.4	1.9	0.9	<0.3	0.6
Cadmium	mg/kg	0.2	0.1	0.2	0.2	0.2	<0.1	<0.1
Chromium	mg/kg	19.1	6.4	6.5	5.9	9.9	6.4	8.7
Copper	mg/kg	259.3	27.9	43	72.2	36.3	5.6	16.7
Nickel	mg/kg	9	3.5	6.2	5.3	5.6	3.1	5.9
Mercury	mg/kg	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
Lead	mg/kg	2.9	1.8	4.3	11.6	5.1	1	1
Vanadium	mg/kg	1.3	1.2	1.2	1.6	4.2	<0.6	4.1
Zinc	mg/kg	18.9	57	64.2	183.4	32	14.9	26.1
Aluminium	mg/kg	32926.8	5311.1	8187.3	8153.9	19530.1	638.7	703.8
Calcium	mg/kg	92861	151730.8	216228.2	240430.8	234986.2	947.7	2186.3
Iron	mg/kg	1279.9	1079.9	1202.3	1347	2346.5	166.5	1554.8
Magnesium	mg/kg	882.8	2094.8	2764.2	3097	4450.7	1578.7	779.1
Silicon	mg/kg	35411.2	9562.1	10980.6	15603.7	29480.8	3694.8	3099.3
Potassium	mg/kg	3038.2	320.4	117	532.9	557	268.1	205
Sodium	mg/kg	814.6	1145.5	2975.8	1905.2	2489.1	706.3	408.8
Titanium	mg/kg	877.7	231.4	687	384.9	804.5	40.8	68.3
SiO2	%	20.7	5.3	4.1	5.2	9.4	46.5	34.9
Al2O3	%	17	2.6	2.7	2.4	5.5	7.1	7
Fe2O3	%	0.5	0.4	0.3	0.3	0.5	1.4	11.7
TiO2	%	0.4	0.1	0.2	0.1	0.2	0.4	0.6
CaO	%	35.5	55	52.8	52.4	49	7.8	16.1
MgO	%	0.4	0.9	0.8	0.8	1.1	15.4	6.8
Na2O	%	0.3	0.4	0.7	0.4	0.5	5.6	2.9
K2O	%	1	0.1	<0.1	0.1	0.1	1.9	1.3
Mn3O4	%	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	0.6
P2O5	%	0.2	0.3	<0.1	<0.1	<0.1	1.9	3.2
SO3	%	2.5	0.4	0.3	0.2	0.4	4.1	6.2

Heavy metals with density < 5000 kg/m^3 were found in very low quantities. Especially mercury which is < 0.1 mg/kg except for PDE which was 0.2. Other elements such as aluminium, calcium, iron, magnesium, silicon, potassium, sodium and titanium are present in higher quantities. The percentage of total elemental oxides that make up the inorganic minerals is also given in the table. SiO_2 and CaO are the most present from coating and fillers used. Titanium Dioxide (TiO_2) is used in bleaching paper hence its presence in the PMS. TPK and UPH have the least total inorganic content of 8.1 and 9.1 g/kg of PMS. The inorganic mineral composition corresponds with the analysis of ash content.

4.3 Fibre length classification of PMS

PMS fibre length was determined in accordance with TAPPI 233 method-fibre length of pulp by classification (Technical Association of Pulp and paper Industries, 1998). The method employs a Bauer-McNett classifier shown below in figure 27. The classifier has 4 tanks with mesh screens 14, 28, 48 and 100 to collect fibres of different sizes 1.19 mm, 0.595 mm, 0.297 mm and 0.149 mm respectively.

Figure 27: Bauer-McNett classifier for fibre length analysis

Each tank has a cylindrical agitator inserted vertically rotating at 500 rpm to allow laminar flow in the tank. The water flow rate in the tank is 10 l/min. The tanks also have an outlet with a filter cloth for collecting fibres. The system has a drainage at the end to allow the water flow out. 10 g of dried PMS was diluted in 3333 ml of water and dispersed at 3000 rpm in a Lorentzen and Wettre pulp disintegrator (ABB, Switzerland). Water is supplied to all 4 tanks and the agitator is turned on, the diluted PMS is poured into the classifier which is left to run for 20 mins +/- 10 s. The fibres move from one tank to the next until the shortest fibres or fines end up in the last tank. The tank outlet is opened, and fibres are collected from the filter cloth. Any excess fibre in the mesh screen is flushed with a water hose. The fibre from each tank is dried in an oven at 105 ºC +/- 3ºC for 1 hr and then weighed.

The fibre length is calculated based on the weight of dried fibre collected from each tank using the equation 4.1 below

$$w_5 = W - (w_1 + w_2 + w_3 + w_4) \quad \text{equation 4.1}$$

W_5 is fibre lost through the last screen (< 0.149), W is oven dried weight of PMS sample and W_1, W_2, W_3 and W_4 are the clarifiers. The fibre length found in each classifier is shown below in figure 28 for each mill.

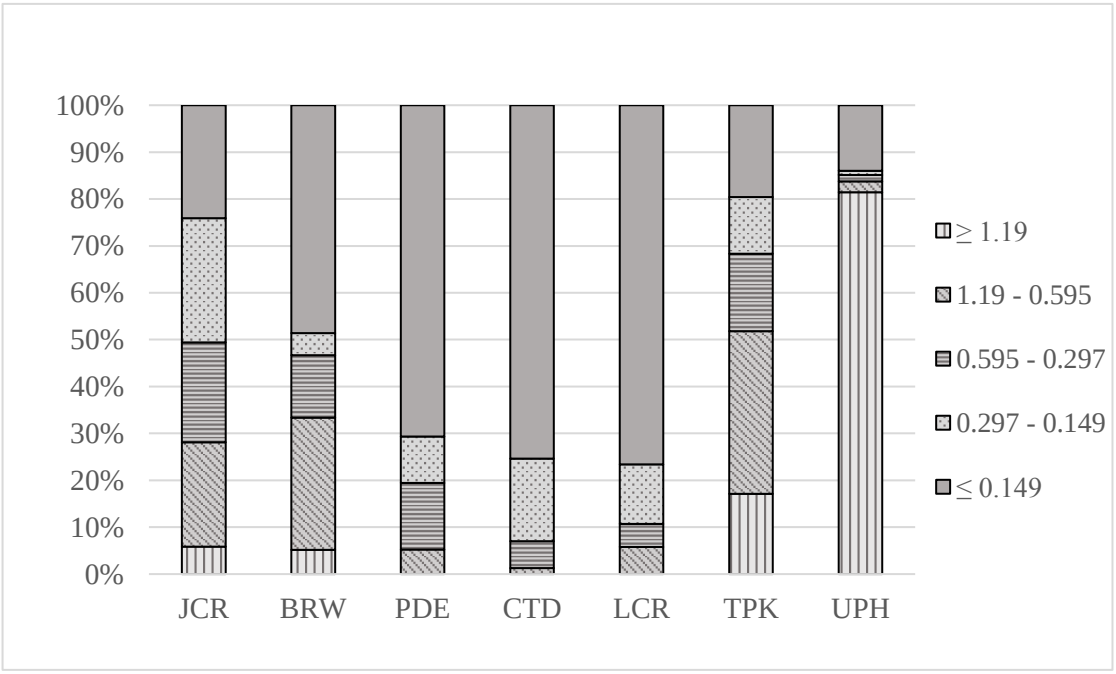


Figure 28: Percentage of PMS fibre length.

JCR sludge was distributed across the classifier with 27% of the sludge found between 0.297-0.149 mm. Sludge UPH had the longest fibres as 80% of fibres where ≥ 1.19, UPH mill uses abaca pulp which results in long fibres. Mills PDE, CTD and LCR had up to 75% of the sludge ≤ 0.149 which is mainly due to this mineral fillers and pulp fines. TPK sludge was also distributed across the classifier 35% of the sludge was 0.19 -0.595 mm in length. TPK sludge also made up of 20% fines which were less than 0.149 mm.

4.4 Analysis of organic contents in PMS

The organic chemicals C, H, N, S and O is determined using PerkinElmer series II CHNS/O analyser. Mass balance equation is used to calculate percentage of the chemicals. The composition of organic chemicals in the sludge is given in table 9.

Table 9: Organic composition of PMS.

	Unit	**JCR**	**BRW**	**PDE**	**CTD**	**LCR**	**TPK**	**UPH**
Carbon	%	34.8	33.44	27.17	24.52	23.65	48.07	51.85
Hydrogen	%	4.24	4.05	2.75	2.47	2.07	7.04	7.45
Oxygen	%	43.4	45.01	45.45	45.78	44.75	43.15	35.11
Nitrogen	%	0.31	0.28	0.26	0.02	0.03	0.82	4.54
Sulphur	%	0.44	0.06	0.04	0.04	0.03	0.11	0.14

The chemical composition refers only to the organic portion of the PMS; i.e excluding mineral content. As seen in the table, PMS is often low in nitrogen but contains carbon and oxygen. It also contains small percentage of Sulphur if the pulping process used chemicals such as Na_2S H_2SO_3 and bisulphite ion, H_SO_3.

To determine organic compound in biomass extractive contents are removed first. Extractive content is usually determined prior to other organic content. Extractives ae the non-structural components contained in biomass such as waxes, fatty acids, resin and tanins. Most of these are dissolved during pulping however studies on PMS characterisation have shown extractive content. TAPPI 204 cm-97 for solvent extractives of wood and pulp can be used for PMS. The method is based on Soxhlet extraction and using solvents such as dichloromethane and acetone to dissolve the extractive. However, Soxhlet extraction process consumes large quantities of solvent and require long waiting times. Thurbide and Hughes (2000) showed that Dionex 150 accelerated solvent extraction (ASE) equipment can be used to determine extractive content 10 mins and uses

75% less solvent. Extractives from PMS were determined with 12 ml HPLC grade acetone (Fisher scientific, UK). 1 gram of grounded PMS sample is filled in a stainless-steel extraction cell with a glass fibre filter. The acetone is flushed into the extraction cell and extraction parameters 15.19 MPa (150 atm) and 100 ℃ was used. Acetone is used as the carrier and the extractive content is purged through the system into a collection vessel. The analysis was repeated 3 times for each sample. The acetone is left to evaporate, and extractive content is determined by weight. Extractive content of PMS is listed in table 10.

Table 10: Extractive content of PMS

	Unit	JCR	BRW	PDE	CTD	LCR	TPK	UPH
Extractives	%	12.31	11.98	10.90	12.60	10.70	6.40	16.47
SD	%	3.2	2.8	4.7	3.5	4.1	0.8	0.4

The extractive content of PMS is affected by the pulping process; thermomechanical pulping leads to higher extractive compared to kraft and chemical pulping processes (Mabee, 2001; Ridout, Carrier and Görgens, 2014). Extractives removed from PMS samples are shown in figure 29.

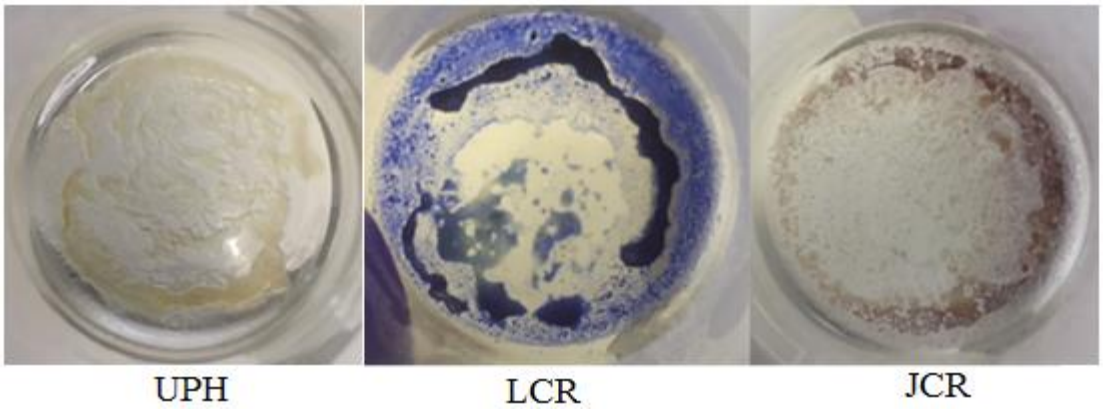


Figure 29: Extractives removed from PMS samples

UPH sludge contained higher amounts of extractives as the fibres were not as bleached compared to the other mills. Acetone also dissolved some ink in the PMS which affects the determination of extractives in PMS.

Paper is obtained from lignocellulose biomass hence it made up of cellulose, hemi-cellulose and lignin. Lignin is an amorphous phenolic polymer found in the

secondary cell wall. Unlike cellulose which has repeating glucose unit, lignin has no regular repeating unit and the structure of lignin vary depending on its origin. It plays a vital role in plant growth by enhancing the strength of fibrous tissue, improving water conduction and fighting against pathogens (Lu and Ralph, 2010). Lignin forms chemical bonds cellulose and hemicellulose in the plant cell wall which improves rigidity. Hemicellulose is composed of various sugar units; xyloglucans, xylans, mannans and glucomannans, and glucans.

When lignocellulose material is treated with 72% sulphuric acid, Klason lignin is obtained, the TAPPI standard adopts this method to quantify lignin in wood (Technical Association of Pulp and paper Industries, 2011). However, this method is not recommended for bleached pulps as most of the lignin in wood pulp is removed during pulping process (Ligero et al., 2008; McDonougH, 1992). Jackson and Line (1997) showed that the ash content of PMS hinders the removal efficiency of cellulose and hemicellulose thereby leading to an overestimation of lignin An empirical method from Moubasher *et al.* (1982) has been used to estimate the composition of cellulose, hemicellulose and lignin in biomass as illustrated figure 30.

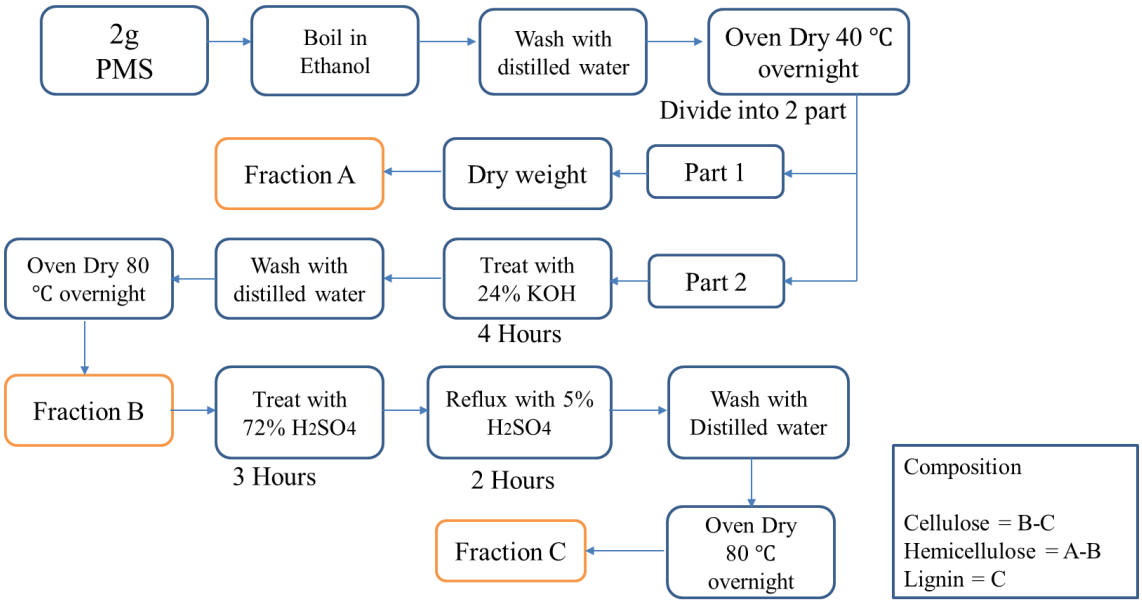


Figure 30: Method for direct estimation of cellulose, hemicellulose and lignin Moubasher et al. (1982).

This method has been used in various studies for characterising biomass (Berglund et al., 2016; Brindha D and P., 2012; Syed, Zakaria and Bujang, 2016). 2 g of

PMS is boiled in distilled water and oven dried at 40 ℃. The PMS samples is divided into 2 equal parts. Labelled as part 1 and part 2, part 1is weighted and labelled as fraction A. Whilst part 2 is treated with 24% potassium hydroxide KOH, washed off with distilled water and oven dried, the sample is weighed and labelled as fraction B. Fraction B is further treated with 72% H_2SO_4 and refluxed with 5 % H_2SO_4. The acid is washed off with distilled water until neutral pH. This fraction is oven dried and weighed as fraction C. The composition of is based on the weight of fraction B-C for cellulose, hemicellulose is fraction A-B and lignin is fraction C. The organic composition of the sludge samples is shown below in table 11.

Table 11: Organic composition of PMS

				B-C	**A-B**	**C**	
	A	**B**	**C**	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**	**Total Organics (%)**
JCR	51.21	48.41	0.69	47.72	2.80	0.69	51.21
BRW	19.02	16.12	0.82	15.30	2.90	0.82	19.02
PDE	14.12	12.02	0.47	11.55	2.10	0.47	14.12
CTD	11.28	8.98	0.26	8.72	2.30	0.26	11.28
LCR	16.34	13.94	0.78	13.16	2.40	0.78	16.34
TPK	75.12	72.52	0.56	71.96	2.60	0.56	75.12
UPH	66.18	62.98	1.78	61.2	3.20	1.78	66.18

The lignin content for all samples were very low < 1 %, although sludge from UPH has a higher lignin content as this is expected of abaca fibres. The highest composition of total organic was found in mill TPK, UPH and JCR at 75.12, 66.18 and 51.2% respectively. Deinking sludges BRW, PDE, CTD and LCR have total organic content 19, 14, 11.3 and 16.3%. The organic composition of primary sludge and deinking sludges follow similar trend with that in the literature (Migneault et al., 2011).The hemicellulose content in all the sludges were very low, it is uncertain if applying the same chemical methods for analysing wood pulp is effective for PMS. Thus, to ensure a reliable quantitative assessment of PMS organic composition, other analytical techniques were used in section 4.5.

4.5 Thermal analysis of PMS

Another approach for determining organic composition of biomass are instrumental methods such as Fourier-transformed infrared spectroscopy (FTIR), used thermogravimetric analysis (TGA) and various spectroscopy techniques. Yang *et al.*, (2006) TGA to determine composition of cellulose, hemicellulose and lignin in biomass samples. Thermal decomposition method was adopted for further analysis of PMS. A Mettler Toledo TGA/DSC analyser was used to heat grounded PMS specimen from 25 ℃ to 600 ℃ at a heating rate 10 ℃/min in N_2 atmosphere. An aluminium pan was used with 10 mg samples. Figure 31 shows the TGA curve of the PMS samples obtained from each mill.

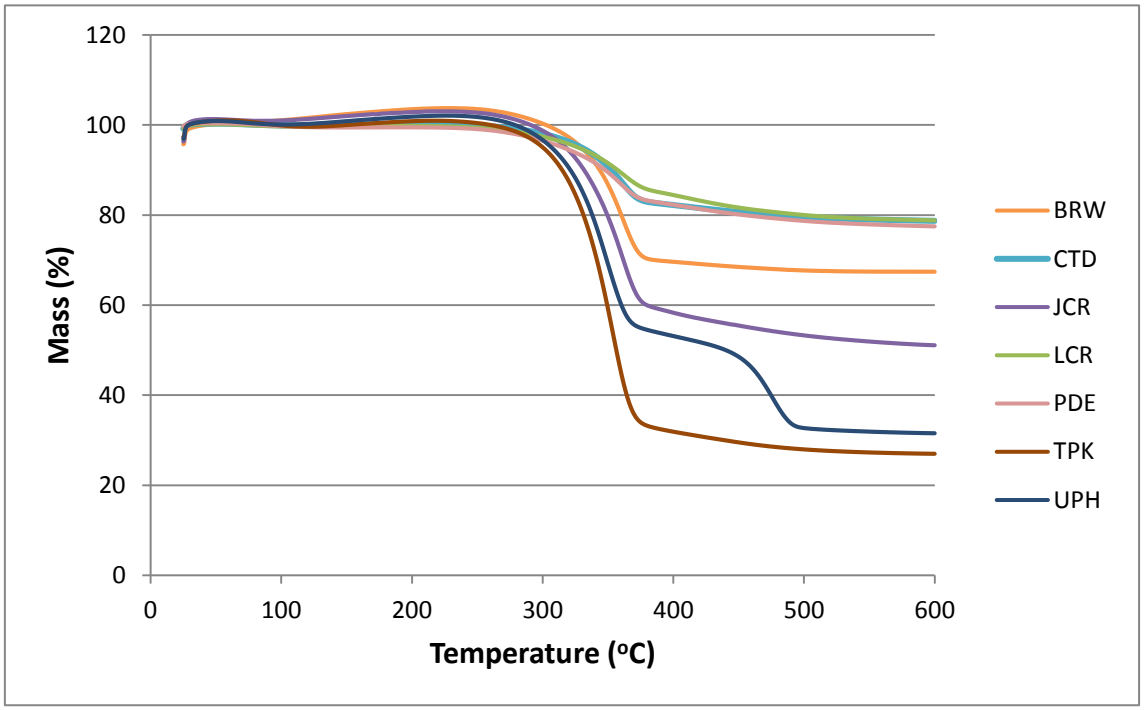


Figure 31: Thermal degradation curve of PMS samples

The TGA curve shows the thermal decomposition of the PMS samples as a function of mass loss. TGA curve of the PMS samples are similar to those found in literature (Lin et al., 2015; Ridout, Carrier and Görgens, 2014). PMS samples showed increasing mass loss starting at ~ 300 ℃ due to decomposition of organic content. The derivative plot of the TGA (dm/dt) is shown in figure 32.

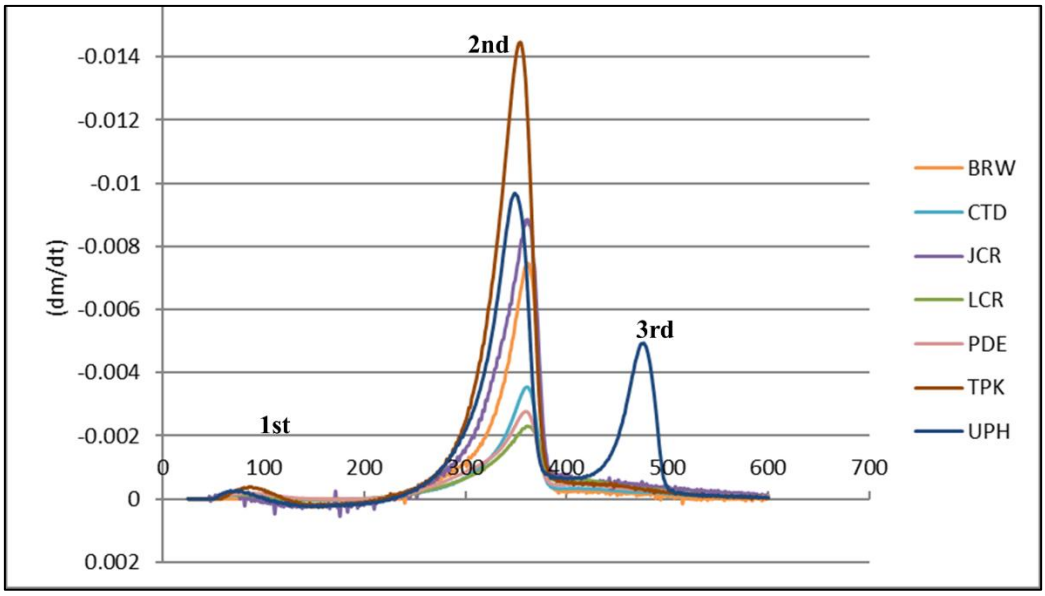


Figure 32: Derivative thermogravimetric (DTG) curve of PMS samples showing degradation peaks.

DTG curve shows the mass loss rate as a function of temperature increase. The first peak at ~ 100 ℃ indicates mass loss from moisture evaporation. The second decomposition peak between 300-400 ℃ indicates the thermal decomposition of the organic content. The third peak appears only for UPH paper mill for the PE content. Table 12 shows the values from the TGA

Table 12: Combustion characteristics parameters of PMS samples.

	Unit	JCR	CTD	BRW	LCR	PDE	TPK	UPH
Mass loss	%	48.9	21.27	32.58	21.17	22.51	73.01	68.46
Mass left	%	51.1	78.73	67.42	78.83	77.49	26.99	31.54
T_1	℃	84.9	83.1	88.5	81.2	85.3	88.7	86.5
T_2	℃	362.7	363.7	361.8	364.8	363.2	356.2	352.7
T_3	℃	-	-	-	-	-	-	477.3
dm/dt max 1	% /℃	8	3.4	7.4	2.2	2.6	14	9.2
dm/dt max 2	% /℃	-	-	-				5

Sludge with higher organic content UPH, TPK and JCR showed the highest mass loss whilst high mineral content sludge LCR, PDE, CTD and BRW had showed highest mass left. The UPH sludge showed another decomposition stage which can be confirmed as thermal degradation of PE fibres (Zheng et al., 2018).

4.6 Microscopy and EDX of PMS samples

Dried PMS were observed with TESCAN LYRA3 (Czech Republic) scanning electron microscope with Energy dispersive x-ray (EDX). EDX was used to obtain chemical analysis of materials in the sludge sample.

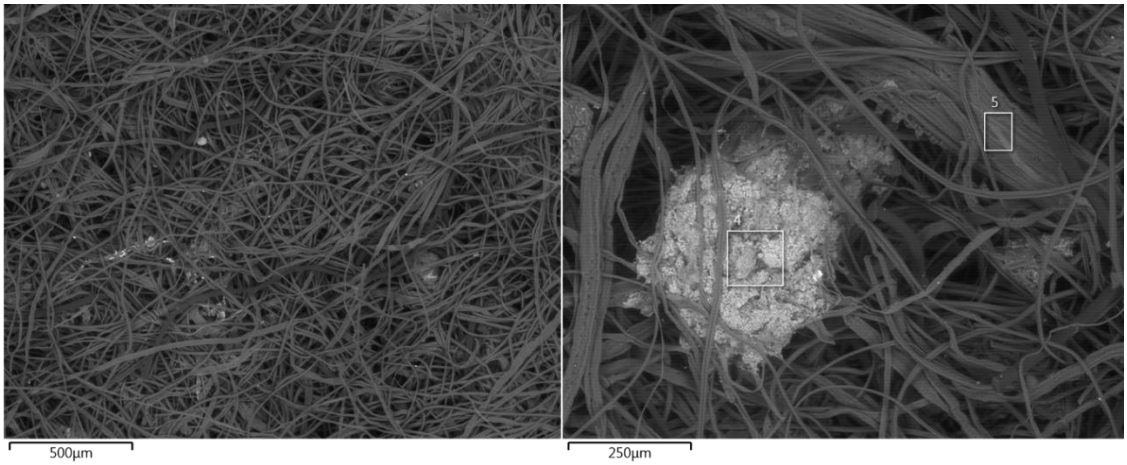


Figure 33: SEM of UPH sludge showing long fibres and mineral filler.

