

# **Valorisation of Paper Recycling Residue Contaminated with Plastic into Valuable Fuel Products by Pyrolysis**

*by*

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## Abstract

The recent drive towards a sustainable green economy, along with changing environmental legislation to combat waste pollution, have promoted the search for alternative disposal techniques. This study focuses on the thermochemical conversion namely pyrolysis of three waste streams from a paper recycling mill contaminated with plastic and a sequential processing route where the three waste streams are first subjected to fermentation to produce bioethanol followed by pyrolysis. The primary objective of this study was to assess different valorisation techniques (pyrolysis and fermentation-pyrolysis) for the disposal of real world industrial waste streams, composed of lignocellulosic fibre and plastic that are currently disposed of at landfill sites, to produce fuel products for energy generation at a paper recycling mill as an alternative to landfilling.

The first part of this study considered standalone pyrolysis (fast or slow) for the valorisation of three different paper mill wastes, classified as rejects. Slow pyrolysis of paper mill waste favoured the production of an energy dense char with an HHV and yield of up to 32.9 MJ/kg and 77.3 wt.% respectively at a conversion temperature as low as 300 °C. The fast pyrolysis resulted in significant yields of the energy dense condensable (liquid) phase (HHV of up to 41.7 MJ/kg), with a yield of up to 53.6 wt.% which being obtained at conversion temperatures of 550 °C, which was ~ 21 wt.% higher than the yield obtained for slow pyrolysis. Increasing the conversion temperature to 550 °C for both slow and fast pyrolysis had a detrimental effect on the quality of the char product, with the HHV of char produced decreasing to between 16.9 to 21.7 MJ/kg for both pyrolysis processes.

The second part deals with converting the lignocellulosic fibrous component in the waste into bioethanol via fermentation. The fermentation of the three waste streams resulted

in only one being chosen for scale up production. As the waste streams (W2 and W3) that contained significant amounts of plastic, resulted in clumping of plastic during fed batch fermentation, which prevented subsequent substrate feeds from reaching the fermentation broth. The waste stream W1 that contained the largest percentage of glucan (56.9 daf wt.%) and the smallest amount of plastic < 5wt.% produced satisfactory results, with ethanol concentration of 39.8 g/l being obtained. Pyrolysis processing of the fermentation residue resulted in the production of an condensable (liquid/wax) energy dense phase with yield of up to 13.2 wt