PMS from UPH mill had the longest fibres (~ 2 mm) in comparison to other sludge samples. The SEM analysis showed very small traces of inorganic fillers scattered in the sludge. The filler can be observed on the left at high magnification. The EDX spectrum confirmed the mineral filler to contain calcium, magnesium, aluminium and sodium as shown in figure 34.

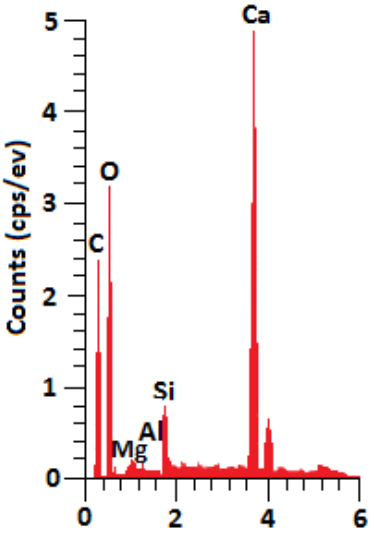


Figure 34: EDX spectrum of UPH sludge

The EDX spectrum also corresponds with the chemical spectroscopy analysis earlier in Table 10. The Sludge samples from deinking mills CTD had fewer fibres and high mineral fillers as shown in figure 35.

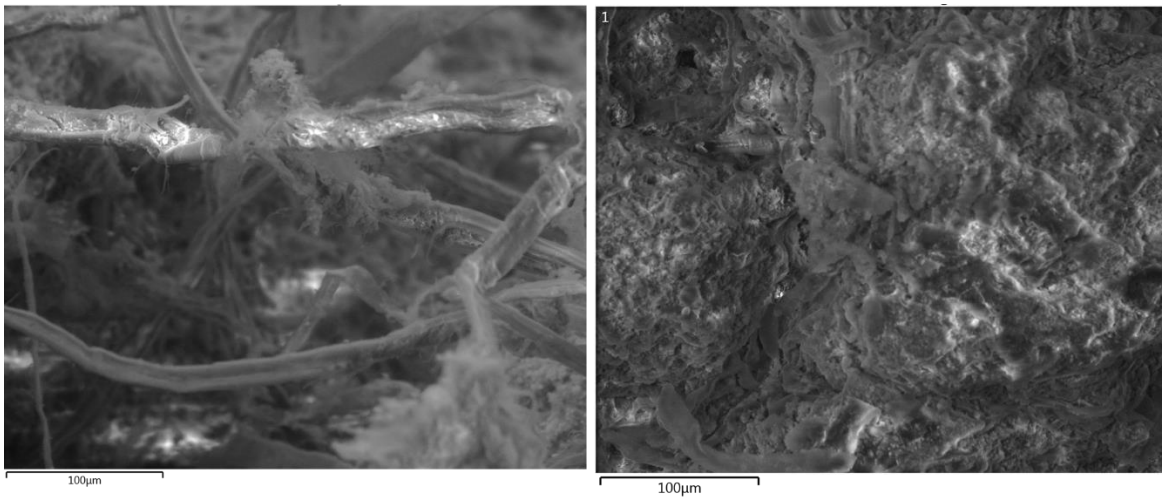


Figure 35: SEM of CTD sludge showing filler content with short fibres.

The sludges obtained from mill BRW, LCR and PDE showed similar microscopy images of higher mineral content with short fibres.

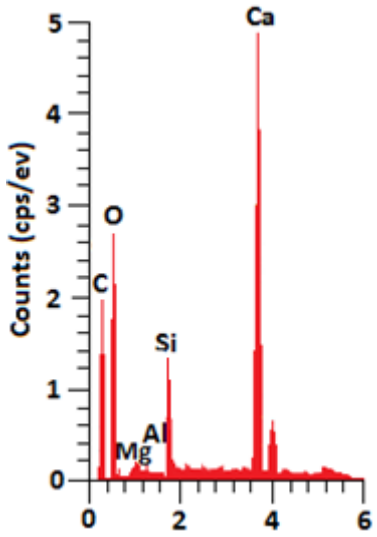


Figure 36: EDX spectrum of CTD sludge.

The EDX spectrum in figure 36 confirmed the entire area to contain high counts of calcium with lower carbon which also corresponds with the IPS analysis in table 9 and organic chemicals in table 10.

4.7 Summary of chapter 4

Chapter 4 completes the objective; to define the properties of paper mill sludge by the characterisation of its organic and inorganic fractionsA summary of the sludge composition is shown in table 13.

Table 13: Summary of PMS composition.

		JCR	**BRW**	**PDE**	**CTD**	**LCR**	**TPK**	**UPH**
Extractive	%	12.31	11.98	10.90	12.60	10.70	6.40	16.47
Total organics	**%**	**51.21**	**19.02**	**14.12**	**11.28**	**16.34**	**75.12**	**66.18**
Cellulose	%	47.72	15.30	11.55	8.72	13.16	71.96	61.2
Hemicellulose	%	2.80	2.90	2.10	2.30	2.40	2.60	3.20
Lignin	%	0.69	0.82	0.47	0.26	0.78	0.56	1.78
C	%	34.8	33.44	27.17	24.52	23.65	48.07	51.85
H	%	4.24	4.05	2.75	2.47	2.07	7.04	7.45
O	%	43.4	45.01	45.45	45.78	44.75	43.15	35.11
N	%	0.31	0.28	0.26	0.02	0.03	0.82	4.54
S	%	0.44	0.06	0.04	0.04	0.03	0.11	0.14
Ash	**%**	**27 ± 2**	**64 ± 8**	**65 ± 2**	**69 ± 2**	**70 ± 5**	**3 ± 1**	**5 ± 2**
*SiO_2	%	20.7	5.3	4.1	5.2	9.4	46.5	34.9
*Al_2O_3	%	17	2.6	2.7	2.4	5.5	7.1	7
*TiO_2	%	0.4	0.1	0.2	0.1	0.2	0.4	0.6
*CaO	%	35.5	55	52.8	52.4	49	7.8	16.1
*MgO	%	0.4	0.9	0.8	0.8	1.1	15.4	6.8
TGA Mass loss	%	48.9	21.27	32.58	21.17	22.51	72.01	68.46
TGA Mass left	%	51.1	78.73	67.42	78.83	22.49	26.99	31.54

* Inorganic compounds are given as a percentage of Ash content

The composition of PMS provides can be used to assess which propped material application in chapter 3 are suitable. PMS from TPK, UPH and JCR are used for fibre-based applications whilst PMS from BRW, PDE, CTD and BRW are proposed for mineral based applications. The Chapter 5 is the ‘Develop’ stage of the research which will focus on the development of materials from PMS and assessment of their technical feasibility.

5 Develop: The conversion of paper mill sludge into value added materials

This chapter address the third objective; To develop paper mill sludge material applications from PMS and assess their technical feasibility. In chapter 5.1 cellulose nanofibres have been prepared from paper mill sludge known as PSNF, in chapter 5.2 the PSNF was spun into long filaments, in chapter 5.3, Foams were produced from the PSNF and in chapter 5.4 the paper mill sludge was used to produce composite panels. *Refer to portfolio submission 3,4, 5 and 6 for more details on this chapter.*

PMS is rich in organic and inorganic compounds that could be developed into materials for other business. After the 'Discover' and 'Define' stage of the design thinking methodology PMS has been recommended for the applications in figure 37.

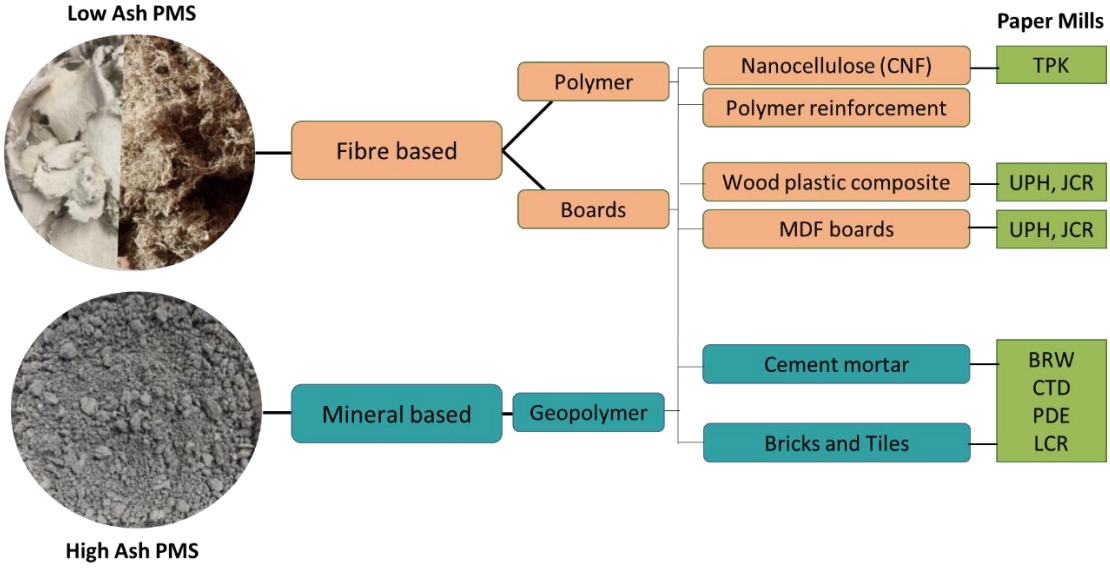


Figure 37: Illustration of proposed material applications for PMS based on characterisation.

In this chapter PMS from TPK will was used to produce cellulose nanofibres, the cellulose nanofibres were spun into long fibres for polymer reinforcement and used to produce foams. PMS was also used to manufacture composite panels however instead of using formaldehyde-based, bio-resin from another industrial by-product was used.

5.1 Cellulose nanofibres (CNF) produced from paper mill sludge

This section is based on research conducted in portfolio submission 4.

PMS provides a sustainable source to produce nanocellulose because it is a free industrial by-product and it does not compete with land resources for growing food crops. In the literature cellulose has been extracted from industrial by-products listed in table 14.

Table 14; Methods used for extracting nanocellulose from industrial by-products**.**

Source	Pre-treatment	Preparation method	Reference
Sugar beet pulp	2% NaOH	Homogenisation	(Dufresne, Cavaille and Vignon, 1997)
Soy bean	NaOH and HCl	Homogenisation	(Wang and Sain, 2007)
Softwood pulp	Enzyme hydrolysis	Homogenisation	(Henriksson *et al.*, 2008)
Bagasse	4% NaOH $NaClO_2$	Homogenisation	(Bhattacharya, Germinario and Winter, 2008)
Pineapple leaf	2% NaOH	Steam explosion	(Cherian et al., 2011)
Jute fibre	H_2SO_4 and NaOH	Ball milling	(Baheti, Abbasi and Militky, 2012)
Dissolving pulp	Pre-bleached	Mechanical grinding	(Jonoobi, Mathew and Oksman, 2012)
Brewery residue	2% NaOH	Mechanical grinding	(Berglund *et al.*, 2016)
Carrot	2% NaOH	Mechanical grinding	(Berglund *et al.*, 2016)
Hemp	4% NaOH $NaClO_2$	Microfluidizer	(Pacaphol and Aht-Ong, 2017)

The different extraction methods for nanocellulose have the same principle to breakdown the plant cell wall and isolate the fibrils. Depending on the source of raw material and if the cellulose is embedded in a matrix, the production of nanocellulose becomes chemically and energy intensive. This also limits the industrial scale production of nanocellulose (Delgado-Aguilar et al., 2015; Oksman et al., 2016). As a result, free

PMS which has already undergone pre-treatment during the pulping process is favourable for nanocellulose production. This section discusses the use of PMS in the preparation of cellulose nanofibres referred to as paper sludge nanofibres (PSNF).

5.1.1 Materials and methods for PSNF preparation

PMS was prepared by mechanical grinding using a supermasscolloider MKCA6-3 (Masuko Sangyo Co. Ltd., Japan). The equipment exerts shear force on the fibres by a rotating silica carbide grinding as shown in figure 38.

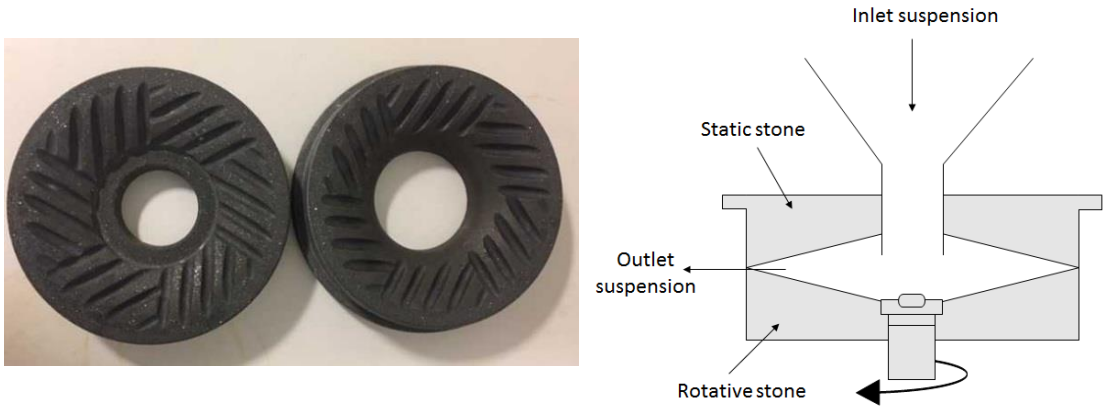


Figure 38: Silica Carbide grinding discs with grooves (left) and schematic of grinder with static upper stone and rotating lower stone (right).

A 2 wt.% suspension of PMS was prepared by dispersing 80g PMS (dry weight) in 4000 ml of de-ionised water. The suspension was processed at a rotor speed of 1500 rpm for 170 mins until a viscous gel was formed as shown in figure 39.

Figure 39: Preparation steps of PSNF showing from left to right, dispersed PMS, mechanical grinder and viscous PSNF suspension at 2 wt.%

Viscosity measurements provide an indication of the fibrillation process. Hence grinding stopped at 150 mins when the viscosity reached a plateau. The PSNF was prepared into films/sheets. PSNF was diluted to 0.2 wt.% suspension dispersed at 10,000 rpm with IKA T25, UltraTurrax, (IKA-Werke GmbH & Co,Germany) for 10 mins. After dispersion the solution was degassed and filtered with a 0.45 mm Whatman filter (GE Healthcare, US). The PSNF network was peeled off from the filter paper with tweezers and heat pressed between stainless steel plates at 110℃ and under 1.1 MPa pressure for 30 minutes based on optimal conditions from Jonoobi, Mathew and Oksman (2012). The PSNF suspension and PSNF film was characterised further to obtain the mechanical properties of the nanofibre network.

5.1.2 Characterisation of PSNF

Apparent viscosity was measured with a Vibro Viscometer SV-10 (A&D company, Japan) at room temperature. The energy consumption of process was measured with EM24 DIN power meter (Carlo Gavazzi Holdings, Italy) and calculated with the following equation

Energy (J) = power (W) x time (h) (5.1)

The morphology of the PMS was observed with polarised optical microscopy (Nikon Eclipse LV100N POL, Japan) and Atomic Force Microscopy (AFM) (Bruker, UK). Light transmittance was measured with a UV-VIS-NIR extended FLAME-S-XRI spectrophotometer (Ocean Optics, UK) between 200-1000 nm. Opacity measurement was obtained with an Elrepho 070 spectrometer (Lorentzen and Wettre, Sweden). The PSNF film was cut into strips of 55 x 5 mm in length and width and mounted unto a cardboard frame for tensile tests. The strips were tested with AG-X universal tensile testing machine (Shimadzu, Japan) at a 2 mm/min extension rate and 1 kN load cell. The tensile index of the PSNF films was measured based on weight per unit area (gsm). Measurements are reported from an average of 8 samples.A Bruker D8 Advance diffractometer (Brucker, Germany) with Cu radiation source was used to obtain the X-ray diffraction (XRD) pattern of the PSNF samples. The range of 2θ scan angles were from 5 to 40° with the equipment operated at 40 kV. The XRD pattern was used to calculate crystallinity index based on the empirical Segal's (1958) method for cellulose and peak deconvolution method (Park et al., 2010).

5.1.3 Results and discussion of PSNF properties

The results based on measurements of viscosity, energy consumption, fibre morphology, light transmittance, opacity, mechanical properties and crystallinity of the PSNF will be discussed here.

Viscosity measurements at different fibrillation intervals is shown in figure 40 along with the energy consumption of the fibrillation process.

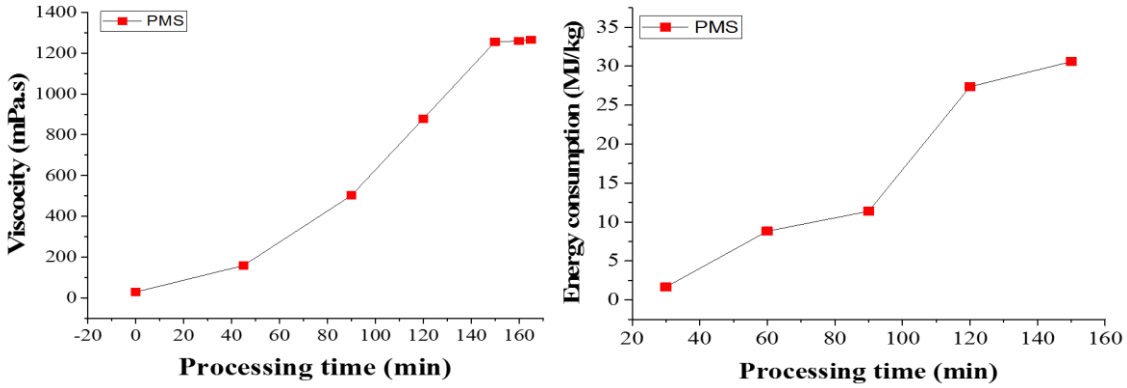


Figure 40: Increase in viscosity (left) and energy consumption (right) at different processing times of PMS fibrillation.

PMS viscosity increased exponentially until it reached a plateau viscosity of 1256 mPa.s after 150 mins of processing. The energy consumption was 30.6 MJ/kg (8.5 kWh/kg). Energy consumption for CNF production varies depending on raw material and fibrillation equipment. Eriksen et al. (2008) used Kraft pulp to produce CNF and energy consumption as high as 252 MJ/kg. Two comprehensive studies on energy consumption based on types of wood pulps reported values from 2 -54 MJ/kg (Lahtinen et al., 2014; Spence et al., 2011). CNF produced with by-products from carrot juicing and brewery process reported energy consumption of 3.34 and 75.6 MJ/kg (Berglund et al., 2016). Jonoobi *et al.* (2012) reported very low energy consumption of 4.7 MJ/Kg and 11.2 MJ/Kg when dissolving pulp sludge was used to produce CNF with at rotor speed of 1400 rpm and 3200 rpm respectively. Compared to these results energy consumption of PSNF processing was average. However, when the process was conducted on a larger l grinder (MKZA10-15JIV) from the same manufacture (Masuko, Japan) and fitted with a recirculating pump; the energy consumption reduced from 30.6 MJ/kg (8.5 kWh/kg) to 16.9 MJ/kg (4.7 kWh/kg) after 150 min processing time and 3 wt.% suspension.

The microscopy images of the PMS are shown below in figure 41. During mechanical grinding the PMS showed consistent size reduction from 0-150 mins.

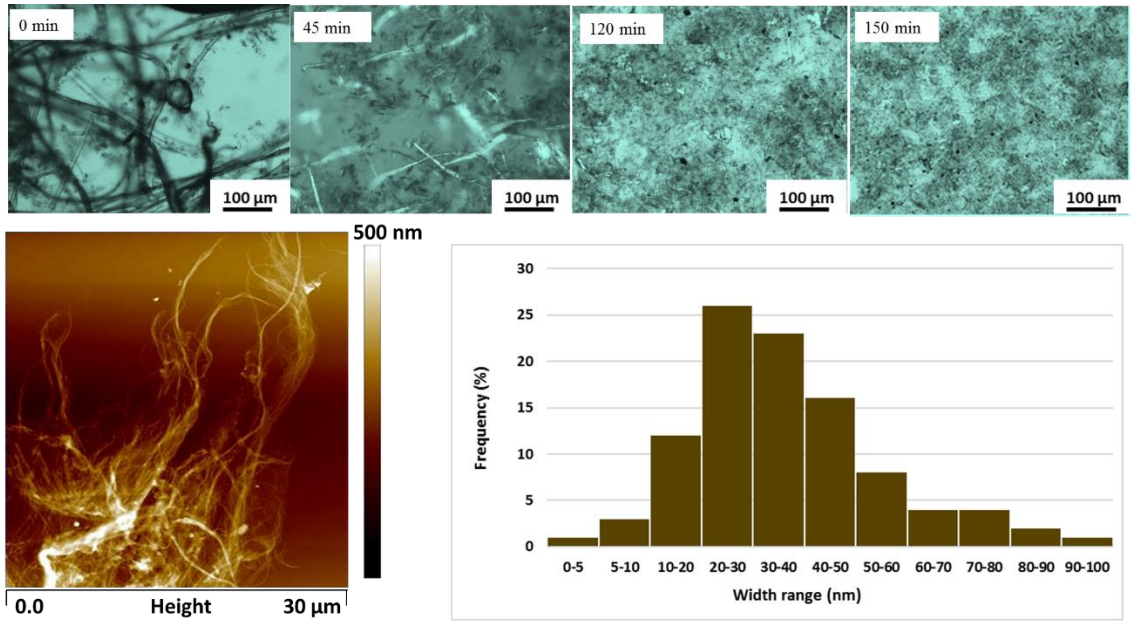


Figure 41: Morphology of PMS fibres during grinding (top), AFM scan of PSNF and width distribution (bottom left to right).

The AFM scan obtained from 0.01 wt.% PSNF on a mic plate which dried at room temperature. Tapping mode was used with a scan rate of 0.4 Hz and scan area of 30 µm. The average fibre width was 34 ± 15 nm. The histogram showed 60% fibre widths ranging between 20-50 nm.

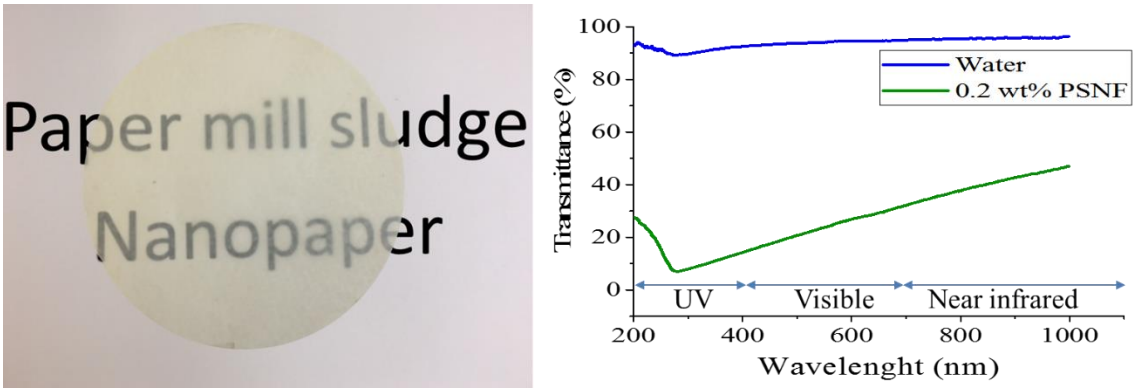


Figure 42: Sheet made from PSNF and, light transmittance of 0.2 wt% PSNF (green) and water (blue).

The opacity of the PSNF sheet shown in figure 42 was recorded as 44 ± 0.3%. The transparency of nanocellulose sheets/films occur when cellulose fibres are less than the wavelength of visible light (400-700 nm) and if air scattering is surprised by densely packed fibres this improves transparency (Nogi *et al.*, 2013). The 0.2 wt% PSNF suspension showed a low visible light transmittance of 32.4% at and 7.4 % in the UV region (300 nm). Low UV light transmission is a beneficial property in packaging of UV-sensitive products. Nanocellulose films with visible light transmittance up to 90% can be used as display screen in electronic devices (Alila et al., 2013; Nogi et al., 2009).

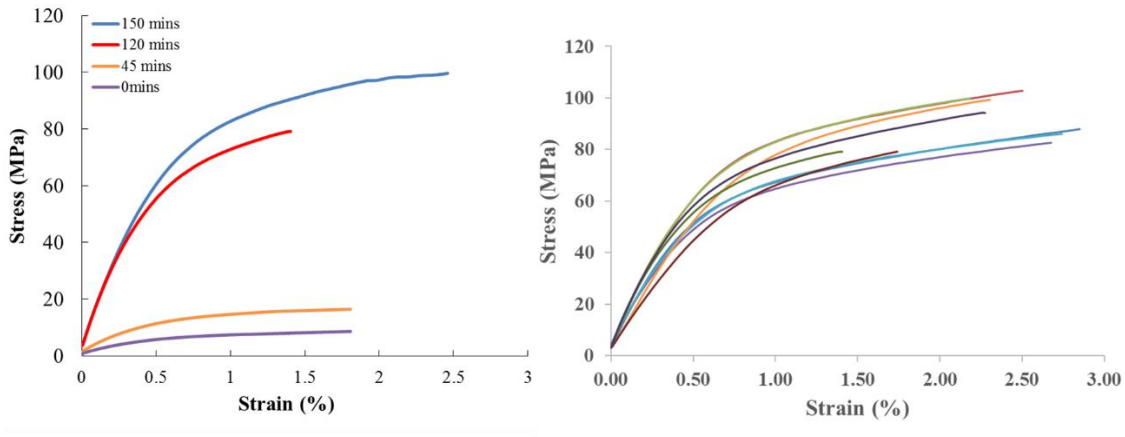


Figure 43: Stress-strain curve of PSNF sheets at different fibrillation times and stress-strain curves of strips cut from PSNF sheets.

In figure 43 (left) an 8-fold increase in tensile strength can be observed from 0 mins to 150 mins. Stress-strain curves of 8 PSNF samples are shown in figure 44 (right) and their elastic modulus was calculated from the slope of the initial portion of the curve. The mechanical properties at PMS before and the PSNF is reported in Table 15.

Table 15: Mechanical properties of PMS and PSNF fibre networks.

	Modulus (E)	Tensile strength	Tensile strain	Tensile index
	(GPa)	(MPa)	(%)	(Nm/g)
PMS	1.7 ± 0.3	8.2 ± 0.3	1.8 ± 0.1	16.4 ± 0.9
PSNF	10.1 ± 0.3	85.4 ± 10.2	2.2 ± 0.4	71.5 ± 5.6

There is a significant increase in the mechanical properties of PMS when prepared into PSNF. The stiffness of the material may have been enhanced by the presence of the mineral fillers. The PSNF is comparable with CNF made from dissolving pulp sludge (Jonoobi, Mathew and Oksman, 2012). However, mechanical properties are also affected by CNF processing methods, material source and film preparation (rapid-kothen, solvent casting, vacuum filtration). If chemical treatment was used the PSNF has potential to reach higher mechanical properties. TEMPO-mediated oxidation of eucalyptus pulp by Gonzalez et al (2014) resulted in strength of 135 ± 18 MPa and modulus of 11.9 ± 0.9 GPa. The degree of polymerisation is affected by the material source, bacteria cellulose with higher DP (8000) have higher aspect ratio resulting in better mechanical properties than lignocellulose source (Yousefi et al., 2013).

The X-ray diffraction patterns is shown in figure 44 for the PSNF film with intensity labelled a-g. Because the PMS contained inorganic compounds their crystalline peaks were shown on the X-ray pattern. Peak (a) at 9.5° and (g) 28.6° are crystalline talc ($MgSi4O10(OH)_2$ confirmed from Frías, Rodriguez and Sanchez de Rojas (2015). Peak (e) is suspected to be calcite material. Only peaks attributed to cellulose were used to calculate crystallinity index (Crl).

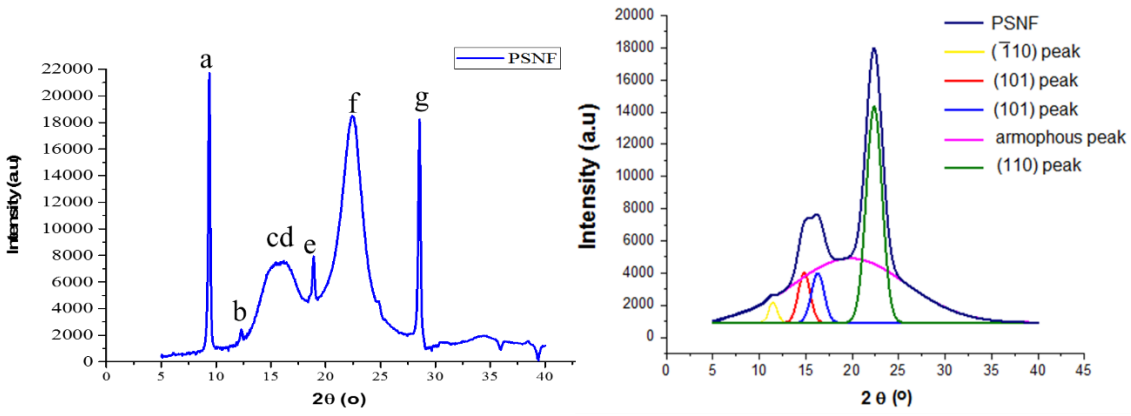


Figure 44: X-ray diffraction pattern for PSNF (left) and deconvoluted peaks (right)

Different polymorphs of cellulose (I and II) can be found in the XRD pattern as PSNF was obtained by grinding (French, 2014). Peak b at 12.8° is indicative of a cellulose II structure ($\bar{1}10$). The amorphous portion of the PSNF is the lowest intensity between peak

b and f. The main crystalline peak (f) at 22.5° is cellulose I structure (110). To calculate the crystallinity index Segal (1958) and Park's (2010) method were used.

Segal's equation (1958) is given in equation 5.2;

$$CrI\ (\%) = \frac{I_{max} - I_{am}}{I_{max}} \qquad \text{equation (5.2)}$$

Where I_{max} is main crystalline peak and I_{am} is the amorphous peak. Park's method applies a Gaussian function to deconvolutes each peak as shown in figure 45 right. CrI is calculated by dividing the total area of each crystalline peak by the total area.

$$CrI\ (\%) = \frac{A_{crystalline}}{A_{total}}$$

The CrI resulted in 69% and 43% for Segal and the peak deconvolution method. The study shows that PMS can be processed into nanocellulose material without any chemical treatments. The mechanical properties of the material render it feasible as reinforcement fillers in polymer composites which will be discussed in sections 5.2 and 5.3.

5.2 Paper sludge nanofibres (PSNF) spun into filaments

This section is based on research conducted in portfolio submission 5

The global fibre production is made up of 60% synthetic fibres such as polyester and nylon, 27% cotton and 8% regenerated cellulose fibres such as viscose and rayon (Freitas and Mathews, 2017). Regenerated cellulose fibres are produced from wood pulp or cotton linter which is arguably more sustainable compared to fossil-fuel also leave microplastics in aquatic habitat. Regenerated cellulose fibres are produced from 120 million trees yearly, under sustainable forestry management. Nonetheless, the global demand for fibres is expected to double by 2050. Therefore, alternative sources of regenerated cellulose production will be beneficial to the industry. Moreover, concerns about unsustainable practices in regenerated cellulose production have been highlighted recently due to use hazardous chemicals, unregulated dumping of factory effluent in public water and high processing temperatures (Changing markets foundation, 2018; Ellen MacArthur Foundation, 2017).

Cellulose molecules are closely packed, with complex a structure of intra/inter-molecular hydrogen bonds making it insoluble in most organic solvents. Therefore, the production of regenerated cellulose fibres applies the viscose or lyocell process where cellulose is treated with sodium hydroxide or amine oxide to produce a spinning dope. Ionic liquids (IL) which are molten salts with low melting points below 100 ℃ have been proposed as benign solvents for producing regenerated cellulose fibres (Swatloski *et al.*, 2002). ILs have hydrogen bond acceptors that have strong interaction with the free hydroxyl groups of cellulose. IL's provide a one-step process, thermally stability, non-flammability and it can be easily recycled (Isik, Sardon and Mecerreyes, 2014; Wendler, Todi and Meister, 2012). In the literature cellulose from various sources have been spun into filaments with and without IL dissolution. Zhu *et al.*, (2016) spun microcrystalline cellulose (MCC) after dissolution in 1-ethyl-3-meth-ylimidazolium diethyl phosphate (EMImDEP). Another study from Zhu *et al.*, (2018) also showed that use of dimethyl sulfoxide (DMSO) as a cosolvent facilitates dissolution. Ma *et al.* (2016) also spun filaments from waste paper dissolved in novel IL 1,5-diazabicyclo [4.3.0] non-5-ene-1-ium acetate ([DBNH]) [OAc]). This chapter investigates the use of PSNF for spinning long filaments after dissolution in ionic liquid. Material and methods for PSNF spinning

5.2.1 Materials and methods for PSNF dissolution and spining

PSNF produced in chapter 5.1 was freeze dried, this prevents the formation of hydrogen bonds with cellulose and water as it will inhibit dissolution in IL (Le, Sescousse and Budtova, 2012).

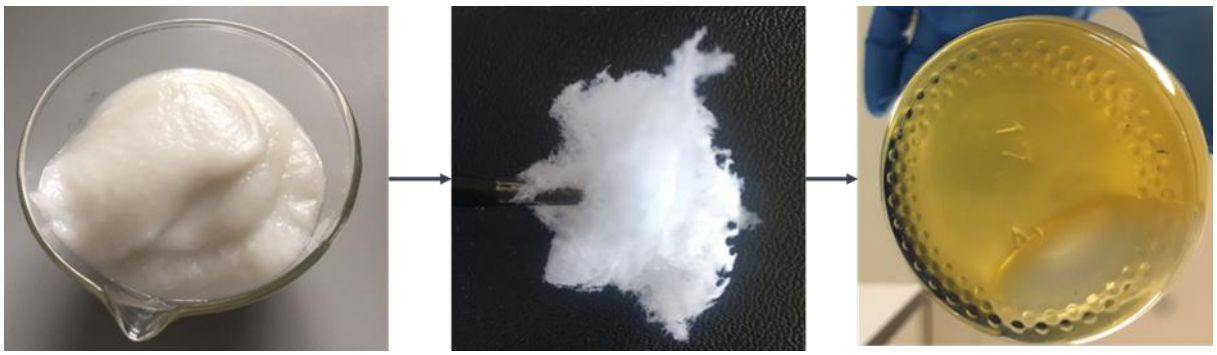


Figure 45: Dissolution steps of PSNF showing PSNF suspension, freeze dried PSNF and dissolved PSNF in EMImDEP ionic liquid.

The freeze- dried PSNF was dissolved with ionic solvent EMImDEP I-ethyl-3-methylimidazolium diethyl phosphate (IoLiTec, Germany) and a co-solvent dimethylsulfoxide (DMSO) from Fisher Scientific, UK. Two samples were prepared 9 wt.% (2.7 g) and 12 wt% (3.7 g) in 30 ml at a ratio of 50:50 EMImDEP:DMSO. The solution was heated at 100 ℃ and stirred at 100 rpm for 8hrs. Dry-jet wet spinning method was used with barrel temperature at 50 ℃. The spinning dope was pushed through 150 μm nozzle and spun at a draw ratio of 2.5 and winding speed of 50 m/min. The filament was soaked for 24 in to remove ionic liquid. The viscosity of the spinning dope was measure before and after spinning with a Discovery HR-1 rheometer (TA instruments, USA). Measurements were made in steady shear and oscillatory shear.

Cross-section and outer surface of 5 samples were observed with JSM-6490LV SEM (JEOL, Japan). EDX was used to acquire the spectra of the fibre. The diameter of the spun PSNF filament were measured with Dia-stron FDAS770 fiber dimensional analyser (Dia-stron, UK) at 5 different locations on the filament. Mechanical strength was measured with Dia-stron LEX820 (Dia-stron, UK) single fibre tester using 20 N load cell. A 2 cm gauge length was used. CrI of single filaments were obtained from powder X-ray diffraction as mentioned in 5.2 and wide-angle x-ray diffraction. WAXD GANESHA 300 XL SAXS (SAXS LAB, Denmark) was used for WAXD. The samples were exposed to Cu Kα radiation with a wavelength of 0.154 nm for 5 hrs.

5.2.2 Results and discussion of PSNF filaments

The physical appearance of the PSNF filament is shown in figure 46.

Figure 46: Physical appearance of PSNF filament.

The steady shear viscosity of the dissolved PSNF spinning dope is shown in figure 47. The spinning dope exhibit a Newtonian region in steady state shear until 10 s^{-1} where shear thinning occurred. The 9 wt.% and 12 wt.% spinning dope reached a viscosity of 39.9 and 248.2 before spinning and 55.9 and 751 Pa.

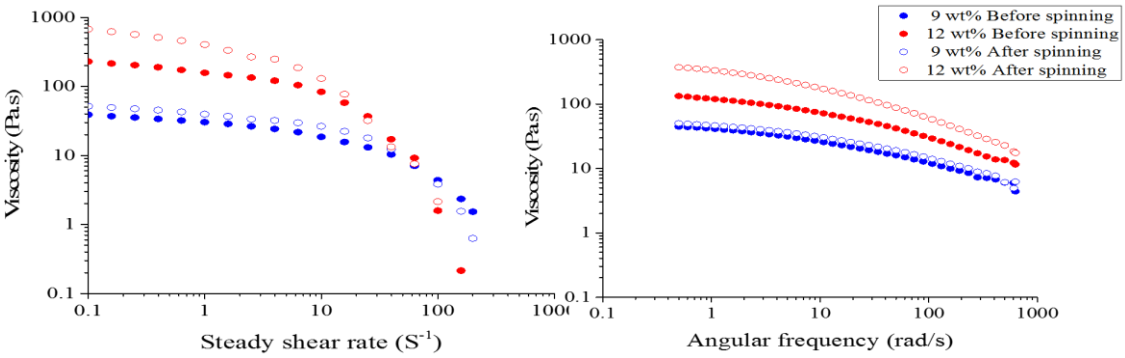


Figure 47: Steady shear and dynamic viscosity for 9 wt% and 12 wt% PSNF spinning dope, before and after spinning.

The dynamic viscosities of the 9 wt% and 12 wt% spinning dopes are 44.6 and 134.1 Pa.s before spinning and, 50.3 and 374.1 after spinning. Viscosity increased after spinning and as the spinning dope concentration increased. This might be due to an increase in concentration and molecular entanglement restricting freedom of movement between individual chains. The SEM of the filaments in figure 48 showed homogenous morphology with longitudinal striations on the outer surface due to filament stretching.

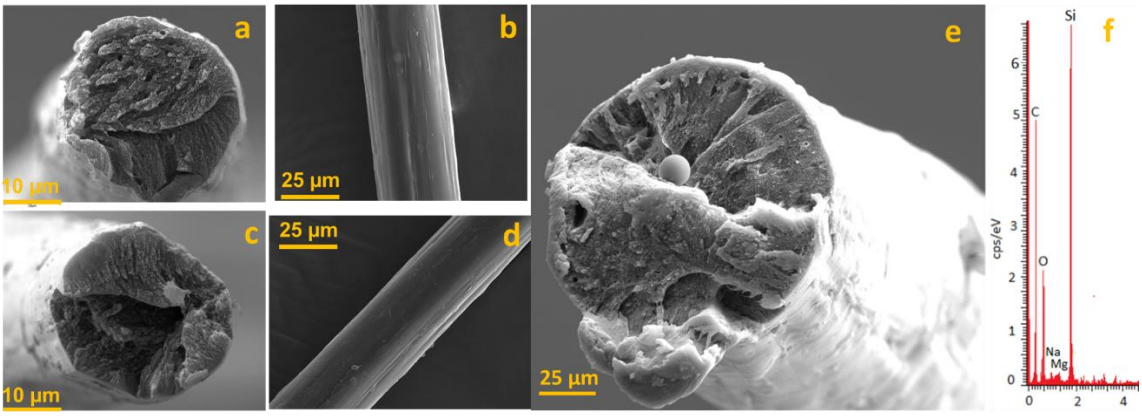


Figure 48: SEM of PSNF filament cross-section and outer surface (a-b: 9 wt.%), (c-d: 12 wt.%), e: broken fibres with spherical particle and f: EDX spectra confirming particle as silica.

The diameter of the PSNF filaments measured from SEM images were 31.3 ± 2.1 and 24.7 ± 1.1 µm for 9 and 12 wt% respectively. Inorganic materials in the PSNF may not fully dissolve in ionic liquid which affects spinnability and properties of the fibre. SEM imaging of filaments after tensile tests showed a spherical particle confirmed as silicon by EDX. The powder X-ray pattern of the PSNF filament in figure 49 was used to calculate crystallinity for 9 wt.% and 12 wt.% resulting in 87.5% and 85.4% using Segal's method and 85.4 wt.% and 44 wt.%.

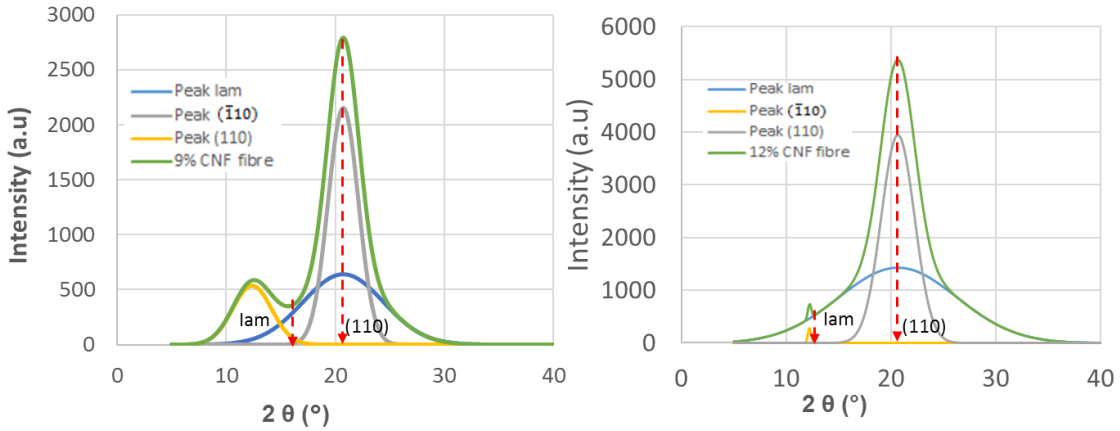


Figure 49: Deconvoluted PWDER X-ray pattern of 9 wt.% and 12 wt.% filament.

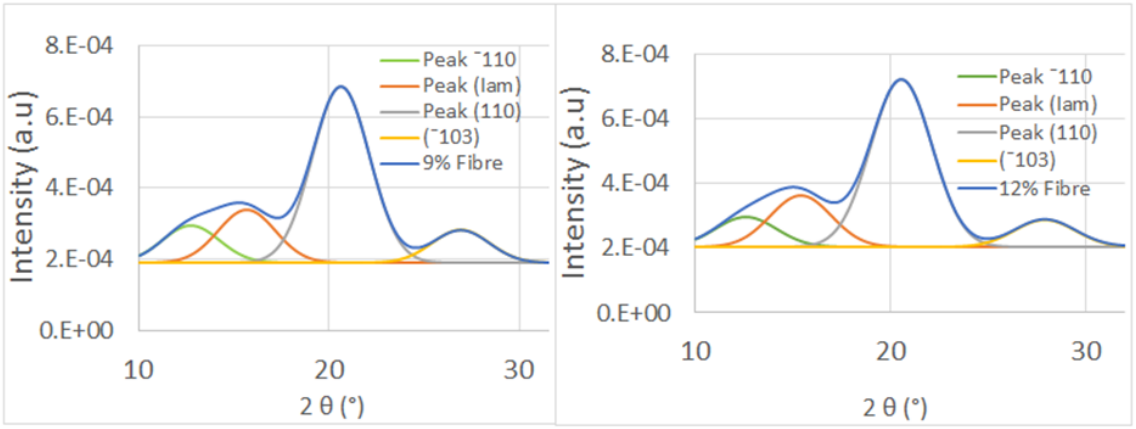


Figure 50: Deconvoluted WAXD pattern of 9 wt.% and 12 wt.% filament.

The crystallinity index calculated from the WAXD pattern is 53.8% for both filaments using Segal's method whilst Park's method is 80% and 79%. There is a reduction in CrI as cellulose concentration increases similar to (Zhu *et al.,* 2018). The FWHM was also calculated from the WAXD azimuthal scanning data shown in figure 51 (left). FWHM

resulted in 29.2° and 27.3° for 9 and 12 wt% filament. A lower FWHM indicated increase in fibre alignment as concentration increased. Increased fibre alignment results in an increase mechanical property as shown in figure 51 (right)

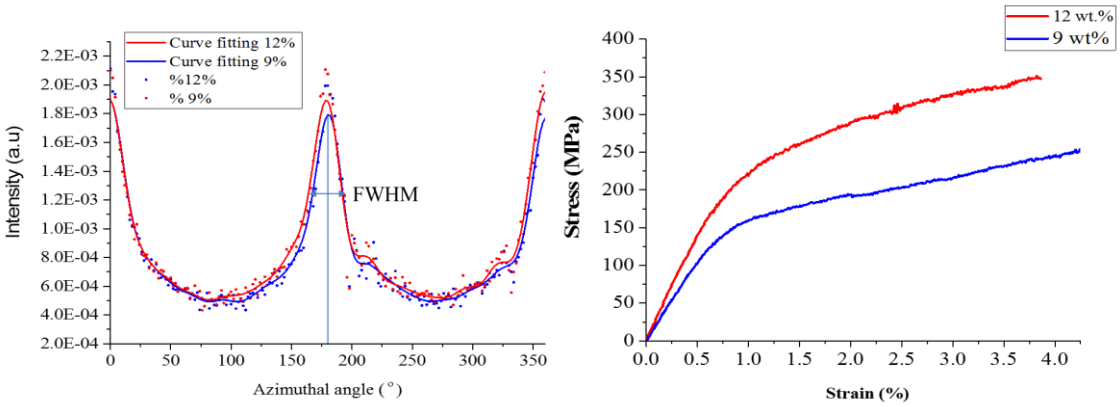


Figure 51: WAXD pattern (left) and stress-strain curve (right) of PSNF filament.

The maximum tensile strength achieved for 9 and 12 wt.% filaments is 347 and 280 MPa respectively which is shown in the stress-strain curve in figure 51 (right). The average results of each PSNF filament is given in table 16.

Table 16: Average mechanical properties of PSNF 9 and 12 wt.% filaments.

	Diameter	Strength	Modulus	Strain	Segal CrI	Park CrI	FWHM
	(µm)	(MPa)	(GPa)	(%)	(%)	(%)	(°)
9 wt.%	31.3	223	19.9	4.0	87.5	62.5	29.2
SD	2.3	3.5	1.3	1.4	-	-	-
12 wt.%	24.7	282	25.9	2.5	85.4	44	27.2
	1.1	39.6	1.75	1.08	-	-	-

The increase in concentration improved the strength and modulus of the filament however this limited the strain. Spinning was conducted 3 times to ensure repeatability of the experiment. Attempts to spin even higher concentration at 15 wt.% was unsuccessful due to increase in impurities which blocked the nozzle during spinning. However Zhu *et al.,* (2018) also dissolved microcrystalline cellulose (MCC) in 7:3 EMIMDEPP: DMSO at 23.6 wt.% which resulted in tensile strength up to 555.9 MPa and a high elastic modulus of 41 GPa as shown in figure 52. There is still opportunity to

achieve higher mechanical strength for PSNF filament if pre-treatment is used to reduce inorganic minerals present in the TPK sludge or use of ionic liquids than can dissolve inorganic minerals. Ma *et al.* (2016) was able to achieve filaments with high mechanical properties from waste paper, by applying several pre-treatment methods and dissolving the waste paper in a novel ionic liquid IL 1,5-diazabicyclo [4.3.0] non-5-ene-1-ium acetate ([DBNH]) [OAc]).

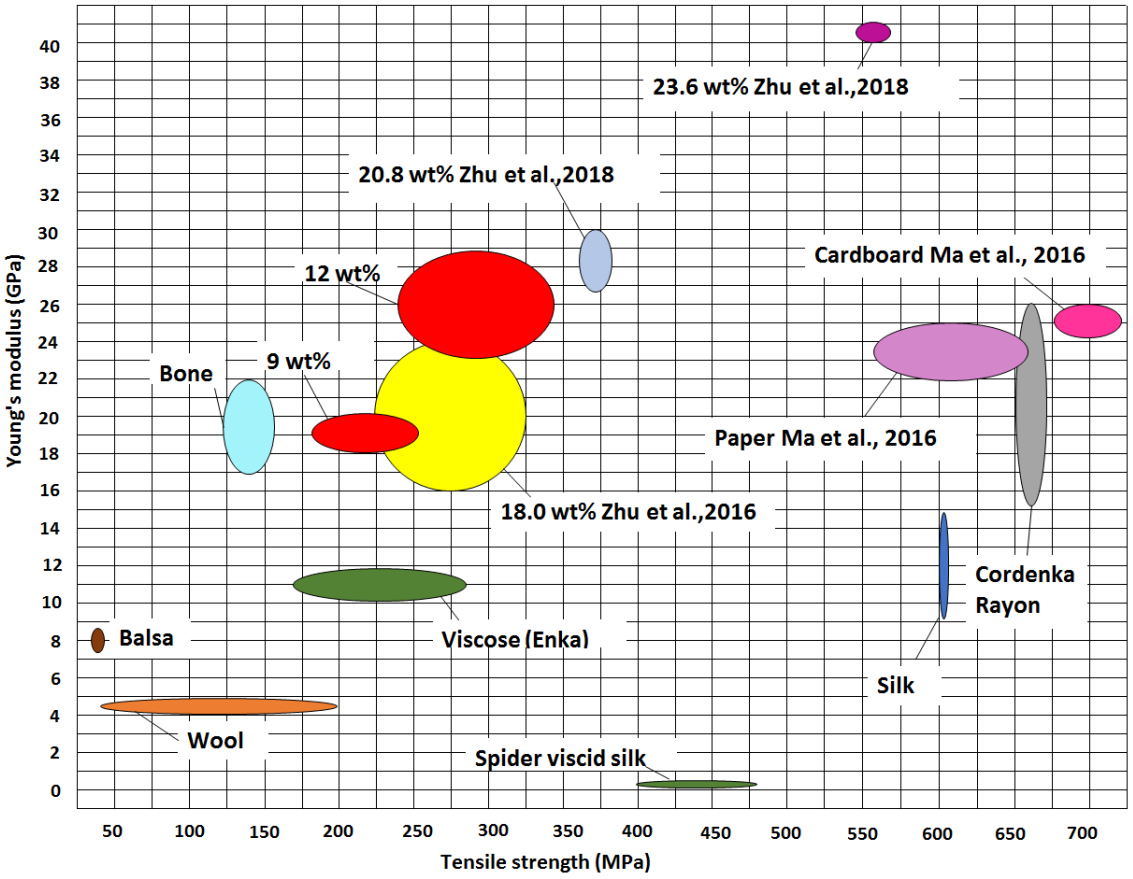


Figure 52: Ashby plot comparing modulus and tensile strength of PSNF filaments in red with commercial fibres.

The modulus of the 9 wt.% and 12 wt.% is higher than commercial viscose Enka (10-12 GPa) whilst the tensile strength of the 12 wt.% filament is competitive. Hence, paper mill sludge with low ash content can be considered a cheap source for producing regenerated cellulose fibres. Moreover, the optimum ratio of EMIMDEP and DMSO for dissolving the PSNF was 50:50 which helps to reduce the cost of materials as ionic liquid is expensive whilst DMSO is cheaper and readily available.

5.3 Foams produced from PSNF and PVA

This section is based on research conducted in portfolio submission 5.

Foams are cellular materials that are relevant in applications requiring light weighting, cushioning, energy absorption and insulation. They can be made from ceramics, metal and polymers, traditionally polymer foams are derived petroleum-based materials like expanded polystyrene (EPS), polyurethane (PU) and expanded polypropylene (EPP). These materials provide beneficial uses in packaging, disposable food containers, insulation, buoyancy, energy absorbance, cushioning, and as filtration media. However, at the end of life they are challenging to recycle and can disintegrate into microplastics detrimental to marine life. This occurs especially for foams used in single-use packaging. There are alternative petroleum bio-polymers Poly Vinyl alcohol (PVA), Poly-lactic Acid (PLA), Polyhydroxyalkanoates (PHAs) however they are limited by their mechanical properties (Duis and Coors, 2016; Reddy *et al.*, 2013). In the literature, reinforcement have been achieved with fillers such as silica, carbon nanotubes, graphene, nanocellulose (Antunes and Velasco, 2014; Bordes, Pollet and Avérous, 2009; Peng et al., 2016; Raquez *et al.*, 2013).

Therefore, the PSNF prepared in this study will be used as a reinforcement filler to enhance the mechanical properties in PVA porous foams. The conventional method for producing expanded polymer foams requires the use of chemical blowing agents Hydrofluorocarbons (HFCs). HFCs are being phased out because of their ozone depletion potential, global warming potential (Cady-pereira and Bailey, 2015; United Nations, 1987) and high flammability unsuitable for building specifications. Additionally, efforts to achieve flame retardancy have led to the use of Hexabromocyclododecanes (HBCDs) which have been detected in aquatic habitats, fishes and water sediments (Rani et al., 2014). In this research, the foams will be prepared by ice-templating method which does not require any blowing agent. Moreover, ice-templating is suitable for cellulose as it is typically in an aqueous suspension, it has no melting point and it's susceptible to agglomeration.

Ice-templating is used to derive porous materials by the dispersion of a solid in a solvent. The solution is frozen and sublimated; the formation of ice-crystal during freezing leaves a porous structure after sublimation. Hence, the term 'ice-templating'

although terminologies such as freeze-casting, phase separation, uni-direction freezing have been used to describe the method. It has been researched mainly in ceramics industry (Deville, 2010; Launey *et al.*, 2009; Munch *et al.*, 2009) for preparing porous foams. However, it is now used being in polymer foams (Dash, Li and Ragauskas, 2012; Gentile *et al.*, 2018; Han *et al.*, 2017; Liu, Medina and Berglund, 2017; Song, Tanpichai and Oksman, 2016). There are different techniques applied in ice-templating that can be used to manipulate the pore formation and microstructure such as cooling rate, freezing direction, cross-linking, particle-size, viscosity and they type of solvent used. Primarily water is the most common solvent use. The common microstructure found in ice-templated materials are lamellar, dendritic, honeycomb, equiaxed and cellular as shown in figure 53 (Scotti and Dunand, 2018). The pore structure also depends on the freezing method i.e. isotropic or anisotropic. Isotropic method shown in figure 54 (top) requires a solution to be placed in an environment < -10 ℃. Nucleation occur and forms crystals in the solvent which solidify and sublimate. Cellular microstructure is common for isotropic freezing method because the pore formation is random.

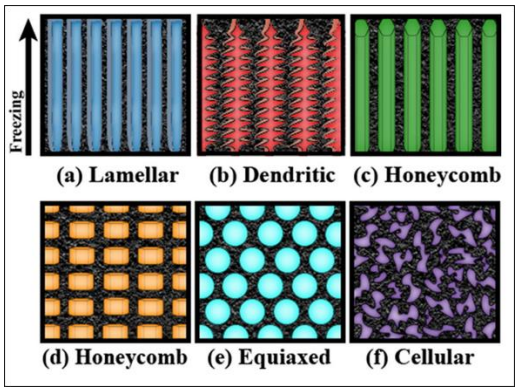


Figure 53: Pore structures found in ice templated materials. Scotti and Dunand (2018).

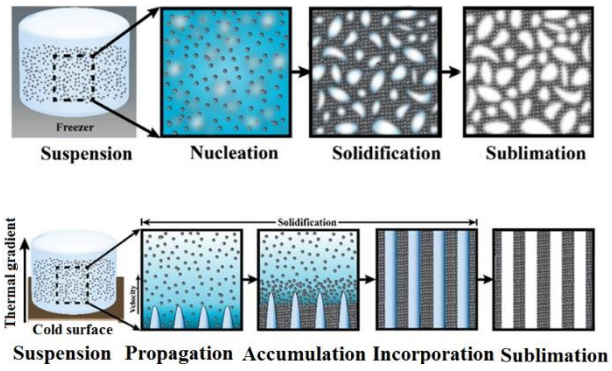


Figure 54: Illustration of isotropic (top) and anisotropic (bottom) ice-templating method Scotto and Dunand.

In the anisotropic method shown in figure 55 (bottom), the solution is placed on a cold surface and nucleation occurs with ice-crystals propagating in the direction of the temperature gradient. Some particles are pushed away which forms a region of accumulated particles. The suspension eventually solidifies leaving a lamellar structure of aligned pores after sublimation. This method is also referred to as uni-directional freezing. Both isotropic and anisotropic freezing method was used to prepare foams with 50:50 PSNF:PVA suspension.

5.3.1 Materials and methods for PSNF/PVA foams

PVA MW 89,000-98,000 g/mol and Sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) also referred to as Borax, where purchased from Sigma Aldrich. 200 ml of 2 wt. % PSNF prepared in chapter 5.1 was used and distilled water was used as a solvent. A 200 ml 2 wt% PVA solution in water was prepared. A 0.5 wt% concentration of borax was prepared by dilution in water. The PVA and PSNF was mixed together under magnetic stirring of 800 rpm and the solution was dosed with 20 ml of the borax to obtain a master batch solution which was stirred vigorously for 12 hrs. Borax was used as a cross-linking agent which improved the miscibility of the PVA and PSNF. The solutions were ice-templated using isotropic method in a freezer at -20 ℃ (Foam I) and -80 ℃ (Foam II). Anisotropic method with liquid nitrogen was used to prepare (Foam III) as shown below in figure 55. The anisotropic method employs a liquid nitrogen bath with a copper rod acting as a cold finger to create a temperature gradient. A PTFE tube is fitted on the shoulder of the copper rod and the PSNF/PVA suspension is poured inside. The thermocouple is used to measure the cooling rate. The sample was removed after it completely froze to the top. 10 samples were made for each method and all frozen samples were made of 10 ml PSNF/PVA solution and freeze dried at -52 ℃ and 0.1 Pa using an ALPHA 1-2 LD plus freeze dryer (Martin Christ, Germany).

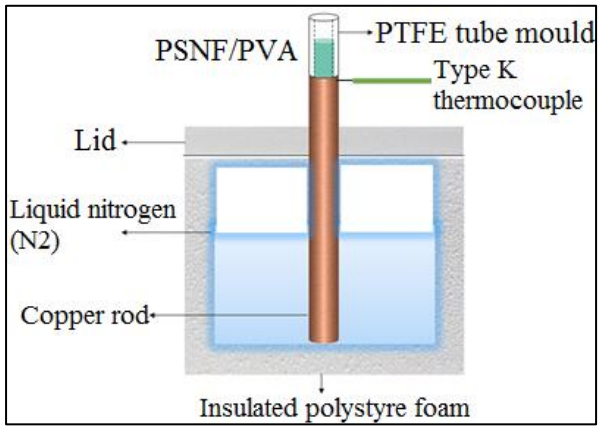


Figure 55: Ice-templating equipment set up for anisotropic ice-templating.

Figure 56: Image of physical foam sample

The outer surface of the foam samples appeared the same as shown in figure 56. The apparent density was calculated from dividing the foam mass by volume. Instron

5500R universal testing machine was used for compression test at 100 N load cell at 1mm/min. The test was conducted in a conditioned room at 23 ℃ and RH 51%. The vertical and horizontal cross-sections of the foams were observed with TESCAN Lyra 3 SEM (TESCAN, Czech Republic).

5.3.2 Results and discussion on PSNF/PVA foams

The foams I, II and III weighted an average of 0.22 ±0.01, 0.23±0.02, 0.24± 0.03 with an apparent density of 26.2 ±0.9, 26.6 ±0.4 and 27.8 ±4. The foam pore structure is shown in figure 57 shows at different magnifications Foam I showed no orientation or hierarchical structure. At 5000x Foam I eventually showed a homogenous cellular structure from entanglement of the nano-fibres and PVA.

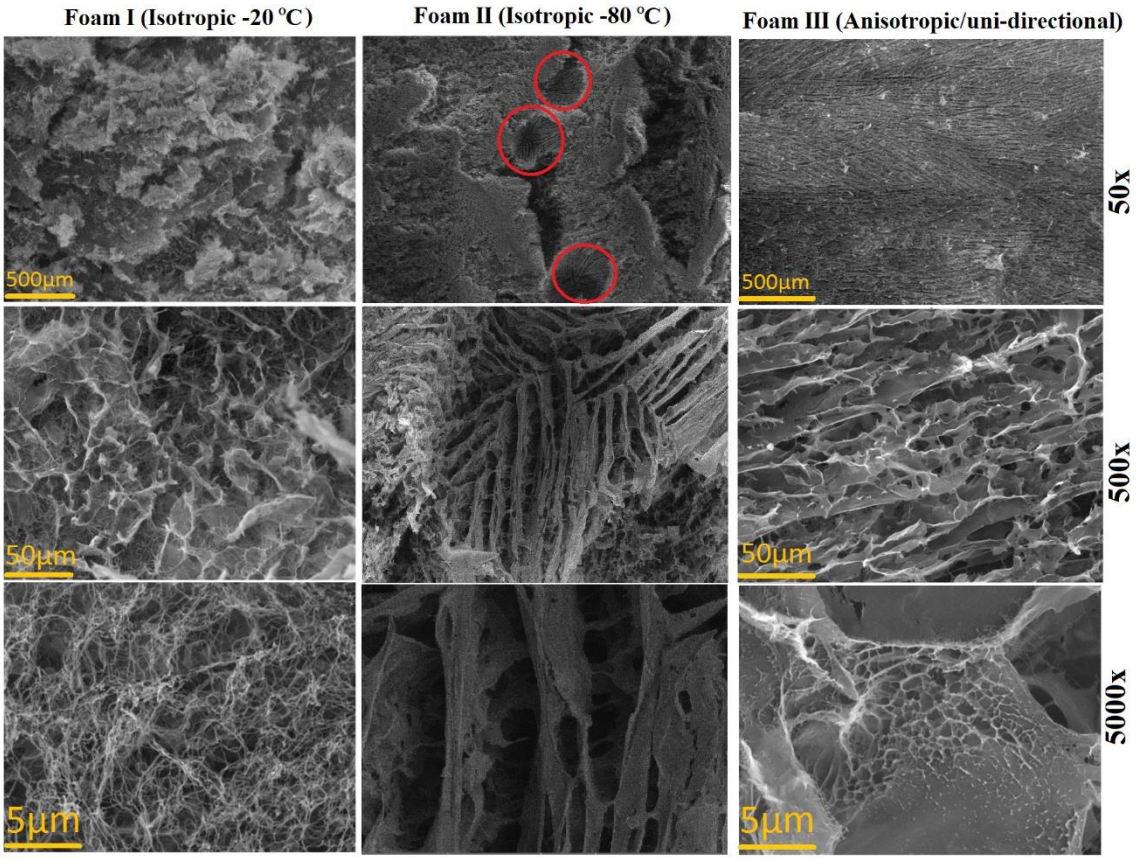


Figure 57: SEM of the PSNF/PVA foam cross-section at 50, 500 and 5000 magnification.

Foam II showed very small regions with lamellar structures (circled in red). This lamellar structure is prominent in Foam III were unidirectional ice-templating method was used, a linear pattern can be observed at 50x magnification. At higher 500x magnification the

cell walls have dendrites connecting them which act as reinforcement in the cell wall. The failure mechanism of the foams shown in figure 58.

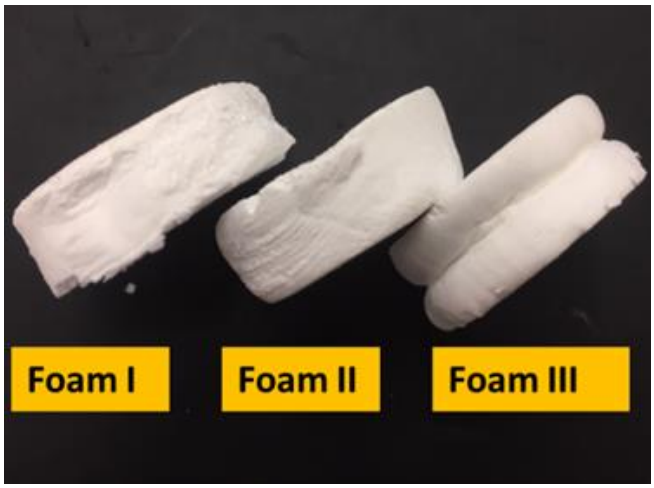


Figure 58: Failure mechanisms observed in PSNF/PVA foams.

The stress-strain curve of a foam under compression has 3 regions; linear elastic region where the cell edges bend, plateau whereby the cell walls collapse and elastic buckling, yielding or crushing may occur and lastly the densification region which is noted by a steep increase in stress (Gibson, 2005).

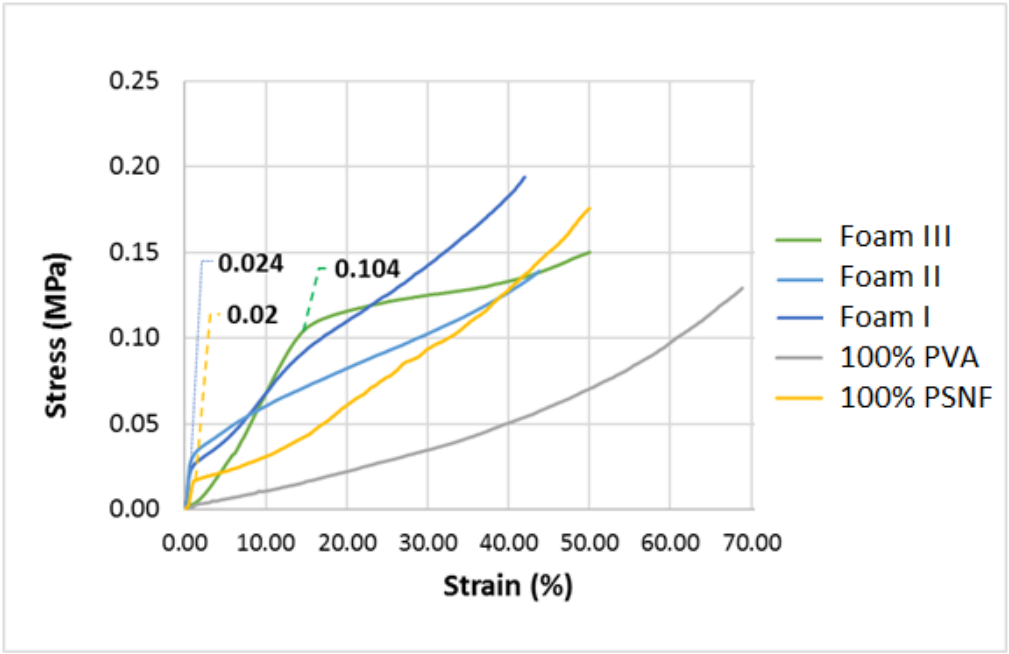


Figure 59: Stress-strain curve of PSNF and PVA foams.

Foam III showed elastic buckling due to orderly cell walls. The linear elastic region was present in Foam I, II and III. However, foam III which was made with the uni-directional method showed significant increase in the linear region up to 0.104 MPa. When comparing stress-strain curve of the PSNF/PVA foams with the 100% PVA and 100% PSNF, it is evident that the reinforcement with the PSNF has greatly improved the strength of the foam.

The average mechanical properties of the foam are shown in table 17. Isotropic foams, I and II showed a higher modulus compared to Foam III made by the uni-directional freezing method. This is because their cell walls were randomly oriented whereas Foam III was loaded in the direction of the cell wall growth during compression. This caused the material to buckle as the cell walls bend.

Table 17: Mechanical properties of PSNF/PVA foams

	Maximum strength	Strength @ 10% strain	Strength @ 20% strain	Modulus	Energy absorption
	(kPa)	(kPa)	(kPa)	(MPa)	(kJ/m3)
Foam I	24 ± 10	44 ±15	80 ± 20	1.2 ± 0.3	3.4 ± 0.3
Foam II	24 ± 5	42 ± 8	70 ± 7	1.2 ± 0.6	2.5 ± 0.4
Foam III	104 ± 7	82 ± 7	100 ± 3	0.93 ± 0.1	3.2 ± 0.2

Nonetheless, at 20 % strain Foam III reached an average compressive strength of 100 ± 3 kPa allowing it to be classified for high duty applications in accordance with BS 3837-1:2004. An Ashby plot in figure 60 used to compare the foams with commercial and existing PVA and CNF foams in literature. The foams made in this study are competitive with the commercial foams Jablite EPS 100 (Jablite, 2019) used as floor insulation and Ethafoam (Dow, 2017) used in packaging and cushioning. The effect of the anisotropic ice-templating and crosslinking of PVA and CNF is evident when compared with literature. Foams prepared with only 2 wt.% CNF anisotropic foams from Lee and Deng (2011) reached lower compressive strength of 30.7 kPa. CNF and PVA isotropic foams from Liu et al. (2014) were not crosslinked leading them to have lower compressive strength than the PSNF/PVA foams here. Meanwhile, anisotropic PVA/CNF foams from Han et al. (2017) showed a compressive strength of 150 kPa at 20% strain. However, when divided by the density the specific compressive strength of the foam from

this work is higher 3.5 kPa.m^3/kg. The research shows a possible environmentally friendly alternative to fossil fuel-based foams for protective packaging.

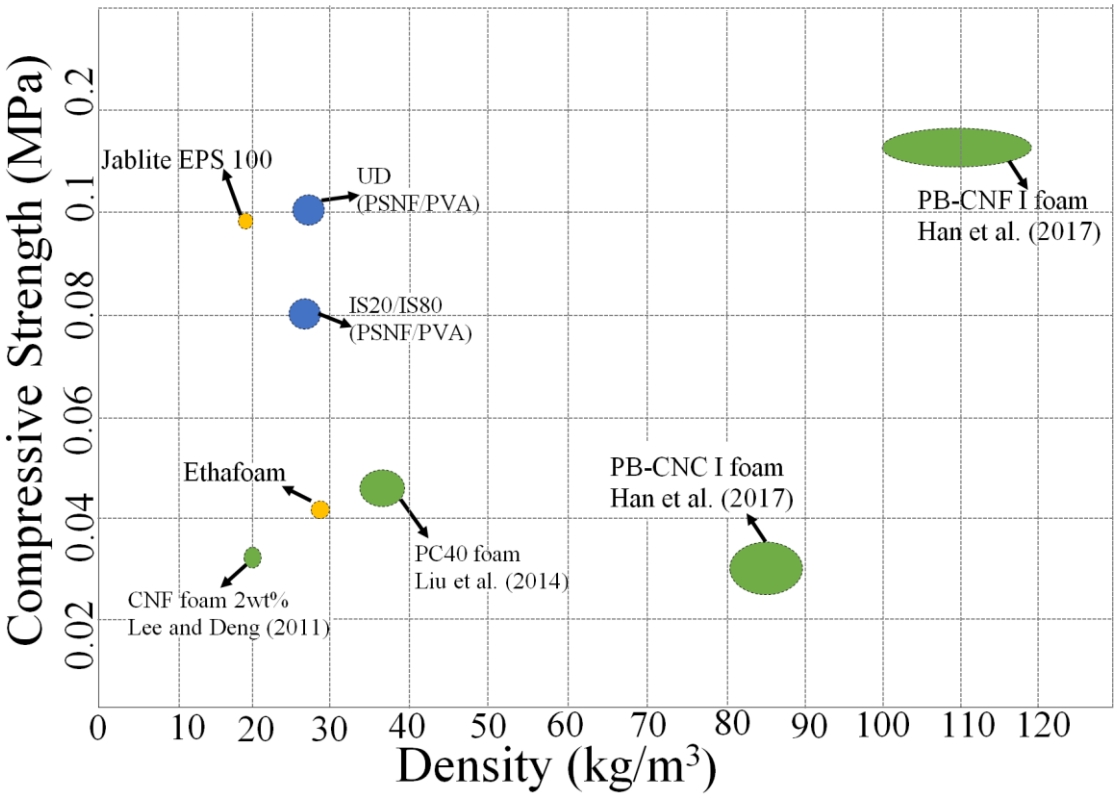


Figure 60: Ashby plot of showing density vs compressive strength of commercial foams (yellow), PSNF/PVA (this work, blue), literature foams (green).

The PSNF/PVA foams are prone to water absorption. This could be an advantage for single use packaging during disposal and decomposition. Both PSNF and PVA are biodegradable. To improve moisture absorption, increasing in borax content and surface coating could be applied.

5.4 Composite panels produced from PMS

This section is based on research conducted in portfolio submission 6.

The life cycle of PMS can be extended if used in the manufacturing composite panels for building, furniture and construction. These applications typically have long product life and would reduce the embodied energy or carbon footprint of the paper mill process if the by-product can be integrated into building materials. Composites panels used in buildings, furniture and construction range across medium density fibre (MDF) boards, particle boards, mineral boards, hardboard and plasterboard. In this section PMS from mills UPH, JCR, LCR and mixture of mills (PDE, CTD and BRW) were used to produce composite panels. Typically, 10-12% urea-formaldehyde (UF) adhesive is used in wood panel production.

Adhesives plays a critical role in panel manufacturing, it affects structural properties, moisture absorption/resistance and processing time. UF adhesive provide advantages in panel manufacturing such as water solubility, colourlessness, tackiness, low flammability and fast curing. However, composite panels containing UF resins emit formaldehyde which affect indoor air quality and health (Pilidis *et al.*, 2009). Indoor air-quality is becoming increasingly important. Hence, manufacturers are also using formaldehyde free resins such as MDI (4,4-diphenylmethane diisocyanate) which also provide better moisture tolerance compared to UF and doesn't emit volatile organic compounds (VOCs) when cured. Nonetheless, in gaseous and droplet form, MDI has a very high toxicity to workers when used in manufacturing composite panels (Vangronsveld, 2012). Because MDI is not a formaldehyde derivative it is marketed as a formaldehyde free resin although it can still release small amounts of formaldehyde during decomposition. MDI is produced from polymeric methylene diphenyl di-isocyanate (pMDI) which is a crosslinker that has been used in the particle board industry. The aldehyde in pMDI cannot be released hence it is formaldehyde free (Solt *et al.*, 2019). These synthetic adhesives are mainly polyurethane derivatives from fossil fuels. Hence, there is still a significant importance in bio-based adhesives derived from natural sources. In the 20th century adhesives were made from protein sources such as gluten, casein, wheat gluten, blood, oil seeds (Frihart, 2015). Some bio-based adhesives have even been prepared from industrial by-products such as waste vegetable oil from restaurants

(Fernandes *et al.,* 2017) and cotton seed meal, a by-product of cotton oil extraction (Liu *et al.,* 2018). Although PMS panels may not achieve mechanical properties required for load bearing applications PMS produced with bio-adhesive may offer a competitive indoor product.

Distillers dry grain and solubles (DDGs) which is a by-product of ethanol distillery was developed into a bio adhesive by Zhao (2015) by CAMBOND LTD UK . DDGs is mainly used as animal feed due to its high protein content. The product DIGLUE was used to bind wood composite panels in addition of pMDI 1-3%. The pMDI acts as a crosslinking agent by forming a water-resistant polymeric network and creating strong internal bonds (Zhao, 2017). The panels with DIGLUE had lower thickness swelling and some also resulted in higher MOE and MOR compared to UF panels.

5.4.1 Materials and methods for PMS board production

PMS from UPH, JCR, LCR and a mix of PDE, BRW and CTD were used to prepare 4 separate composite panels with a target density of 1200 kg/m^3. Dried PMS was agglomerated thus in an electric cereal grinder (Goldenwall, China) was used to disintegrate the fibres at 2800 rpm and 20 seconds. Diglue was provided by CAMBOND, UK and pMDI Suprasec 5025 from Huntsman, UK was used as crosslinker. The adhesive was measured based on mass weight of the PMS, 18 wt.% DIGLUE, 6 wt.% resin and 15 wt% water was diluted and stirred at 800 rpm for 1 hour. The mixture was poured in small doses into the dried PMS whilst mixing with an electric hand mixer. The mixture was then poured into an aluminium mould 210 x 210 40 mm with a piston of 209 x 209 x 50 mm as shown below in figure 61. A release agent, Chemlease^{TM} was applied on the mould (Chemtrend, UK) to prevent adhesion of the PMS mixture to the mould and wearing. Thermocouples were used to measure temperature in the mould. The panels were pressed at 4 MPa, 180 ℃ for 10 mins. Panels were cut to follow BS EN 326-1:1994 *Wood based panels sampling, cutting and inspection* (BSi, 1994). Three panels were tested from each mill. Modulus of rupture (MOR) and elasticity (MOE) was measured following BS EN 310-1993 *Wood-based panels determination of modulus of elasticity in bending and of bending strength* (BSi, 1993a).

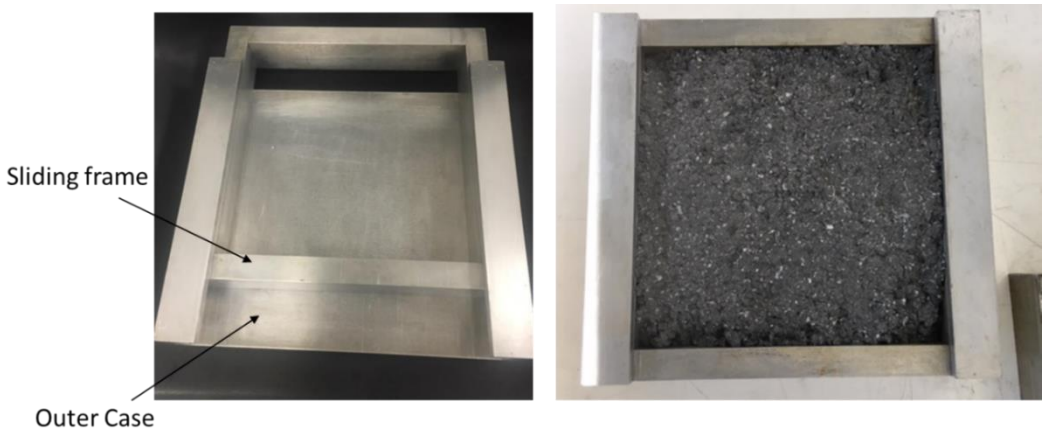


Figure 61: Aluminium mould with sliding frame (left) and mould containing PMS and resin (right).

Panels were tested on an Instron 5500r with a 5 kN load cell using and three-point bend test fixture. The fixture comprised of two 15 ± 0.5 mm roller-bearing and 15 ± 0.5 mm cylindrical loading head. The test standard uses 30 ± 0.5 mm loading head however this was not available. Internal bonding (IB) determines the tensile strength of the panel by adhering a 50 x 50 mm specimen to two metal blocks which is loaded in tension perpendicular to the plane of the board based on BS EN 319:1993 (BSi, 1993b). Thickness swelling (TS) was measured by following by immersing 50 mm x 50 mm specimen samples in still water maintain a pH 7 ± 1 at temperature of 20 ± 1 ℃ for 24 hrs (BSi, 1993c). Thickness swelling is reported as the percentage of increase in thickness of the sample.

5.4.2 Result and discussion of PMS fibre and mineral boards

The panels produced are shown in figure 62. All panels maintained dimensional stability although LCR had small particles shedding from the surface. This is because LCR high ash content with minerals and was finely grounded into particle size of ≤ 200 mesh when supplied by the company. The dark spots on the panels was caused by moisture concentrated areas and droplets of bio-resin which did not mix fully due to high viscosity. Similarly this was found for wood panels made with cottonseed meal bio-adhesive (Liu *et al.*, 2018).

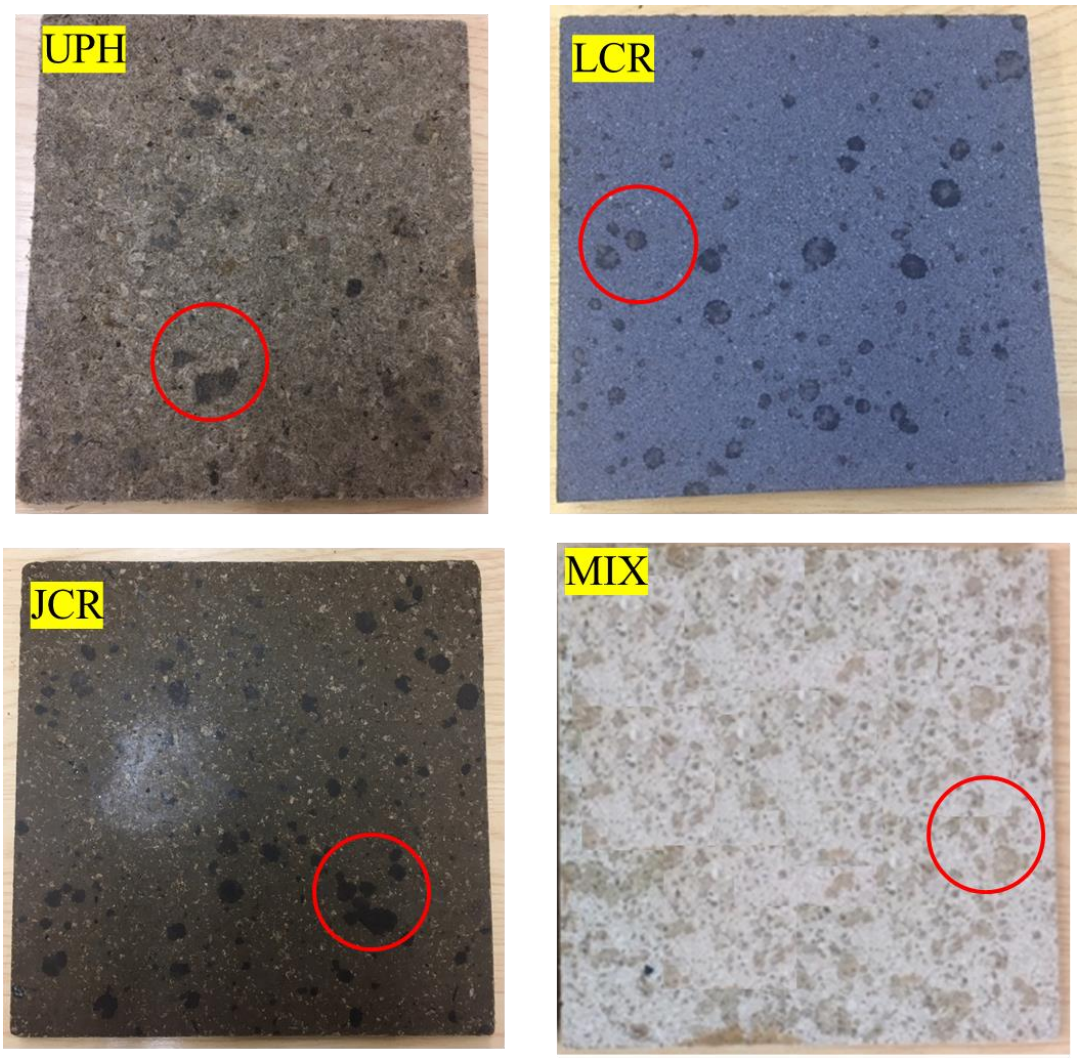


Figure 62: Appearance of PMS composite panels.

The structural properties of the panels are given in figure 63 and compared with technical standards for MDF panels/fibreboard specification. The UPH panel had the highest

mechanical properties as the material contained mainly organic fibres which formed stronger bonds with the bio-resin. The fine PE fibres in the UPH sludge also created interfacial adhesion leading to stronger internal bonds This is similar to with paper mill sludge/wood fibres composites containing polyethylene (Soucy *et al.,* 2014; Turku *et al.*, 2017). UPH sludge also contained lignin (1.7%) which played a role in binding the cellulose fibres.

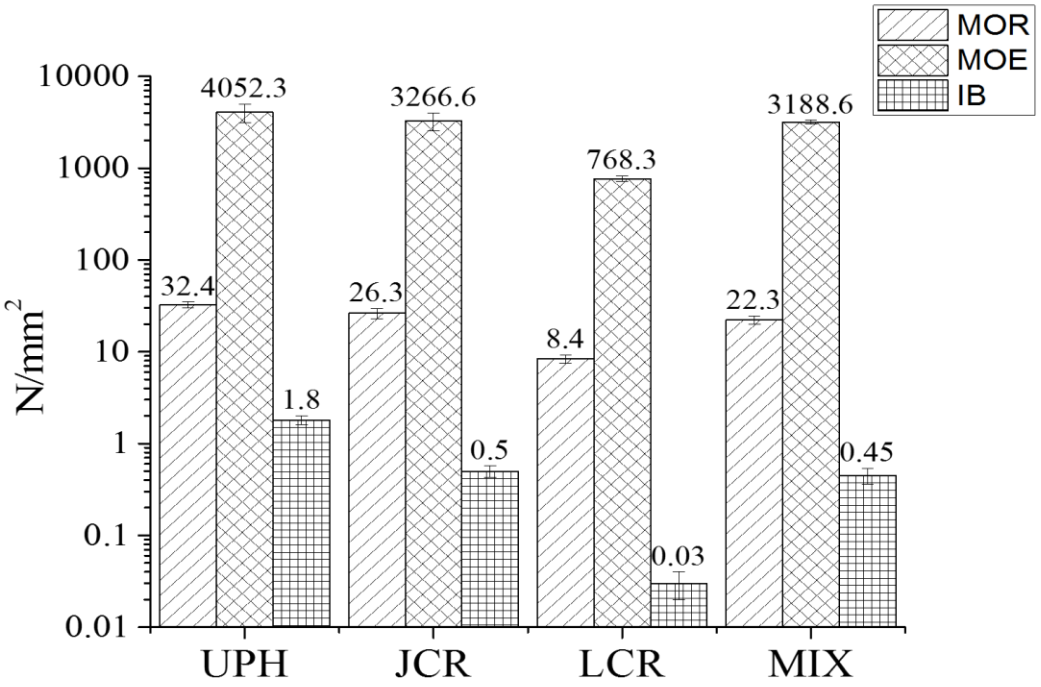


Figure 63: Bar chart showing mechanical properties of PMS panels for MOR, MOE and IB.

Although sludge from JCR was considered a low ash sludge, the mechanical properties were not up to the UPH sludge. This is because JCR contained inorganic mineral that inhibits the bio-resin binding. Similarly, the MIX sludge was affected by poor internal bonding leading to lower properties compared to UPH. The LCR panel had a brittle failure at 8.4 ± 0.9 N/mm2. LCR sludge contained higher mineral content (70 ± 5 %) and fine particle size 200 mesh which resulted in low internal bonding 0.03 ± 0.01. Thickness swelling of the panels were 17.5 ±2.8, 14.4 ±1.3, 3.4 ±0.3 and 7.6 ±0.5 % for UPH, JCR, LCR and MIX respectively. Thickness swelling is caused by porous fibres, hydroxyl group interaction with water and interfacial gaps in the PMS-resin

matrix. The properties of the sludge is listed in table 18 showing comparisons with technical standards BS EN 62205:2009.

Table 18: The properties of the panels are compared with technical standard in table 18

	MOR	**MOE**	**IB**	**TS**
	(N/mm^2)	**(N/mm^2)**	**(N/mm^2)**	**(%)**
UPH	32.4 ± 2.5	4052 ± 908	1.8 ± 0.2	17.5 ± 2.8
JCR	23.5 ± 3.3	3266 ±713	0.5 ± 0.07	14.4 ± 1.3
LCR	8.4 ± 0.9	768 ± 52	0.03 ± 0.01	3.4 ± 0.3
MIX	19.5 ± 2.4	3189 ± 147	0.35 ± 0.09	7.6 ± 0.5
BS EN 622-5:2009	≥	≥	≥	≤
-Non-load bearing dry	23	2700	0.65	17
-Non-Load bearing humid	27	2700	0.80	12
-Load bearing dry	29	3000	0.70	17
-Load bearing humid	34	3000	0.80	12
-Underlay roof/wall	14	1600	0.30	10

The UPH panel reached the required mechanical properties for MDF board, though it was limited by thickness swelling. Thus, it is suitable for applications in dry conditions (load-bearing and non-load-bearing). Mechanical properties of JCR and MIX had low thickness swelling but they were limited by internal bonding which made them only suitable for underlay roof/wall board applications. Maleic coupling agents have been used to improve mechanical properties and reduce water absorption (Keener, Stuart and Brown, 2004; Valente *et al.,* 2017). The LCR panel had significantly low thickness swelling (3.4 ±0.3) due to high inorganic mineral content although it did not meet the strength specification. LCR panel was affected by brittle failure due to poor internal bonding; the DIGLUE bio-adhesive is not a suitable binder for the deinking sludge. Nonetheless, the LCR panel presents an opportunity to produce flooring material if a cementitious binder is used. Producing PMS composite panels with extrusion method would also lead to improved mechanical properties opening avenues for more applications.

5.5 Summary

This chapter 'Develop' focused on the development of materials from PMS and the assessment of their technical feasibility. The materials developed from PMS are shown in figure 64 with a portfolio of applications.

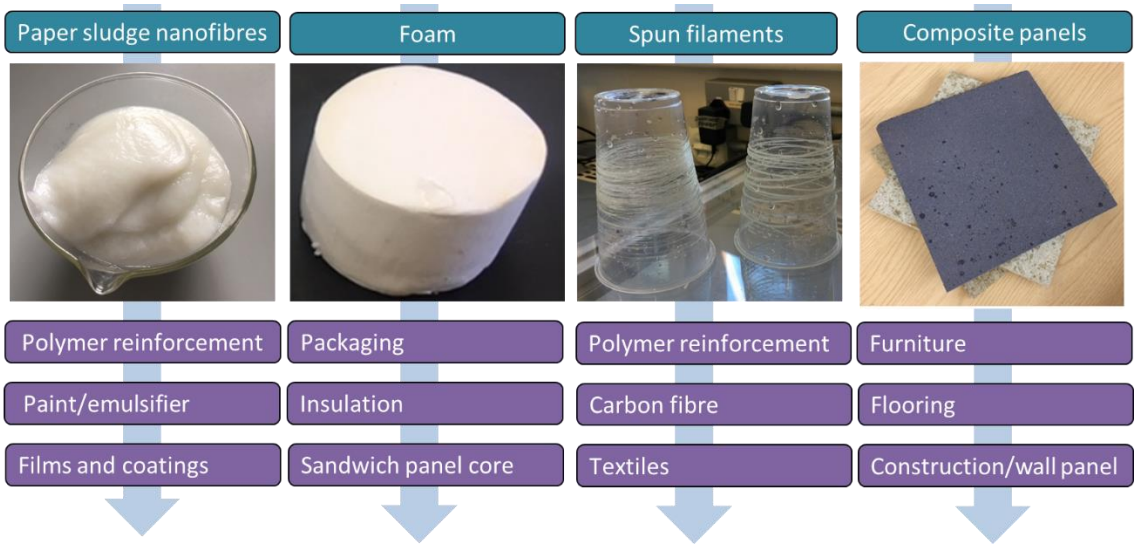


Figure 64: Materials developed from PMS portfolio of applications.

PMS from primary mills using virgin fibres such as TPK was used to produced nanofibres without any chemical pre-treatment. The paper sludge nanofibres had a tensile strength up to ~ 90 MPa and modulus of ~ 10 GPa. The PSNF have a variety of applications such as polymer reinforcement, use in paint, emulsifier, packaging films and coatings. PSNF was used to prepare foams for potential substitution of fossil fuel foams. The foams properties were competitive with commercial polyurethane and polyethene blown foams; thus, they were suitable for packaging, insulation and sandwich core panels.

Finally, the PMS was also used to produce formaldehyde-free composite panels. Some composite panels offered mechanical properties for potential substitution of MDF used in dry conditions. De-inking sludge from LCR was incompatible with the bio-adhesive, although there was a potential to use the panel for flooring applications due to its low water absorption. Spun filaments have properties suitable for polymer reinforcement, preparation of carbon fibre and textiles. These materials will be used to develop a business case in chapter 6.

6 Deliver: Economic and environmental assessment of PMS circular business model.

This chapter is the 'deliver' stage, it addresses the fourth objective; to deliver a circular business case for paper mill sludge based on economic and environmental justification. The materials developed from PMS are proposed as a product portfolio in a circular business model. An economic and environmental assessment of the business model is also conducted. The chapter also provides the company with the next actions/steps to take in adopting the proposed business model.

6.1.1 Paper mill sludge business model

To answer the research question 'How can waste management businesses uncover value from waste/by-product for the circular economy?' The research applied design-thinking methodology which, led to the development of materials from PMS. However, to make these materials into marketable products, a business model is required. The current business model for PMS management is short-sighted as PMS is primarily used for agricultural land spreading. Lewandowski (2016b) argued that existing circular economy business models are not supported by any comprehensive framework and lack transferability. Thus, Lewandoski used Osterwalder's business model canvas (BMC) as a foundation to develop a circular business model canvas. Lewandoski's circular business model canvas has not been rigorously tested. Hence, the commonly applied Osterwalder's business model canvas was used for the PMS case study. A business modelling workshop was conducted on the 6th of February 2019. The participants were;

- Arthur Ready: managing director of Ecoganix.
- Tom Everitt: Head of compliance and technical support, and industrial supervisor of the research.
- Peter Collier: Cranfield university intellectual property and commercialisation manager.
- John Patsavellas: Senior lecturer in manufacturing management, expert in flooring industry and various manufacturing sectors.
- The workshop was facilitated by the author.

The participants were able to provide a wealth of expertise on PMS operations, business insight and innovation knowledge. Ideas were collected on post it notes and discussed with two iterations of the BMC. The current business model of Ecoganix LTD is shown below in figure 65. The value proposition is to divert PMS from landfill by using it as a soil conditioner. The key partners are paper mills who supply the PMS, farmers that use PMS on their land and external contractors.

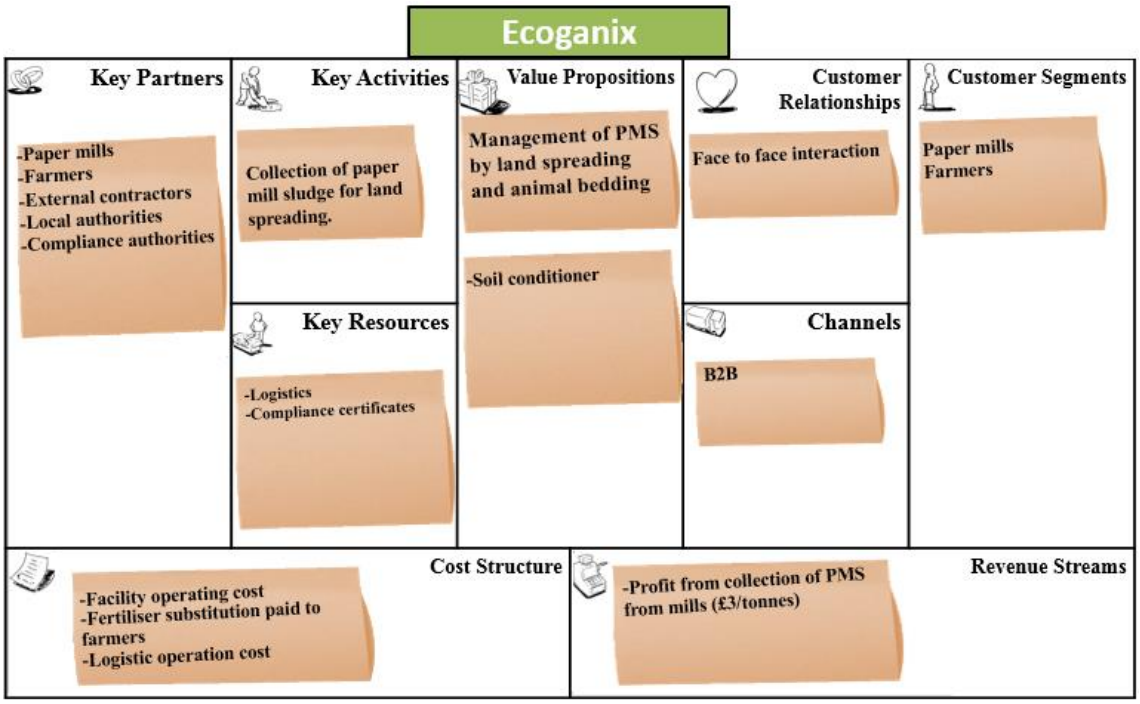


Figure 65: Current business model canvas for Ecoganix.

The customer relationship is a face to face interaction with the farmers. The paper mills play two roles as key partners and customers. The key resources currently used to run the business are the logistic fleets for transporting the PMS and compliance certificates to allow land spreading of PMS. The revenue stream is business to customer sale when dealing with farmers and profit from the collection of the PMS from the mills. This current business model can be compared to a new circular business model in figure 66. The new business proposed will be a spin-off and rebrand from Ecoganix known as Ecoprodux. The value proposition is; alternative products to single use plastics, fossil fuel products and virgin materials. The products offered are dried animal bedding, pelletised cat litter, underlay floor panels, ceiling panels, wall panels, wood-plastic

composite, packaging foams, insulation foams, sandwich foam panels and water-based paint.

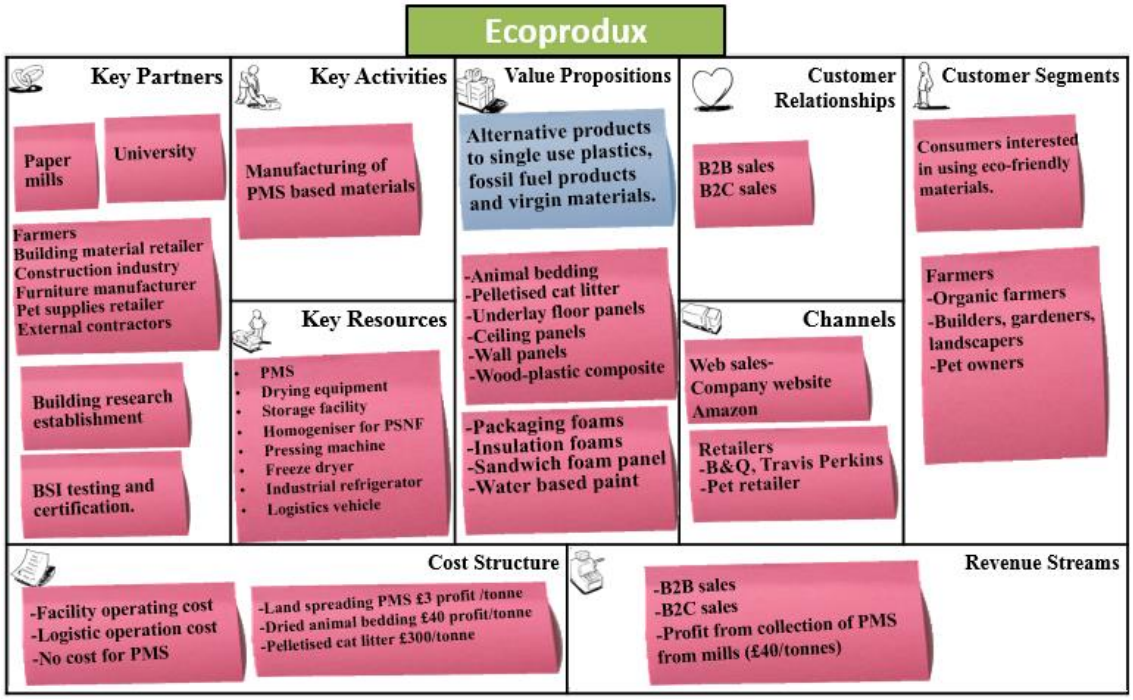


Figure 66: Business model canvas proposed for Ecoprodux.

The customer relationship is B2B and B2C sales through channels such as web sales, company website and amazon. Products will also be sold through retail channels such as B&Q, Travis Perkins and pet retailers. A transition to the new business model will require new resources, forming new partnerships and building new customer relationships. Ecoganix currently has some key resources that can be used to create the new product portfolio. However, the transition to the new business model must be considered with minimum risk.

Ries's (2011) identified that it is challenging for entrepreneurs and start-ups to realise the business model into a viable product. Hence, he created the "lean start-up" model which helps businesses to launch a viable product with minimum resources and risks. The lean canvas was developed as a one-page business plan adopted to Osterwalder's BMC. The lean canvas is a second iteration of the BMC. The lean canvas in figure 67 helps the business to acknowledge potential risks as it focuses on the problems the business aims to solve, the solution, the unique value proposition and unfair advantage.

<table>
<tr>
<td rowspan="2">Problem
• Environmental and economical challenge of paper mill sludge going to landfill.
• Competitive market for managing paper mill sludge as contractors are offering the paper mills lower prices which puts Ecoganix at risk.</td>
<td>Solution
Convert PMS into valuable products that can be used in other industries and can be used to generated business revenue.</td>
<td rowspan="2">Unique Value Proposition
Alternative products to single use plastics, fossil fuel products and virgin materials. All products are from recycled material

Animal bedding
-Pelletised cat litter
-Underlay floor panels
-Ceiling panels
-Wall panels
-Wood-plastic composite
-Packaging foams
-Insulation foams
-Sandwich foam panel
-Paint/emulsifier</td>
<td>Unfair Advantage
-10 years experience on managing PMS
-Established connections with paper mills
-Can collect PMS from mills at £0 cost
-Compliance certificate allowed to handle PMS.</td>
<td rowspan="2">Customer Segments
-Farmers
-Organic farmers
-Pet owners
-Builders
-Gardeners/landscaper
-DIY
-Procurement department in construction</td>
</tr>
<tr>
<td>Key Metrics
• Annual Tons of PMS
• PMS inorganic and organic composition</td>
<td>Channels
E-commerce
-Company website
-Amazon

Retailers
-B&Q
-Retailers of gardening supplies
-Travis Perkins
-Pet retailer</td>
</tr>
<tr>
<td colspan="3">Cost Structure
-Facility operating cost
-Raw material cost
-Logistic operation cost
-No cost for PMS</td>
<td colspan="3">Revenue Streams
-Dried animal bedding £40 profit/tonne
-Pelletised cat litter £300/tonne
-Bulk supply product to external retailers
-Profits from E-commerce sales</td>
</tr>
</table>

Figure 67: Lean Canvas for Ecoprodux.

The lean start-up approach recommends the business to develop a minimum viable product (MVP) that can be sold to customers before scaling up. Taking this into consideration, the pyramid showing the MVP leading up to future products is shown in figure 68.

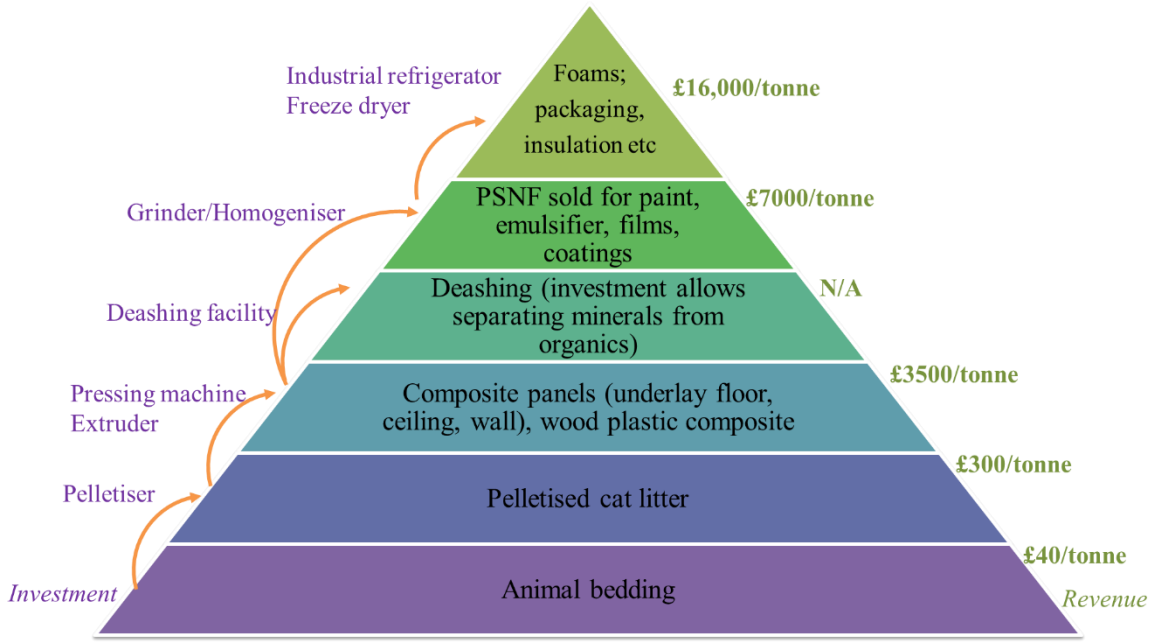


Figure 68: Ecoprodux scale up pyramid showing investment required to increase revenue from products.

The business is expected to start with products that require low investment cost and scale up gradually by investing the profits into resources that will increase the profit margin. Currently the business generates profit of £3/tonne from land spreading of wet PMS on agricultural farms. The next feasible products are dried animal bedding and pelletised cat litter. Prepared animal bedding at 10 % moisture content cost £90–100/tonne (AHDB, 2011). Composite panels from PMS will extend the life cycle of PMS and increase profits for the business to £3000/tonne. Investment is required for a de-ashing facility to separate the inorganic fillers in PMS. This will allow for more PMS to be processed and opportunity to also used waste paper materials instead of sludge. With further investment in technology, the low ash PMS can then be used for producing foams and PSNF. The profit values are explained in chapter 6.2 with the environmental assessment.

6.2 Economic and environmental assessment of PMS business case

The revenue from the different product offerings are estimates based on figures from market research, product pricing websites and discussions with the business clients. The average market price for cat litter/animal absorbent is between £100-£500/tonne (Grand View Research, 2018). The innovation of the product is focused on eco-friendly absorbents, biodegradable materials. The cost of composite panels was estimated base on £3/panel as shown in table 19 below.

Costs	**(£/ton)**
Paper mill sludge	0
Cambond bioresin	200
Manufacturing cost	500
PMDI (crosslinking)	1000
Selling price £2/panel of 380g	5263
Revenue	**3,563**

The revenue from composite panels is estimated at £3,500/tonne. An extensive market research on cellulose nanofibres reported that most producers sell nano-fibres between £40-£80/kg (Future Markets, 2019). The PSNF is from a waste source hence it's minimum selling price was estimated at £8/kg. The cost of processing CNF from sludge was estimated at £235/tonne based on energy consumption of 16.9 MJ/kg (4.7 kWh/kg)

calculated in chapter 5.1 and average UK wholesale electricity market price £50/MWh (1000 kWh) (OFGEM, 2018). Based on the processing cost (£235/tonne) and minimum selling price (£8000/tonne), the revenue was estimated at £7000/tonne. The price of the foam was calculated based on a minimum unit price of a 25 kg/m^3 Polyurethane foam block of 500 x 400 x 25 mm (LWD) costing £0.20, hence 1 tonne of the foam would generate revenue of £16,000.

The EMF is developing a Material Circularity Indicator (MCI) which generates a score from 0 to 1 based on a scale of linear to circular (Ellen MacArthur Foundation, 2014). The MCI tool shown in figure 69 provides an insight on how much the materials circulates in the system.

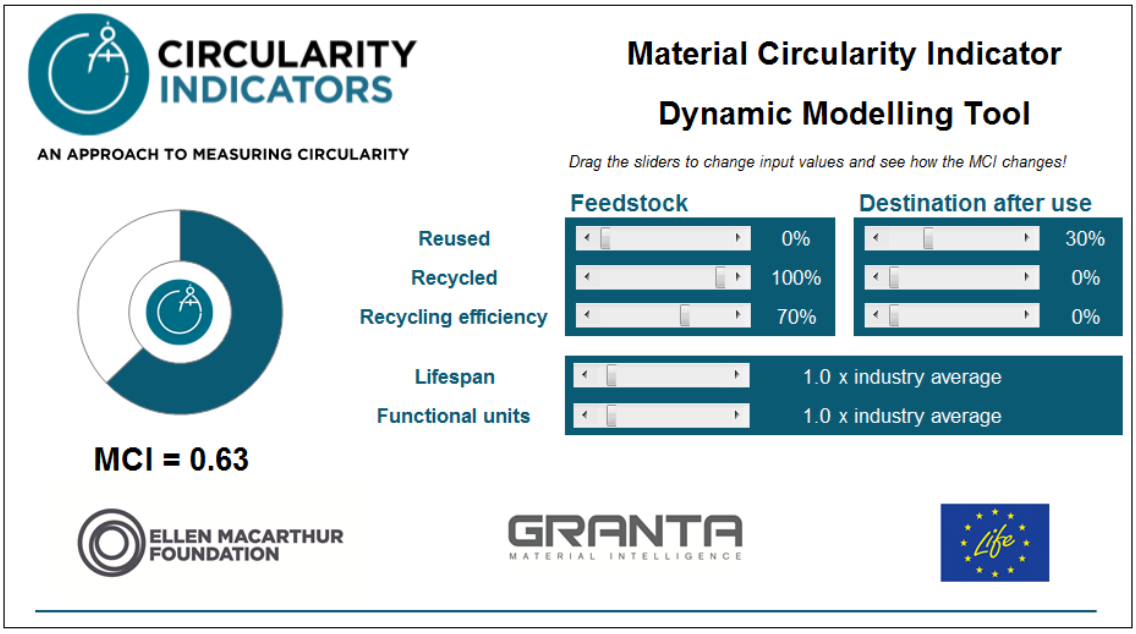


Figure 69: Material circularity index tool(Ellen MacArthur Foundation, 2014).

The MCI tool collects data on the feedstock and destination of the material after use based on their reusability, recyclability and recycling efficiency. The feedstock of the product considered to be 100% recycled, as PMS is from the recycling of paper. The recycling efficiency used was 60% based on current recycling rate of paper in the UK. Using the circularity index tool, the following circularity index were calculated for the products, animal bedding, pelletised cat litter, composite panels, PSNF foam as shown in table 19.

Table 19: Circularity index of PMS products

	Animal Bedding	Pelletised cat litter	Composite panels	Spun PSNF	PSNF Foam
Feedstock	%	%	%	%	%
Reused	0	0	0	0	0
Recycled	100	100	100	100	100
Recyling Efficiency	70	70	70	70	70
Destination after use					
Reused	0	5	10	30	30
Recycled	0	0	5	10	100
Recyling Efficiency	0	0	5	5	0
Lifespan (1 x industry average)	1	1	1	1	1
Function Unit (1 x industry average)	1	1	1	1	1
Circularity indicator	0.51	0.53	0.55	0.64	0.63

The values for destination after use are different depending on the final product of PMS. PMS animal bedding has 0 % reuse and recycling, PMS cat litter has very low reuse of 5 % as some consumers may use them in compost and gardening. PSNF spun into filaments was given a reuse of 30% if used in textile fibres. The lifespan and functional unit are based on the industry average. Despite PMS coming from the waste-water treatment process of recycled paper the circularity indicators for PMS products were between 0.5-0.6. The MCI tool does not consider how many times the material feedstock has been recycled, embodied energy, embodied carbon and other environmental impact categories such as ozone depletion, ecotoxicity.

Whilst the MCI tool is being developed further there are traditional environmental assessment methods such as life cycle assessment (LCA), Mass Flow Analysis (MFA) and environmental performance standard ISO 14000 which provide a more robust environmental assessment. These methods are challenging to apply comprehensively on the proposed business model, because specific design parameter, production process data, transportation data are unknow. However, it is still beneficial to understand the environmental impact of the business model, potential areas of hotspots and areas that can deliver environmental benefit Bocken *et al.* (2016). Life cycle assessment method looks at the product life cycle in the following phases of raw material extraction, manufacturing, transportation, use and end-of life. Faubert *et al* (2016) reviewed the challenges to assess environmental impact of PMS management practises, further noting

that only Likon's (2011) study calculated the GHG emissions from PMS landfilling. Likon's study estimated of 2.7 t of CO_2 and 0.24 t of CH_4 for landfilling 1 t of low ash PMS due to aerobic and anaerobic decomposition. The lack of data limits the scope of the PMS environmental impact assessment. Nonetheless, in table 20 below the areas to consider for the environmental impact assessment is addressed. Transportation stage is not considered in the LCA as it is dependent on the locations within the system boundary, at this stage of the business model transportation routes to customers are undefined

Table 20: Areas to consider for PMS product environmental assessment.

PMS product	**Raw material extraction**	**Manufacturing**	**Use**	**End of Life (EoL)**	**Avoided impacts**
Animal bedding	PMS	Dried to < 10% moisture.	Manual spreading	Use on soil Composting	Landfill
Pelletised cat litter	PMS	Drying Pelletising	Manual spreading	Use on soil Gardening	Landfill
Composite panels	PMS pMDI DiGlue	Drying Disintegration Hot pressing	In building applications.	Reuse Long life (> 5yrs)	Extended life UF emissions VOC emissions Replace virgin material
PSNF	PMS	Grinding	Various application	Compostable Biodegradable	Replace virgin material
Foam	PMS PVA Borax	Grinding Freezing Freeze drying	Packaging Insulation	Compostable Biodegradable	Landfill HFC Microplastic PU/PE foams

Drying of PMS for animal bedding consumes energy. Thus can be calculated based on a specific energy consumption of 0.6 $kWh.kg^{-1}$ H_2O (Mäkelä, Edler and Geladi, 2017). Thus, drying wet PMS of 60% moisture content will consume 0.36 $kWh.kg^{-1}$ of PMS.

The environmental impact given by energy consumption depends on the electric energy mix of the region. Here, UK electricity green-house gas conversion factors for 2019 shown in table 21 (DBSEI, 2019).

Table 21: Emission conversion factors for UK energy consumption.

	kg CO_2e	**kg CO_2**	**kg CH_4**	**kg N_2O**
Emission conversion factors	0.26	0.25	7.E-04	1.E-03

The global warming potential (GWP) of the material is measured in kgCO_2e. The emission conversion factors are used in table 22 to calculated GHG emissions based on energy consumption of the manufacturing processes.

Table 22: Energy consumption and greenhouse gas emissions from manufacturing PMS products per tonne.

Energy consumption	**kWh/tonne**	**kgCO_2e**	**kgCO_2**	**kgCH_4**	**kgN_2O**
Drying PMS/tonne	360	92.0	91.3	0.23	0.49
Grinding (PSNF)	4700	1201	1192	3	6
Disintegration (composite panels)	80	20.5	20.3	0.05	0.11
Pelletising (Cat litter)	136	92.0	91.3	0.23	0.5
Freezing (Foam)	82.5	21	20.9	0.05	0.11
Refrigerant (Foam)	N/A	0.3	N/A	N/A	N/A
Freeze drying	2	0.51	0.51	0.001	0.003
Hot pressing (Composite panels)	140	35.8	35.5	0.09	0.19

Emissions from drying PMS were calculated based on the energy consumption of PMS grinding 16.9 MJ/kg (4.7 kWh/kg). Energy consumption for disintegration of PMS was calculated based on 100 g PMS, power of the grinder 2800 W multiplied by grinding time (0.0028 hrs).

$$\frac{2800\,W \times 0.0028}{1000} = 0.008\,kWh\ per\ 100g, \therefore 1\ Tonne = 80\ kWh\ per\ Tonne$$

The electricity consumption for pelletising was 490 MJ/tonne (136 kWh/tonne) was taken from industry surveys (Pa *et al.*, 2012).

The energy consumption of freezing was calculated based on average energy consumption of industrial refrigerator system (Cascini *et al.*, 2016). The volume of 25 kg/m^3 PSNF foam is 40 m^3, based on Polar U635 industrial freezer (Polar) capacity of

1200 litres, power of 700 Watt and freezing time of 5 hours. The energy consumption of 1 tonne of foam was calculated as follows;

40 m^3 = 40,000 litres; $\frac{40{,}000}{1200} = 33$ freezing cycles

$$\frac{700\ W \times 10\ hours}{1000} = 2.5\ kWh\ \times 33 = 82.5\ kWh/tonne$$

The refrigerant used in the system (R290) is also considered as this also contribute emissions. R290 is a propane refrigerant not part of the Montreal and Kyoto restricted HFCs or CFCs, as it has 0 ozone depletion potential (Choudhari and Sapali, 2017). The UK emission conversion factor for R290 is 3 $kgCO_2e/kg$ of refrigerant. This value is multiplied by the mass of refrigerant top-up per year. an annual refrigerant leakage of 10% is the average for a commercial system (Cascini et al., 2016). The energy consumption of freeze drying was calculated based on commercial industrial freeze dryer FD1000 (Cuddon, New Zealand). The energy consumption of the freeze dryer is 2 kWh based on 1000 kg of ice over 24hr period (Cuddon, 2018).

The energy consumption of hot pressing was calculated based on life cycle inventory for medium density fibreboard (Rivela, Moreira and Feijoo, 2007). The energy required to produce 705 kg/m^3 was equivalent to 355.79 MJ (98 kWh), this was used to estimate the energy consumption of pressing 1 tonne of PMS (140 kWh/ton). The GWP on manufacturing of the PMS products is lower than the emissions from landfilling PMS. The assessment did not include ILCD impact categories such as land use, ecotoxicity, acidification, eutrophication, human toxicity. However, the diversion of PMS from landfill and substitution of virgin materials will lead to reduction in these impact categories. For example, the GWP of 1tonne of low-density PU foam used in building insulation is between 3180-4007 $kgCO_2e/kg$. The GWP of the PSNF foam is significantly lower because the PU foam uses HFC/CFC blowing agents used have high GWP factor < 1000 $kgCO_2e/kg$ (Kylili, Seduikyte and Fokaides, 2018). The highest GWP comes from the grinding of PSNF; 1200 $kgCO_2e$/tonne PMS.

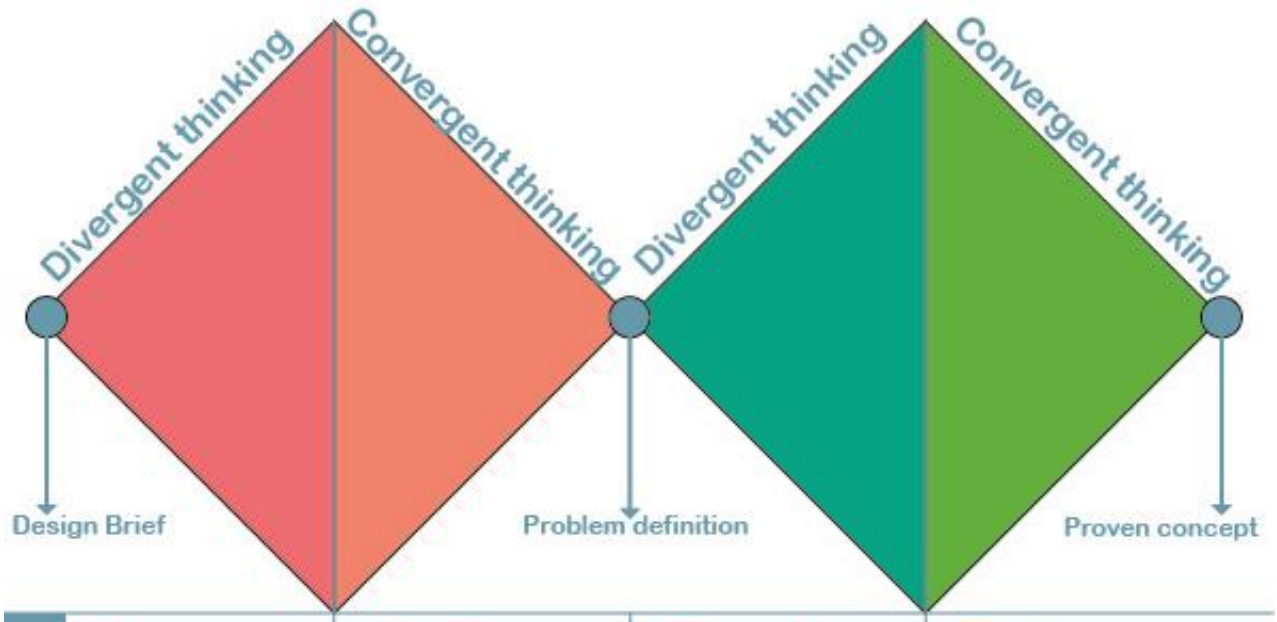
7 Summary

This discussion chapter refers to the research question; ***'How can waste management businesses uncover value from waste/by-products for the circular economy?',*** by providing guidelines for SME waste management based on design thinking methodology and insights from this case study.

The circular economy provides an opportunity for businesses to achieve economic growth without significant detriment to resources. Whilst efforts have been made to guide companies on transitioning to CE business models; there is still a knowledge gap on **'how'** this can be achieved. When it comes to acting, companies find it difficult to identify scope for improvement and transition into a circular business model. For companies who have innovation and product development as their core competencies, it may be less challenging to adopt a circular business model. However, for waste management businesses were disposal and energy recovery are their core competency; it becomes even more difficult to valorise waste into new products. The design-thinking methodology applied to the case study of paper mill sludge can be used as a guideline for waste management to develop circular business models. Thus, in this chapter, the experience of using the design thinking methodology during the research is developed into a set of guidelines to recover value from waste/by-products.

7.1 Guidelines for applying design thinking to create value from waste.

These guidelines are based on the design thinking methodology and include relevant methods which can be applied at each stage of the process. There are various techniques to use in each stage of the design thinking method as shown in figure 71. Design thinking is generic and ambiguous thus each stage of guidelines given below includes methods, tips and results that can be followed.



	Discover	Define	Develop	Deliver
objectives	Collect ideas, explore options & gather information	Characterise materials, link results from the define and discover stage.	Prepare materials from define stage and assess their technical feasibility.	Design a business model, based on proposed products, consider environmental and economic aspects.
Methods	Field study Rapid prototyping Brainstorming Literature review	Mass-spectroscopy Electron microscopy Organic composition Thermal analysis	Material design Manufacturing Material testing Technical standards	Business model canvas Lean stat-up model Environmental assessment Material circularity indicator
Tips	Use data visualisation tools to collate themes. Brainstorm with participants from diverse fields.	Identify variability of the waste/by-product.. Understand if they should be mixed or seperated for proposed ideas.	Collaboration is important if the resources and skills required to prepare materials are unavailable.	Collect data for the business model by using the products to communicate with potential partners and customers.
Results	A list of potential ideas supporting scientific literature, visible prototypes to help communicate idea..	Characterisation Data Shortlisted materials that will be developed.	Physical materials and proposed product/application based on the material technical ability.	Business plan and product portfolio for leverage funding.

Figure 70: Proposed guidelines for applying design thinking to create value from industrial by-products.

8 Conclusion and further work

The circular economy concept requires businesses to adopt a resource-efficient model that decouples economic growth from resource depletion. Whilst the circular economy literature increases exponentially most studies focus on conceptual frameworks and the development of CE business models for the technical cycles. However, there is limited research on the application of design tools to create value from industrial by-products. Waste management companies have a crucial role to play in the circular economy, and there is a lack of evidence-based research that informs such businesses on how to use design to approach CE problems. Thus, the research tackles the question; ***'How can waste management businesses uncover value in waste/by-products for the circular economy?'*** This research question was addressed based on a case study of Ecoganix, an SME organic waste management company managing PMS from 7 UK paper mills. The research applied the four stages of design thinking methodology; discover, define, develop and deliver, which led to the following conclusions;

- The study demonstrates the possibility of upcycling paper mill sludge into functional materials for applications in cellulose nanofibres, foam packaging, spun PSNF filaments and composite panels.
- Cellulose nanofibres ~50 nm in width can be produced from low ash PMS without chemical treatments, their network had a strength of ~92 MPa and modulus ~10 GPa.
- Spun PSNF filaments showed increase in tensile strength as concentration increased from ~ 220 MPa for 9% to ~ 280 MPa for 12% CNF. The modulus of the spun PSNF (25 GPa) was higher than commercial viscose Enka (10-12 GPa).
- Foams produced from PSNFs and Poly-vinyl alcohol were competitive with commercial packaging foams and can serve as possible replacement of expanded polystyrene/polyurethane foams.
- PMS composite panels bonded with bio-resin proposed were suitable for panels used in dry conditions and floor tiling.
- The research proposed a new business model with potential revenue based on products derived from mill sludge.

The new business model proposed by the research shows an opportunity for valorising paper mill sludge. However, it is no denial that there are barriers to transition into a circular business model;

- Financing of the new business model

There will be challenges for an SME waste management company to invest in the resources required to make the business model transition. The scale-up pyramid in figure 68 showed how the business can invest gradually in developing new products. However, given the processing equipment and raw material cost, the time frame to move from one product to the other will depend largely on the success of the predecessor product.

- Consumer perception

Consumers may expect a cheaper price for products derived from industrial by-products/waste materials, they may also be perceived as low quality despite the product meeting the same technical requirement. There will be a challenge here is products from the business should be marketed as recycled materials or if any mention to PMS should even be made.

- Current linear system

The infrastructure required to manage products that are biodegradable/compostable is not consistent in all geographical regions, even within in the same country. This implied to the foams prepared in the research for replacing fossil fuel foams in packaging applications. Although the PSNF/PVA foams are derived from biodegradable materials, when it comes to packaging materials there is an ongoing debate on biodegradable vs recyclable.

Nonetheless, the products developed in this research show the capability of future paper recycling to go beyond fibre recovery. Thus, there is a potential to transform not just PMS but paper waste into functional materials and biological nutrient for the circular economy. Collaborations with paper mills that have the capacity to scale-up.

8.1 Future work

Some of the applications such as animal bedding, cat litter, PSNF and packaging foams are ready for market if the production facility is set up. However, composite panels from PMS require further testing on fire classification and slip resistance to meet technical standards for the built environment. Additionally, the separation of mineral from organic fibres in the PMS can contribute significantly to the valorisation of PMS. Removal of inorganic minerals will aid the dissolution and spinning of PSNF with higher concentration (>12%). Further, research into bespoke ionic solvents that can dissolve the inorganic minerals may also improve spinnability of the filaments and their mechanical properties.

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10 Appended papers

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Current Opinion in Green and Sustainable Chemistry

Exploring new horizons for paper recycling: A review of biomaterials and biorefinery feedstocks derived from wastepaper

Cynthia Adu[a], Mark Jolly[a] and Vijay Kumar Thakur[b]

Paper is a perfect example of the circular economy as it remains the furthermost recycled product in Europe, creating significant environmental benefits and raw materials resources to the industry. Indeed, maintaining a consistent level of quality whilst limiting the environmental footprint of the product has become a major challenge for the industry. In this direction, paper is proving to be the promising feedstock for biorefinery and biomaterials. The future of paper recycling is slowly going beyond fibre recovery to address the needs of other industries because for the earth's environmental well-being various paper products need to be recycled and reused persistently. In this article, we outline the ambitious use of wastepaper (WP) for high-value applications such as; production of cellulose nanocrystals (CNC), composite reinforcement, high performance electrical components and biofuels.

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Edited by **Avtar Matharu** and **Vijay Kumar Thakur**

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Introduction

Paper recycling is a major process in the manufacturing of paper products. Europe boasts of 72% recycling rate recorded in 2012 and a 74% target is set for 2020 [1]. Although, paper can be recycled an average of 5 times, most paper products have a very short lifespan (days) which may not justify the amount of resources consumed for its production and its use in low value applications. The expectations for paper recycling rates to increase, requires the use of recycled fibers in high quality grade paper. However, these fibers become shorter and reduce the properties in swelling and flexibility which cannot meet the standards desired by customers. Furthermore, the demand for high quality paper products containing recycled fibers rely on the increasing use of chemical additives and fillers which produce large quantities of by-products posing serious environmental and economic challenges [2].

An overview of publications on paper recycling is illustrated in Figure 1. The authors reviewed publication overtime on Scopus database which showed that, early studies were focused on fiber recovery from wastepaper which included fiber bleaching methods and deinking technologies to allow the reuse of secondary fibers in papers, an increasing demand for deinking equipment was also noted in the early nineties. Publications on paper recycling peaked in year 2000 perhaps in response to the European declaration on paper recycling released the same year [3]. In 2001–2010 publications were still dominated by fiber recovery. Nowadays circular economy principles are becoming attractive within regulators and policy makers, as the substitution of fossil fuel based products with bio-based or biodegradable materials is strategic for mitigating climate change. Thus, the current landscape on wastepaper recycling is populated with recovery of biomaterials and bio-refinery feedstock from waste paper which will be discussed in this review.

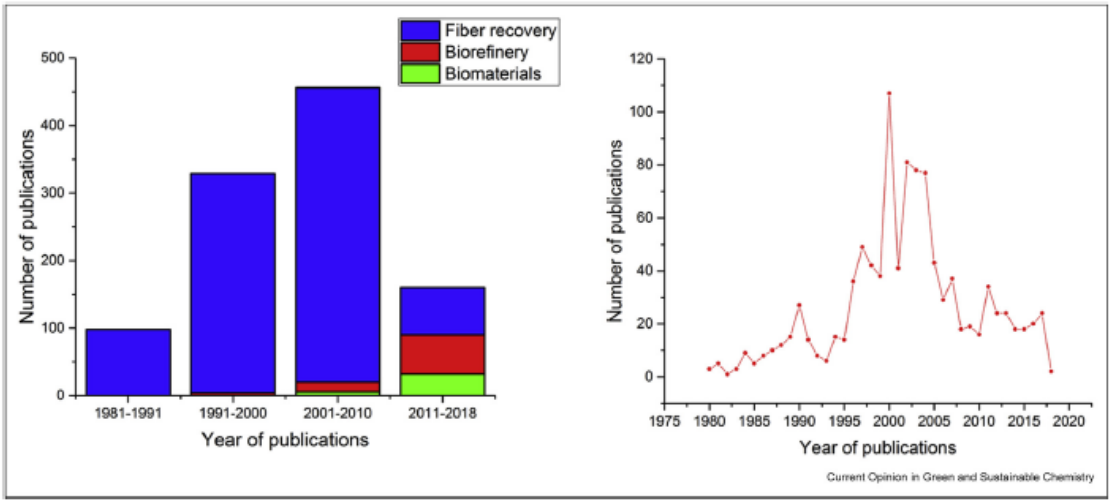
Bio-materials synthesised from wastepaper

Paper is primarily a plant/wood based product containing high amount of cellulosic biomass desirable in a diverse range of industries. Cellulose is an abundant natural polymer consisting of crystalline and amorphous regions [4]. Over the past few years, there has been several research breakthroughs in the industrial production of cellulose nanofibers (CNF) and cellulose nanocrystal (CNC) proposing it's use in high added value applications [5,6]. Wastepaper has been used in the literature for the extraction of CNC/CNF, preparation of polyhydroxyalkanoate (PHA), carboxymethyl cellulose and polymer composite matrix. Meanwhile materials prepared from the synthesis of wastepaper have also been explored for producing high performance electronic components such as supercapacitors.

Cellulose nanocrystals

Cellulose contains amorphous regions known as hemicellulose which can be removed by acid hydrolysis or mechanical grinding resulting in the formation of a highly crystalline or semi crystalline structure exhibiting elastic modulus as high as 137 GPa. Cellulose

Figure 1



Publications on paper recycling: yearly publications showing increase in 2000 (left), publications by topic or research area (right).

nanocrystal has been produced from various wastepaper sources such as: old news print (ONP), recycled newsprint (NP), old corrugated container (OCC) and office waste paper (OWP). Cellulose can be obtained from pre-treatment of the wastepaper with sodium hydroxide (NaOH) to remove hemicellulose and bleaching with sodium hypochlorite (NaClO) to remove lignin. Nanocellulose crystals can be prepared with the renowned sulfuric acid hydrolysis method or enzymatic hydrolysis. The resulting properties of the CNCs derived from wastepaper is compiled in Table 1.

The dimension of the wastepaper CNCs obtained above are comparable to CNCs prepared from material sources such as cotton, tunicate, bacteria, ramie and sisal. The CNCs derived from some wastepaper showed aspect ratio between 10 and 70. CNC vary from 10 to 100 nm in length and 4–70 nm in diameter although the crystallinity of CNC (95.5%) derived from pure cellulose is higher. It was shown that with direct acid hydrolysis and no bleaching of the newsprints the CNCs produced had similar properties to bleached newsprint (NP-B) [10]. Thus, waste paper presents a cheap source for CNC production especially in application whereby the presence of ink, colouring and impurities is of less importance.

Composite reinforcement

Fibers are commonly used as reinforcing materials in composite applications because of their high aspect ratios which provide high tensile strength and other material properties. Wastepaper (WP) was used as a filler in samples of polyester (P) and polyurethane (PU) as a matrix, with matrix to filler ratio of 20:80 [12]. The tensile strength for the P/WP composite reduced from 17.8 ± 0.5 MPa to 4.4 ± 2.5 MPa whilst modulus increased from 2286 ± 751 MPa to 3144 ± 248 MPa. Nevertheless, another study with 50:50 P/WP ratios reported a significant increase of 30% in the material tensile strength [13] which signifies that there might be an optimum point whereby further addition of wastepaper causes reduction in tensile strength. For the PU/WP, composite strength increased slightly from 1.2 ± 0.2 MPa to 7.8 ± 0.7 MPa whilst elastic modulus increased greatly from 13 ± 3 to 741 ± 113. The mechanical properties in both studies were reduced by 20–30% with increasing moisture uptake due to high cellulose content. The interfacial adhesion of wastepaper in polymer composite matrix can be enhanced by polymer grafting. Maleic anhydride grafted linear low density polyethylene (LLDPE-g-MA) reinforced with WP composites showed significant improvement in tensile strength (88%) and elastic modulus (409%) caused by increased interaction between the wastepaper hydroxyl groups and the anhydride groups [14]. CNC of 20 nm–60 nm widths obtained by acid hydrolysis of wastepaper were used to substitute carbon black for natural rubber (NR) reinforcement which showed few effects on the mechanical properties and improved the processing properties of the NR [15]. Inorganic fillers in recycled paper such as kaolin clay and precipitated calcium carbonate (PCC) have been replaced with CNF which were proven to have a higher bursting and tensile strength [16,17]. Waste paper fibres have also been incorporated into building materials such as concrete, mortars, bricks and cement based composites [18–20].

Table 1

Characteristics of CNCs prepared from various wastepaper sources.

Source Material	Diameter (nm)	Length (nm)	Cri[a] (%)	Treatment	Ref
ONP	3–10	100–300	75.9	Alkali and acid hydrolysis	[7]
NP	5.8 ± 2.2	121 ± 32.5	82.0	Alkali and acid hydrolysis	[8]
OCC	15–80	100–400	57.8	Enzymatic hydrolysis[b]	[9]
ONP	2.9 ± 0.99	371 ± 74	92.6	Direct acid hydrolysis	[10]
NP	3.26 ± 2.90	218 ± 49	93.4		
NP-B	4.40 ± 3.91	356 ± 137	94.8	Direct acid hydrolysis Alkali and acid hydrolysis	
OWP	33 ± 5	238 ± 72	84	Alkali and acid hydrolysis[c]	[11]
OWP	32 ± 5	196 ± 61	73	Alkali and acid hydrolysis[d]	

[a] Crystallinity index.

[b] 60% phosphoric acid was used for pre-treatment prior to enzymatic hydrolysis and sonication.

[c] 2 wt% sodium hydroxide solution treatment.

[d] 7.5 wt% sodium hydroxide solution treatment.

Bio-polymer

CNC films exhibit high transparency, light weight, biodegradability and barrier properties proposing them for packaging applications [21]. Transparent CNC films prepared from OWP were used to coat poly-ethylene terephthalate (PET). The coating with CNC resulted in improved water vapour barrier thought to be beneficial for elongating the shelf life of packaged food products [22]. It was also found that some films appeared dark however still had higher transparency (65%) than others which appeared clear (59%). Sodium alginate/carboxymethyl cellulose (NaCMC) bio-composite films were prepared from old NP. Although the tensile strength of the films (2 MPa) was lower than LDPE and HDPE, the materials were deemed suitable for low mechanical packaging applications [23]. The enzymatic hydrolysis of office waste paper produced fermentable sugars used in preparation of Poly (3-hydroxybutyrate) (PHB), a short chain length PHA [24]. Poly-hydroxyalkanoates (PHAs) are a family of biodegradable polyesters produced by the microorganisms synthesised in presence of excess carbon source [25]. Although PHAs have their limitations in comparison to synthetic plastics which include high production cost, incompatibility with legacy processing techniques and chances of thermal degradation, improved mechanical properties have been identified when blended with other polymer materials or after chemical modification.

Electronic components

Hybridisation of Li-ion batteries with electrochemical capacitors require the use of carbonaceous materials with high surface area such as graphene, activated carbon, biomass derived activated carbon for electrode material [26,27]. Such Li-ion hybrid electrochemical capacitors (Li-HEC) are regarded as potential avenue for efficient energy storage systems. Porous carbon derived from hydrothermal processing and pyrolysis of OWP was used as a cheap source for cathode material in Li-HEC. The material had a high surface area porosity of 2341 m^2/g with energy storage capacity of 61 Wh Kg^{-1} [28]. Wastepaper converted into graphene-tethered carbon fibre composite paper (GCCP) demonstrated high electrical conductivity and electrochemical stability for electrodes [29]. Flexible supercapacitors were derived from anchoring reduced graphene oxide-manganese dioxide (RGO-MnO_2) onto OWP. The electrode material exhibited energy storage capacity of 19.6 Wh Kg^{-1} and was proposed for wearable electronic device [30]. Cyanoethyl cellulose derived from waste paper can also be used for organic field-electric transistors (OFETs) [31,32], such organic based components are receiving attention for their low-cost, ease of processing, flexibility and lightweight circuits suitable in applications for ultra-low power electronics such as radio frequency identification (RFID) tags, biodegradable electronics for medical implant, sensor devices and so on.

In recent years, advanced hybrid devices are the most promising storagesystems for large scale smart-grid and industry applications. Compared to secondary batteries, Li-ion hybrid electrochemical capacitors (Li-HEC) possess high energy density, high power capability, and long-term stability [3].

Generally, Li-HECs are constructed with electrical double layer (EDL) materials as the positive electrode (supercapacitor component) and Li-intercalation-type materials as the negative electrode (Li-ion battery).

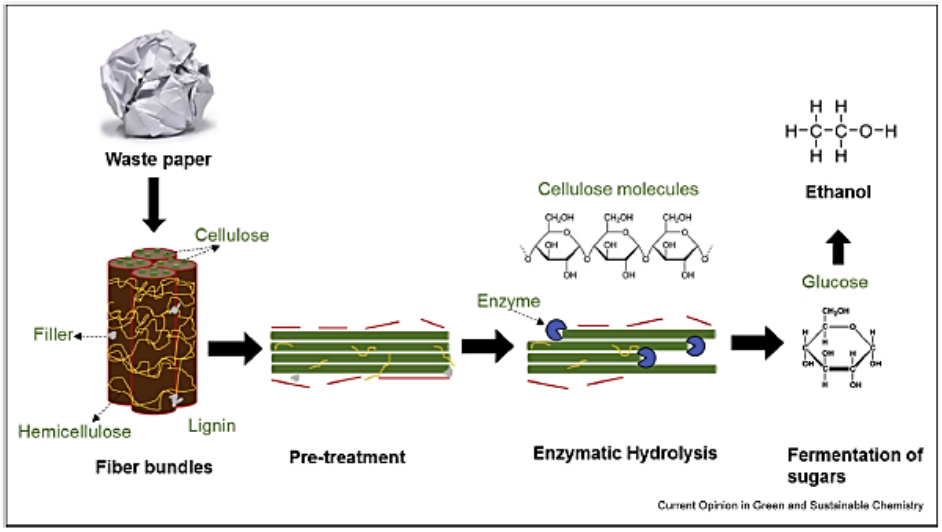
Wastepaper derived biofuels

The biofuel potential of wastepaper is estimated to replace up to 5% of fossil fuel consumption [33]. In recent studies, the use of wastepaper as feedstock for various energy production such as ethanol, methane and hydrogen has shown promising results.

Bio-ethanol from wastepaper

Wastepaper has been used as feedstock in anaerobic digestion to produce bio-ethanol and methane through enzymatic hydrolysis [34,35]. Enzymatic hydrolysis uses enzymes to degrade the cellulose and lignin which produces reducing sugars such as glucose, the fermentation of the glucose produces bio-ethanol which can

Figure 2



A schematic of the enzymatic hydrolysis of wastepaper to produce fermentable sugars.

also be converted to methane [36] as illustrated in Figure 2.

The efficiency of hydrolysis process on glucose yield is affected by costly enzymes and long retention times. Recently pre-treatment methods have been shown to improve process yield by disrupting the crystalline structure and increasing the surface area. This enhances the enzymes accessibility to cellulose and reduces enzyme loading. Chemical and physical pre-treatment methods were evaluated to show their effect on glucose release after enzymatic hydrolysis of WP. The maximum glucose yield after milling the WP to 10 mesh was <0.5 g/L whilst 25 g/L was obtained after sulfuric acid treatment leading to reduction of enzyme loading by 50% [37]. Nevertheless, another study showed that mechanical pre-treatment of WP with Hollander beater prior to enzymatic hydrolysis increased methane yield in anaerobic digestion by 21% at 254 mL/g VS [38], Nishimura *et al* reported higher methane yield of 270.5 mL/g VS when yeast was used for presaccharification prior to simultaneous scarification and fermentation (SSF) [39,40].

Hydrogen production

Hydrogen gas is a clean fuel source due to its non-polluting nature during combustion. Biological production of hydrogen through dark fermentation is less energy intensive compared to steam reforming of hydrocarbons and water electrolysis [41]. Fermentation of sugars derived from acid hydrolysis of wastepaper has been proven to produce hydrogen gas. However a limitation in hydrogen yield is the inhibition of the fermentation process caused by furfurals generated during acid hydrolysis stage [42]. Activated carbon has been effective for the removal of Hydroxymethylfurfural (5-HMF) from media after the hydrolysis of wastepaper [43] another study also used lime treatment to reduce 5-HMF from 2.48 g/L to 0.35 g/L [44]. Botta *et al*, applied rumen fluid as an inoculum in wastepaper fermentation, this enriched fermentative spore forming bacterial capable of producing hydrogen. Additionally acid pre-treatment of the rumen fluid reduced the hydrogen consuming cultures [45].

Conclusions

Recycling of paper offers several benefits including cost-effectiveness of the process and new emerging market applications. This article highlights that the future of paper recycling will go beyond fiber recovery to recycling wastepaper into functional materials and biorefinery feedstock of higher value. The most prevalent method in the literature for converting wastepaper into CNC is the acid hydrolysis process, however from green chemistry perspectives, more sustainable approaches such as ionic liquid treatment and mechanical refining requires investigation for CNC production from wastepaper. From the energy perspectives, whilst derivation of methane from AD of wastepaper is not especially new, efforts such as pre-treatment, presaccharification and co-digestion have been applied in the literature to improve the process yield and plant economic feasibility.

On the bio hydrogen production from wastepaper, the dark fermentation produces mixed gas streams which require improved gas separation technologies to obtain pure hydrogen.

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Properties of cellulose nanofibre networks prepared from never-dried and dried paper mill sludge

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ABSTRACT

Paper mills yield large volumes of sludge materials which pose an environmental and economic challenge for disposal, despite the fact that they could be a valuable source for cellulose nanofibres (CNF) production. The aim of the study was to evaluate the production process and properties of CNF prepared by mechanical fibrillation of never-dried and dried paper mill sludge (PMS). Atomic force microscopy (AFM) showed that average diameters for both never-dried and dried paper sludge nanofibres (PSNF) were less than 50 nm. The never-dried and dried sludge nanofibres showed no statistical significant difference ($p > 0.05$) in strength ~92 MPa, and ~85 MPa and modulus ~11 GPa and ~10 GPa. The study concludes that paper mill sludge can be used in a dried state for CNF production to reduce transportation and storage challenges posed on industrial scale.

1. Introduction

Biopolymeric materials derived from environmentally friendly sources are gradually becoming competitive with traditional polymers derived from non-renewable sources (Pickering et al., 2015; Montoya et al., 2014; Thakur, 2014). Agricultural crops have been suggested as a raw material to produce biodegradable polymers. However, in the present era of limited resources, there is a competition of using land to grow lignocellulose biomass instead of food crops (Valentine et al., 2012). The circular economy principles promote the optimisation of resources by extracting valuable biochemical feedstocks from existing industrial processes. For example, agro-industry waste such as sugar cane bagasse, carrot residue and brewery waste has been used to produce nanocellulose (Berglund et al., 2016; Golbaghi et al., 2017; Nuruddin et al., 2016).

Ideally, nanocellulose is produced from cellulose sources such as plants, wood, tunicate and algae by the breakdown of their structure, either by chemical and/or mechanical means to produce cellulose nanofibres (CNFs), or by acid hydrolysis to form cellulose nanocrystals (CNCs) (Eichhorn et al., 2010; Hsieh et al., 2008; Moon et al., 2011). These cellulose nanofibres are characterised by their high aspect ratio, high stiffness and crystallinity. The elastic modulus of the crystalline regions of cellulose was first determined from the deformation of bleached ramie fibres resulting in a value of 137 GPa for the crystal modulus (Sakurada et al., 1962), further research on modulus of cellulose reported values ranging from 100 to 140 GPa (Northolt et al., 2005; Sturcova et al., 2005). The specific mechanical properties, when divided by the density of cellulose (~1.5 g cm^{-3}), are comparable to engineering materials such as steel, glass or aluminium. Hence, they can be used in high value applications such as automotive, packaging materials, biomedical applications, sensors and membranes (Trache et al., 2017). However, the application of CNF in industry is limited by availability as the mass production of nanocellulose is hindered mainly due to its high production costs (Delgado-Aguilar et al., 2015; Oksman et al., 2016).

Nevertheless, to reduce cost and scale up production of nanocellulose, Paper mill sludge (PMS). has been proposed as a cheap and sustainable raw material for producing CNFs. PMS is an industrial effluent of paper mills produced in large volumes; one million tonnes is produced in the UK alone. Disposal of PMS poses an economic challenge of £82.60/tonne and risks potential release of 2.60 tonnes of CO_2 if not managed to environmental disposal

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standards (Adu and Jolly, 2017; Faubert et al., 2016; Likon et al., 2011). Despite being rich in cellulose, PMS is currently used in low value applications for land spreading (Monte et al., 2009; Phillips et al., 1997) and animal bedding (Villagrá et al., 2011). Moreover, using PMS means no chemical pre-treatment is required to dissolve lignin unlike other biomass residues, and it can be obtained free of charge from the mill thereby reducing cost. However, a foreseeable industrial challenge of processing large quantities of PMS into cellulose nanofibres is the high chance of microbial activity during storage and transportation as the sludge is often obtained never-dried/wet from the paper mills with up to 80% moisture content (Ghribi et al., 2016).

In the literature, never-dried sludge has been used to produce CNF with widths 5–30 nm by high pressure defibrillation at 138 kPa and chemical bleaching with NaOH (Leão et al., 2012). Never-dried sludge from a dissolving cellulose mill was also used to produce CNF (<100 nm) by mechanical fibrillation (Jonoobi et al., 2012). The use of never-dried/wet cellulose material is highly desirable for CNF production in comparison to once dried material. This is because of the phenomenon known as hornification, which promotes an irreversible bonding between fibrils thus leading to reduced mechanical properties in dried pulp (García et al., 2002; Spinu et al., 2011). However, the use of dried sludge provides an advantage to prevent bacterial degradation, reduces transportation costs and storage challenges. The use of dried sludge as opposed to never-dried sludge for producing CNF has not been investigated in the literature. Thus, this study draws a comparative evaluation between the production process and properties of CNFs obtained from never-dried and dried paper mill sludge. The nanofibres obtained from the sludge are referred to as paper sludge nanofibres (PSNF); never-dried ($PSNF_{ND}$) and dried ($PSNF_{D}$).

2. Materials and methods

2.1. Material

Never-dried sludge was obtained from a paper mill producing kitchen towel rolls with hardwood and softwood pulps such as eucalyptus or pine. One batch of the same sludge was also dried for 24 h in an oven and stored for 3 months. The paper mill yields 4000 tonnes of PMS annually, which is used for agricultural land spreading or animal bedding.

2.2. Chemical composition of sludge

The ash content of the sludge sample was determined using TAPPI 211 standards ash in wood, pulp and paperboard at 525 °C (TAPPI, 2004). Hemicellulose, cellulose and lignin were tested using direct chemical methods (Moubasher et al., 1982). Ethanol was used to treat 2 g of PMS, two parts of 1 g each. Part 1 is dry weighed as fraction A, while part 2, namely fraction B, was treated with 24% KOH. After dry weighing, fraction B was further treated with 72% H_2SO_4 and refluxed with 10% H_2SO_4; this was labelled as fraction C. After each stage, all fractions were washed thoroughly in distilled water and dried overnight at 80 °C before weighing. Deductions of the weighed fractions (A, B and C) were used to calculate the organic composition of the sludge. The cellulose content is given by fraction B–C, hemicellulose (A-B) and lignin (C itself). The morphology of the PMS was studied using Scanning Electron Microscopy (SEM) JSM-6490LV, JEOL (Japan) with a 12 kV acceleration voltage, in back-scatter electron (BSE) detector mode, to obtain a chemical analysis of inorganic minerals in the sample. Oxford instruments Aztec™ EDS element mapping software was used to process the data. Thermogravimetric analysis (TGA) was also used to confirm the organic composition of the sludge, and the presence of inorganic material (Lin et al., 2015; Yang et al., 2006). TGA of PMS was determined in accordance with the ASTM-E1131-03 standard test method for compositional analysis of thermogravimetry using a Mettler Toledo TGA/DSC analyser. TGA/DSC was used to measure the mass change of the specimen in an increasing temperature range from 25 to 600 °C, at a heating rate of 10 °C/min.

2.3. Processing of cellulose nanofibres from never-dried and dried PMS

Never-dried and dried PMS was fibrillated using a super mass collider MKCA6-3 (Masuko Sangyo Co, Japan), at a consistency of 2 wt%. Prior to the ultrafine grinding process, the suspension was dispersed in deionised water using a shear mixer Silverson L4RT (Silverson Machine Ltd. England). The dried PMS required a 24 h soaking before dispersion in deionised water. The grinding stones used were coarse silicon carbide (SiC) with several grooves on the surface. Centrifugal forces from the repeated cyclic pressure and shearing stress cause the microfibre suspension to move outwards from the grooves. The forces on the fibre suspension result in the defibrillation of the fibres by setting the grinding stones in contact mode after the initial feeding and gradually adjusting them to −90 μm. The rotor speed was set to 1500 rpm. The energy consumption for the mechanical separation was based on the direct measurement of power in Watts, using a power meter produced by Carlo Gavazzi (model, EM24 DIN, Italy). The energy consumption for the grinding process is converted to kWh per kg of the nanofibres' dry weight, calculated using the equation.

$$\text{Energy (J)} = \text{power (W)} \times \text{time (h)} \quad (1)$$

To assess the degree of fibrillation, viscosity measurements were carried out using a Vibro Viscometer SV-10, (A&D Company, Ltd., Japan). The details of the fibrillation process are shown in Fig. 1. The viscosity measurements were conducted at room temperature (22.5 °C) based on testing three samples each collected from different intervals during the fibrillation process until reaching a plateau in the viscosity. The plateau viscosity was reached after a 150 min processing time.

The microstructure of both materials was also studied during fibrillation at different time intervals using polarised microscopy (Nikon Eclipse LV100N POL, Japan) and the imaging software NIS-Elements D 4.30. The PMS fibre dimensions were measured with a Metso FS5 fibre image analyser (Metso Automation, Finland) in accordance with the ISO 16065–2:2007 determination of fibre length by automated optical analysis, using unpolarised light.

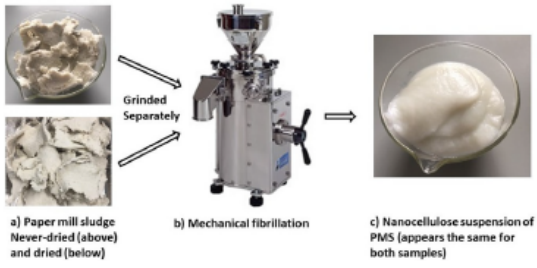

Fig. 1. Schematic of the preparation steps for a cellulose nanofibre suspension produced from paper mill sludge with mechanical ultrafine grinding (suspension appears the same for both sample).

2.4. Preparation of nanofibres networks

Nanofibre networks were prepared by using the CNF suspension to fabricate nanopaper sheets. The CNF suspension was adjusted to 0.2 wt%, after which it was dispersed at 10,000 rpm for 10 min, using a shear mixer, IKA T25, UltraTurrax, (IKA-Werke GmbH & Co., Germany). The dispersed CNF solution was de-gassed and vacuum filtration undertaken with a 0.45 μm and 125 mm diameter membrane filter. The gel formed was placed between two metal plates lined with a stainless-steel mesh and hot pressed at 110 °C and 1.1 MPa for 30 min using Fortune presses, LP300, (Fontijne Grotnes, The Netherlands). Under the same conditions, but for 10 min, a surface finishing was carried out by replacing the mesh lining with polyester films.

2.5. Characterisation of paper sludge nanofibre

The PSNFs were characterised to obtain fibre dimensions and mechanical properties of sheets of the material. Atomic force microscopy (AFM) was carried out using a digital instruments Dimension 3100 AFM equipped with Veeco Nanoscope IV controller (Bruker, UK). AFM was performed in tapping mode at the resonance frequency of the cantilever with a scan rate of 0.4 Hz and a scan size of 8.8 μm. Samples for AFM were prepared by depositing a dilute drop of 0.01 wt% fibrillated sludge fibres on a freshly cleaved mica plate, and allowing this to dry at room temperature. The fibre dimensions were measure from the AFM using Veeco Nanoscope analysis software and images were collected from independent scans. AFM measures the diameter of the fibres by scanning the tip across the surface of the specimen with a scan size of 30 μm. Height measurements were taken from individual fibres protruding out of a network within four different scan areas with 100 fibres measured in total. Areas with agglomerated fibres were not considered in the measurement analysis. X-ray diffraction analysis of the nanopaper was conducted using a Bruker D8 ADVANCE X-ray diffractometer (Bruker Co., Germany), multiple nanopaper samples were mounted and exposed to Cu Kα radiation with a step size of 0.03° at $2\theta = 5-40°$. The diffraction pattern for never-dried and dried PSNF were used to calculate crystallinity index (CrI) based on Segal's method (equation (2)) (Segal et al., 1958)

$$CrI(\%) = \frac{I_{total} - I_{am}}{I_{total}} \quad (2)$$

where I_{total} is calculated from the maximum scattered intensity from the main peak (110) and I_{am} is the minimum scattered intensity between the main and secondary peaks for cellulose. A peak fitting method (equation (3)) has also been used to calculate *CrI* as Segal's method has been known to underestimate the amorphous fraction. This method deconvolutes each peak using a Gaussian function after which the amorphous region is subtracted and the *CrI* is calculated by dividing the total scattered intensity area of each crystalline peak by the total scattered intensity area of the diffraction spectra (Park et al., 2010).

$$CrI(\%) = \frac{A_{crystalline}}{A_{total}} \quad (3)$$

The transmittance of a PSNF suspension (0.2 wt%) was measured using a UV-VIS-NIR extended range FLAME-S-XR1 spectrophotometer (Ocean Optics, UK) set in the range of 200–1000 nm with distilled water used as a reference. The opacity of the nanopaper was measured using a Elrepho 070 spectrometer (Lorentzen and Wettre, Sweden) in accordance with British Standards (British Standards Institution BSI, 2008). Tensile tests were conducted on the nanopaper samples using a universal testing machine manufactured by Shimatzu AG-X (Japan) using a 1 kN load cell, and an extension rate of 2 mm/min and a 20 mm gauge length between the clamps. All samples were conditioned in an environmental cabinet, which maintained 50% relative humidity (RH) and 23 °C, 24 h before testing. The reported results were obtained from 8 test specimens that failed in the middle of the gauge length. Tensile strength was calculated from the force and cross-sectional area of the paper. Tensile index was calculated in accordance with (TAPPI, 2006) standards which considers the weight per unit area of the paper (g/m^2) instead of the thickness. Results of tensile index for mechanical fibrillated CNF have been reported by Yousefi et al. (2013) as 87.7 Nm/g.

3. Results and discussions

3.1. Chemical composition and thermal analysis of sludge

A summary of the PMS chemical composition is illustrated in Table 1, The composition results of both never-dried and dried samples of PMS are the same as they were collected from the same batch.

The EDX spectrum in Fig. 2 (left) shows that the major component of the sludge is organic (C, O) although trace elements of magnesium (Mg), aluminium (Al), Silicon (Si) and Calcium (Ca) are present. These inorganic components may come from fillers, sizing agents, possible contaminants and trace elements present in the waste-water. The TGA analysis in Fig. 2b is as expected for the sludge. The organic content of PMS, which is mainly cellulose and hemicellulose, thermally decomposes at ~300 °C, whilst the mineral fillers remain thermally stable after 500 °C.

3.2. Microscopy of nanofibres

Polarised light micrographs of the paper sludge showed changes in the fibre size at different time intervals during fibrillation (Fig. 3). After 45 min fibrilation the dried PMS fibre showed no obvious reduction in fibre size compared to the never-dried PMS at 45 min. The microscopy image for the dried sludge presented a few large fibres circled in red at 120 min and 150 min.

During the mechanical grinding process, an increase in viscosity gives an indication of the degree of fibrilation. The viscocity and energy consumption of never-dried and dried PMS at differing intervals of fibrillation is shown in Fig. 4.

The starting viscocity for the never-dried PMS (5 mPa.s) was lower than the dried PMS (28 mPa.s). Both PMS showed an exponential increase in viscocity until reaching equilibrium. The never-dried PMS showed a higher viscocity (1256 mPa.s) than the dried PMS (1124 mPa.s). The energy consumption of never-dried PMS was 30.6 MJ/kg whereas the dried material consumed 33.5 MJ/kg of energy due to a higher rotor speed required to process it.

3.3. AFM imaging of paper sludge nanofibres

Fig. 5 shows the morphology and width distributions of the paper sludge nanofibres (PSNFs). The average nanofibre diameter for $PSNF_{ND}$ was found to be 34 ± 15 nm, with more than 60% of

Table 1
Chemical composition of paper sludge.

Ash	Cellulose	Hemicellulose	Lignin	Ca	Si
1.3%	74%	2.6	1.3	2.4	<1%

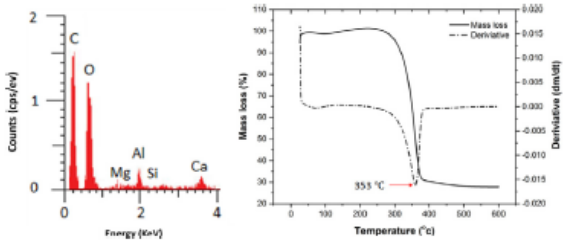

Fig. 2. A typical EDX spectrum showing peaks of elements contained in a PMS sample (left), themogravimetric traces and a derivative curve (dotted line) of the PMS showing the highest degradation peak at 353 °C attributed to the thermal decomposition of cellulose (right).

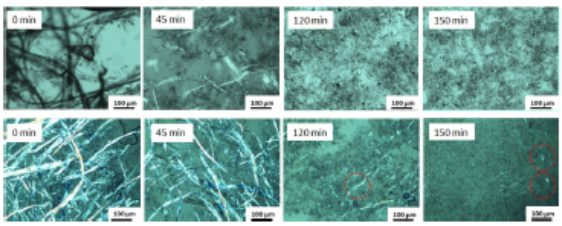

Fig. 3. Typical polarised microscopy images of PMS fibres at fibrillation time intervals showing a reduction in fibre/nanofibre widths for never-dried sludge (above) and dried sludge (below).

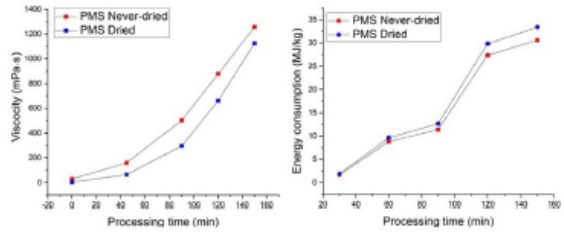

Fig. 4. Increases in viscosity (left) and increase in energy consumption (right) as a function of processing time for never-dried and dried PMS (to convert MJ/kg to kWh/kg divide by 3.6).

these values being between 20 and 50 nm whilst the $PSNF_D$ showed comparable fibre width of 41 ± 13 nm.

3.4. Powder X-ray diffraction (XRD) analysis of sludge nanofibres

The X-ray diffraction patterns for both $PSNF_{ND}$ and $PSNF_D$ exhibited a number of intensities within the 2θ angle range (Fig. 6 left). The intensities labelled (a), (e) and (g) are attributed to crystalline talc ($MgSi_4O_{10}(OH)_2$), which is a common filler used in the paper industry; the presence of this compound can also be confirmed by the observation of these elements in the EDX spectrum. Similar peaks have also been identified in XRD of paper sludge (Frías et al., 2015) and talc used as a filler in polylactic acid (PLA) exhibited the same intensities (Buzarovska et al., 2016).

Fig. 6 (right) shows the deconvolution of cellulose intensities used to calculate the *CrI*. The intensity ($\bar{1}10$ at 12.8° is indicative of a cellulose II structure. The (101) intensity at an angle 14.8° and 16.8° respectively are related to intermolecular hydrogen bonds. Both PSNF show an intensity (110) at an angle 22.5° which is

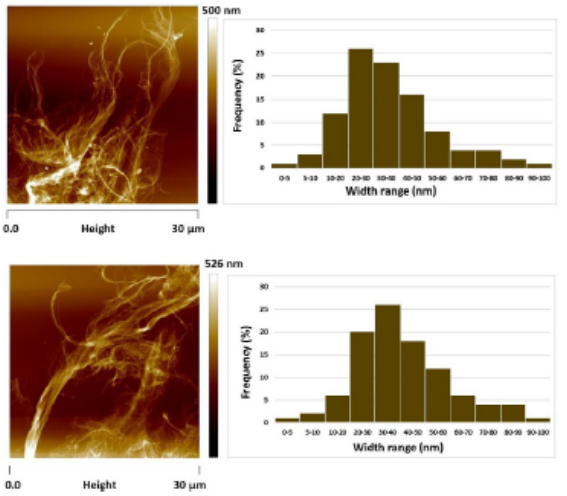

Fig. 5. AFM height of paper sludge nanofibres (PSNFs) and width distribution of PSNF; $PSNF_{ND}$ (above) and $PSNF_D$ (below).

characteristic of a cellulose I structure; this becomes a double peak around 20.6° if regeneration occurs and the cellulose structure changes to cellulose II (Sharma et al., 2015). A broad peak at 20.6° was chosen for the amorphous region. The *CrIs* for $PSNF_{ND}$ and $PSNF_D$ were calculated as 69% and 67%, based on Segal's method, whereas the peak fitting method resulted in *CrIs* of 43% and 46% respectively.

3.5. Optical properties of paper sludge nanofibres

Nanopaper exhibits excellent transmittance properties depending on how small the nanofibre diameters are, in comparison to the wavelength of visible light. Additionally, if the CNFs are densely packed, air scattering can be supressed thereby improving the transparency of the material. Fig. 7 shows the transmittance spectrum of 0.2 wt% suspension of PSNF. Both nanopapers prepared from never-dried and dried PSNF showed a low visible light transmittance of 32.4% (at 600 nm wavelength). CNFs has shown up to 90% transmittance in other studies making materials suitable for applications in electronic devices (Alila et al., 2013; Isogai et al., 2011; Nogi et al., 2009). Nevertheless, the PSNF nanopapers exhibit 15.8% transmittance of UV light at 300 nm, which is a desirable property for UV absorption in packaging applications. This low UV transmittance has been previously noted by other work on nanopapers made from bacterial cellulose impregnated with gelatin (Quero et al., 2015). Hot pressing the PSNF suspension into nanopaper increases the transparency of the sheet as shown in Fig. 7; the opacity test resulted in 44 ± 0.3%. The increased transparency is due to capillary action during water evaporation from the sheets causing the fibres to be densely packed together allowing more light to pass through the sheets. In addition the surface roughness is also reduced (Nogi et al., 2013).

3.6. Mechanical properties of paper sludge nanofibres network

PSNF samples were collected at different time intervals and prepared into sheets for tensile tests as shown in Fig. 8. All samples exhibited non-linear stress-strain curves typical for nanopaper sheets. An increase in the fibrillation time resulted in a proportional increase of tensile strength in the nanopaper sheets. $PSNF_{ND}$

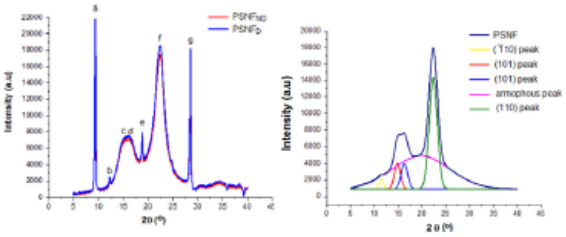

Fig. 6. X-ray diffraction patterns of nanopapers prepared from $PSNF_{ND}$ and $PSNF_{D}$ highlighting crystalline peaks from talc (left) and X-ray diffraction pattern of PSNF nanopaper after peak fitting (right).

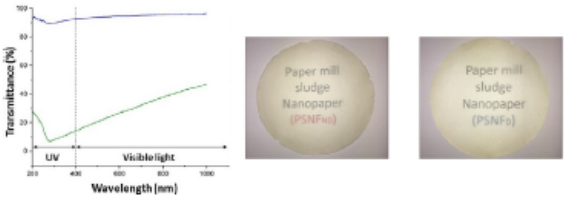

Fig. 7. (From left) Typical light transmittance spectra of PSNF suspension (green line) with water (blue line) for reference, and typical images of nanopaper prepared from $PSNF_{ND}$ and $PSNF_{D}$.

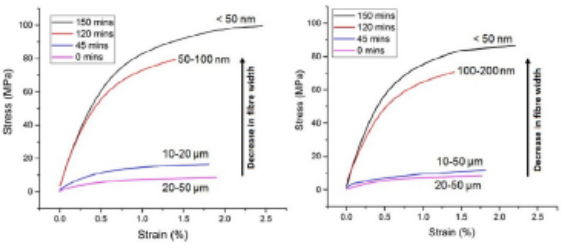

Fig. 8. Typical stress-strain curves of nanopapers produced from PSNFs collected at different fibrillation times showing the effect of a decrease in fibre/fibril width (from 20 to 50 µm to <50 nm) on tensile strength $PSNF_{ND}$ (left) and $PSNF_{D}$ (right).

showed double increases in tensile strength after 45 min of fibrillation whereas the $PSNF_{D}$ increased slightly as larger fibres were still present. After 150 min of fibrillation tensile strength values of ~ 92 MPa and ~ 85 MPa were ultimately achieved for dried and never-dried sludge. An increase in the mechanical properties of the cellulose paper is attributed to an increase in the amount of fibril-fibril bonding; this effect is thought to be due to an increased surface to volume ratio of the fibrils as they are processed.

Mechanical properties of paper sludge nanopapers were found to be similar to a previous study on nanocellulose derived from dissolving cellulose sludge (Jonoobi et al., 2012); data are shown in Table 2. Previous studies of cellulose nanopapers prepared from

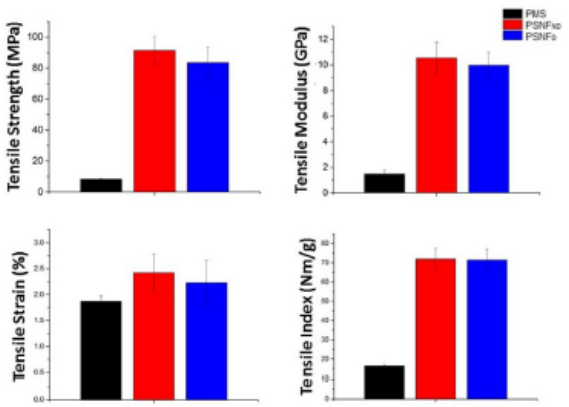

Fig. 9. Mechanical properties of the nanopapers derived from paper mill sludge; tensile modulus, tensile strength, maximum strain and tensile index.

chemical treatment of wood pulp have reported values of 135 MPa and 11 GPa for tensile strength and elastic modulus (González et al., 2014). Additionally, different variations in the tensile modulus of cellulose nanopapers have been reported in the literature; values range between 9.4 GPa and 14 GPa (Henriksson et al., 2008; Lee et al., 2012; Quero et al., 2010).

Fig. 9 shows that the $PSNF_{D}$ exhibited mechanical properties comparable to $PSNF_{ND}$, the results show an 8-fold increase in the mechanical properties of nanopapers from raw sludge fibres to nanofibres. Based on the null hypothesis that there is no significant difference between the mechanical properties of the $PSNF_{ND}$ and $PSNF_{D}$ samples. A Students T-test revealed P values of 0.32, 0.11, 0.85, 0.37 for tensile modulus, tensile strength, tensile index and tensile strain. The ($p > 0.05$) indicated no statistical significant difference in the mechanical properties.

3.7. Cost evaluation

The end-use price of CNF remains difficult to assess due to varying production methods influencing costs. The average selling price of CNF is estimated to range between $700-$1200/ton (Nechyporchuk et al., 2016). Moreover, market research has shown that the production of nanocellulose is currently valued at $65 M with an annual growth rate of 30% estimated to reach $530 M by 2021 (Zion research analysis, 2016). Thus the 4000 tonnes of PMS produced annually at the mill has a potential revenue worth $2.8 M. Sludge can also be considered a free raw material which makes up for some of its production cost. A major barrier for the commercialisation success of CNF is the high energy cost required for mechanical disintegration. The energy consumption of the PMS fibrillation process was recorded as 30.6 MJ/kg (8.5 kWh/kg) for never-dried sludge and 33.5 MJ/kg (9.3 kwh/kg) for dried sludge. These results are similar to fibrillating process of various wood pulps which averaged 36 MJ/kg (10 kWh/kg) (Lahtinen et al., 2014).

Table 2
Average mechanical properties of paper mill sludge sheets.

	Modulus E [GPa]	Tensile Strength [Mpa]	Tensile Strain [%]	Tensile Index [Nm/g]
PMS_{ND}	1.7 ± 0.3	8.2 ± 0.3	1.8 ± 0.1	16.4 ± 0.9
PMS_{D}	1.5 ± 0.4	7.9 ± 0.2	1.9 ± 0.3	14.3 ± 0.7
$PSNF_{ND}$	10.6 ± 1.2	91.5 ± 8.8	2.4 ± 0.4	71.9 ± 5.6
$PSNF_{D}$	10.1 ± 1.0	85.4 ± 10.2	2.2 ± 0.4	71.5 ± 5.6
(Jonoobi et al., 2012)	8.0 ± 1.0	96 ± 4	1.5 ± 0.5	–

Table 3
Cost evaluation of never-dried and dried PMS.

	PMS_{ND}	PMS_D
Transport (£/ton-km)	1.33	0.53
Storage (£/ton)	9	18
Fibrillation (£/ton)	425	465
Total Cost (£/ton)	435	483

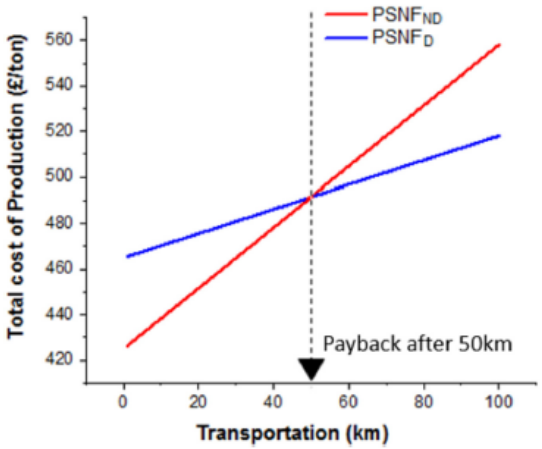

Fig. 10. Payback evaluation for producing CNF from dried PMS in comparison with never-dried PMS.

However, in comparison to a previous study of nanocellulose derived from dissolving pulp sludge, less energy was reported 4.68 MJ/kg (1.3 kWh/kg) (Jonoobi et al., 2012). Nevertheless a higher energy consumption of 108 MJ/kg has also been reported for wood pulp fibrillated using a homogeniser (Eriksen et al., 2008). The cost for processing CNF from never-dried and dried sludge is £425/ton and £465/ton respectively based on average the UK wholesale electricity market price of £50/MWh (1000 kWh) (OFGEM, 2018). The high water content in PMS up to 60% largely determines transport and storage (Ochoa de Alda, 2008). The cost evaluation is shown in Table 3, where the cost of transportation is 0.53 £/ton-km calculated based on a UK-based average heavy goods vehicle consumption of 15 mpg (Department for Transport, 2016), a labour rate of £10/hr and a fuel cost of £1.10/litre. The cost of storage was calculated based on an energy consumption of 180 kWh/ton for cold storage and 360 kWh/ton for drying based on a specific energy consumption of 0.6 kWh kg^{-1} H_2O (Mäkelä et al., 2017).

To highlight the advantage of using dried PMS over never-dried PMS, the cost savings made during transportation of dried sludge must pay back the £40/ton increase when fibrillating dried PMS. The payback is calculated in Fig. 10, by plotting the transport distance against total cost of producing PSNF from PMS_{ND} and PMS_D. The evaluation revealed that the use of dried sludge for CNF production is favourable over never-dried sludge in situations when the sludge material is transported over 50 km from the mill for processing or kept in cold storage longer than 14 days.

4. Conclusions

A major limitation of industrial scale utilisation of biomass waste is in the transportation cost and microbial degradation. This study draws comparison between the production of CNF from dried and never-dried paper mill sludge which showed no significant difference in these materials in terms of their mechanical performance. Hence, dried sludge offers an economic advantage to alleviate challenges of microbial activity, storage and transportation, without compromising on the properties of the CNF. The nanopapers produced from both never-dried and dried PSNF showed high stiffness (~11 GPa and ~10 GPa) which could be used to improve mechanical properties of polymers limited by low mechanical strength such as polyvinyl alcohol (PVA). The low opacity (44%) and low UV transmission of the PSNFs sheets also reveal potential application in the packaging field. Sludge obtained from various paper mills creates an opportunity for largescale valorisation to produce CNF with a free raw material. However, the variability in sludge composition from different mills poses a disadvantage in scaling up production. Thus, further investigation on the effect of the fillers contained in the sludge will provide more knowledge on developing a consistent product.

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Structural packaging foams prepared by uni-directional freezing of paper sludge cellulose nanofibres and poly (vinyl alcohol)

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ABSTRACT

Porous foams from cellulose nanofibres (CNF) and poly-vinyl alcohol CNF/PVA were prepared by uni-directional freezing to create a homogeneous pore structure. The CNF was derived from paper mills sludge (PMS), a by-product of paper manufacturing waste-water treatment. Sodium tetraborate decahydrate (borax) was used as a crosslinking agent. The density of the CNF/PVA foams were 0.03 g cm^{-3} with a compressive strength of 116 kPa at 20% strain. The foams were competitive to commercial expanded polystyrene (EPS) foam.

1. Introduction

Polymer foams produced from polyurethane (PU), polystyrene (PS) are rigid, lightweight and energy absorbent desirable for packaging applications. However, these materials largely rely on petroleum crude oil as feedstock, use blowing agents that emit greenhouse gases and leach out microplastics in aquatic habitat. Thereby leading to significant environmental impacts [1,2]. Meanwhile, environmental friendly alternatives such as petroleum based bio-polymers; Poly (Vinyl alcohol) PVA and renewable resource based bio-polymers; Poly-lactic Acid (PLA), Polyhydroxyalkanoates (PHAs) have limitations in foam applications due to their low mechanical properties [2,3]. Thus, researchers have employed reinforcement fillers like silica, carbon nanotubes (CNT), cellulose nanofibers (CNF) and graphene to aid their performance [4–6]. Particularly, CNF is an interesting material for reinforcement in foams due to its high aspect ratio, biodegradability, flexibility and crystallinity [7]. However, CNF is limited by agglomeration if used in foam production processes such as compression moulding, injection moulding, extrusion, solvent exchange and spin coating [8]. To improve dispersion and increase the addition of CNF, ice-templating can be used for fabrication of polymer foams. Therefore, this study investigates the use of ice-templating to prepare packaging foams from CNF and PVA to be compared with commercial petroleum based foams. The fundamental process of ice-templating (IT) is based on the growth of ice crystals in a solvent which sublimates, leaving an orderly pore formation in the material [9].

CNF was derived from paper mill sludge (PMS) a by-product of paper mills proven to be a successful source of nanocellulose production due to its reduced processing cost, and no requirement for chemical treatment [10]. The CNF and PVA solution was crosslinked with Sodium tetraborate decahydrate and using the uni-directional freezing method. This entails a liquid nitrogen bath <−180 °C in an insulated polystyrene vessel, a copper rod used as a localised cold surface allowing the solution to freeze from the bottom up (Fig. 1). This freezing method influences the ice growth, pore formation and mechanical properties of the foam [11].

In the literature, ice-templated PVA foams have been prepared with CNF, chitin nanowhiskers, montmorillonite (MTM) clay, crosslinking agent to enhance the pore structure of foams [12–15]. Uni-directional freezing method has also been used to produce fire retardant phosphorylated-CNF foams [16] and graphene oxide CNF foams [17]. However, uni-direction freezing of CNF/PVA has not been studied, most studies employ fast freeze method by dipping the solution in liquid nitrogen or slow freezing whereby the solution is refrigerated at −20 °C for 24 h [15,18]. Slow freezing hinders the orderly growth of ice crystals as the sample is frozen from all directions which in turn affects the mechanical properties of the foam.

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2. Materials and methods

2.1. Materials

PMS obtained from a UK mill producing kitchen towel rolls was mechanically homogenised using a supermass colloider MKCA6-3 (Masuko Sangyo Co, Japan), details on CNF preparation can be found in our previous study [10]. The CNF had an average width of 50 nm, crystallinity index of 43%, chemical composition of 74% cellulose and 2.6% hemicellulose. PVA was purchased from Sigma Aldrich with MW 89,000–98,000 g/mol, 99+% hydrolysed. Sodium tetraborate decahydrate ($Na_2B_4O_7{\cdot}10H_2O$) also known as borax, was purchased from Sigma Aldrich with MW: 381.37 g/mol.

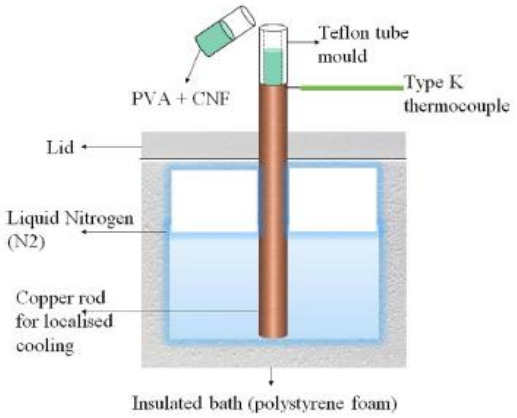

Fig. 1. Experiment set-up for uni-directional freezing.

2.2. Preparation of CNF/PVA foams

The PVA solution was prepared by diluting 2 g of PVA in 100 ml of distilled water (2 wt%) at 80 °C, vigorously stirred for 4 h. 5 mg/ml of Borax was added to the PVA solution as a crosslinker at. 100 ml 2 wt% suspension of CNF was added to the PVA and borax solution and vigorously stirred for 12hrs. Each foam was prepared from a 10 ml (2 wt% PVA, 2 wt% CNF and 0.5 wt% borax) solution of 50:50 CNF/PVA using the directional freezing method. Each sample was frozen after 10 mins and placed in a freeze dryer at −52 °C and 0.1 Pa.

2.3. Characterisation of CNF/PVA foams

Compression test was conducted using an Instron 5500R universal testing machine with 100 N load cell at 1 mm/min crosshead speed in a conditioned environment of 23 °C and RH 51%. After conditioning, the apparent density (ρ app) of the samples were calculated. Eight cylindrical shaped specimens were tested. Compres-

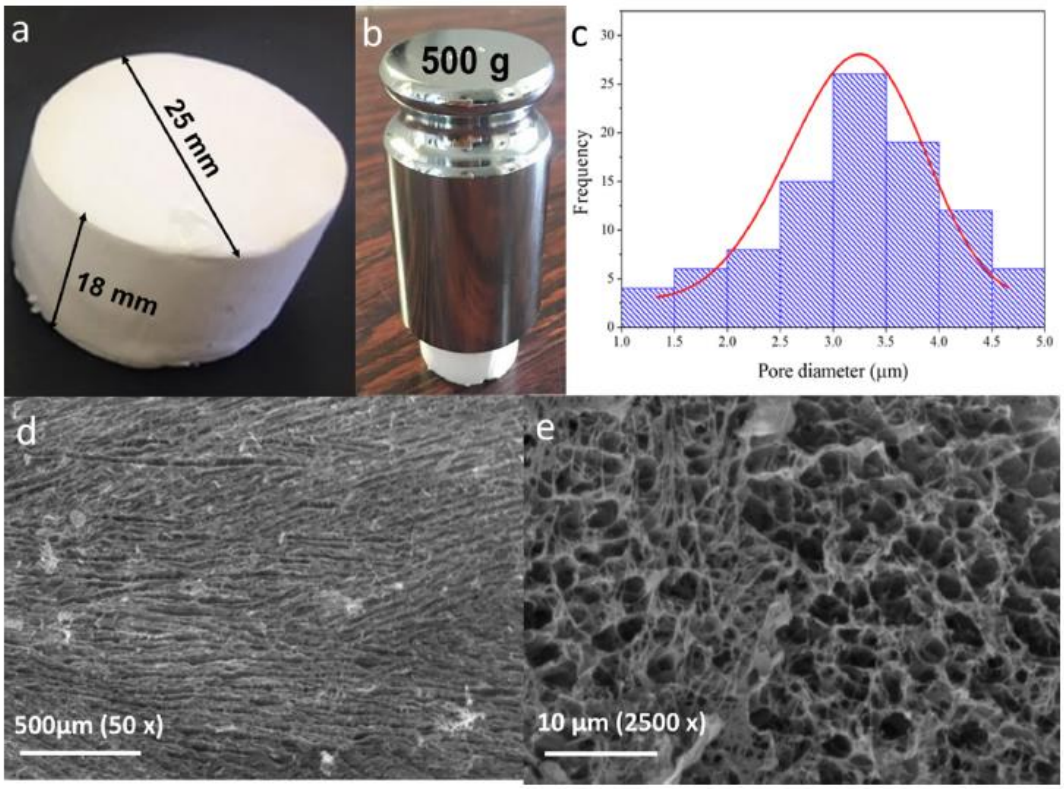

Fig. 2. (a) Physical foam sample (b) Foam sample supporting over 2000 times its weight (c) histogram of foam pore size with normal distribution curve (d) SEM scan of foam at 50x magnification (e) 2500x magnification.

sive strength was calculated at 10% strain and compressive modulus calculated from the linear portion of the stress-strain curve. The foams were cut vertically along the direction of freezing and coated with gold particles to observe their pore size using Scanning Electron Microscope (SEM) JSM-6490LV, JEOL (Japan) and measured using imageJ software (USA).

3. Result and discussion

3.1. Morphology

The foam weighted an average of 0.238 g, 25 mm in diameter and 17.3 ± 1.4 mm in height which was used to calculate the apparent density (ρ_{app}) of 28 kg/m^3. The foam porosity is calculated using the equation $(1-\rho_{rel})$ where ρ_{rel} is the quotient of (ρ_{app}) divided by the cell-wall density (ρ_{cell}) [19]. The cell-wall density is taken as the 50:50 ratio of 1500 kg/m^3 for cellulose and 1190 kg/m^3 for PVA. The average porosity of the foams resulted in 97.9 ± 0.3%. Unidirectional freezing allows the foam to exhibits a lamellar channel structure in the direction of freezing [11,20], this can be observed at a lower magnification in Fig. 2c. At higher magnification (Fig. 2d) the foam shows cellular pores with honeycomb-like structure with an average pore size of 3.2 ± 0.9 μm. The higher aspect ratio of CNF and entanglement affects the orientation of the pores which plays a major role in the morphology of the cell wall and enhances reinforcement of the PVA foam. This effect was explained in an early study of CNF reinforced starch foams [21].

3.2. Mechanical properties

The stress-strain curve of the foam (Fig. 3a) exhibits a linear-elastic region up to 10% strain followed by a plateau in stress expected of a rigid polymer foam [22]. The average compressive strength of the foam at 10% and 20% strain is 0.082 MPa (82 kPa) and 0.100 MPa (100 kPa) respectively. In (Fig. 3b) an Ashby plot of the density vs compressive strength of CNF/PVA foams in the literature prepared by the slow freezing is shown [12,23]. PB-CNF I foam prepared by Han et al., despite being 3 times denser (110 kg/m^3) revealed a compressive strength of 0.150 MPa. The CNF/PVA foams in this work show competitive compressive strength at 10% strain. Hence this implies the influence of the unidirectional freezing method on the foams mechanical properties.

The elastic modulus was determined from the slope of the linear portion of the curve resulting in an average of 930 ± 10 kPa. Energy absorption was calculated from the area under the stress-strain curve reaching an average of 3.2 kJ/m^3 at 30% strain.

3.3. Comparison with commercial EPS

The CNF/PVA foam can be classified for high duty in accordance with BS 3837-1:2004 [25]. The CNF/PVA foam was compared with compressive strength data of commercially available foams (Table 1). Jabfloor EPS100 (Jablite, UK) is expanded polystyrene foam used as floor insulation in offices and schools [26]. Ethafoam™ 180 (Dow Chemicals, USA) is a polyethylene foam used in packaging applications and for cushioning [27].

4. Conclusions

Paper mill sludge processed into cellulose nanofibres was cross-linked with polyvinyl alcohol to produce a sustainable polymer foam capable of supporting over 2000 times its weight. The foam is suggested as protective packaging. However, the CNF/PVA foams is prone to water absorption, increasing the content of borax in future study could improve moisture absorption. Coating the foam surface with a hydrophobic film or spray may aid reduction in water absorption. Nonetheless, water solubility is an advantage

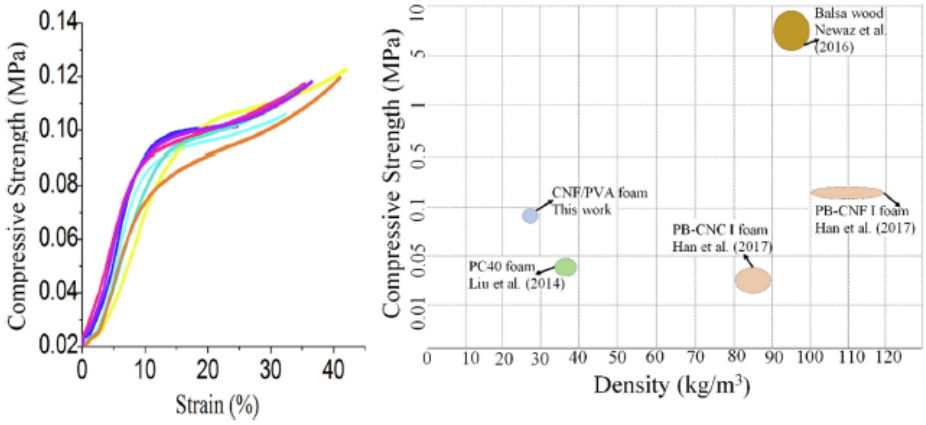

Fig. 3. Mechanical properties of CNF/PVA foams (a) Compressive stress-strain curve (b) Density vs compressive strength of foams and balsa wood as reference [24].

Table 1
Comparison of CNF/PVA to commercial EPS.

Foam type	Material	Density (kg/m^3)	Compressive strength @ 10% strain (kPa)	Compressive strength @ 20% strain (kPa)
Jablite EPS 100	Polystyrene	20	100	–
EthafoamTM	Polyethylene	29	30	50
This work	PVA-CNF	28 ± 3	82 ± 7	100 ± 3

during disposal and decomposition in single-use packaging applications.

Declaration of Competing Interest

There authors declare that there are no known conflict of interested associated with the work.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.17862/cranfield.rd.7993436.v1.

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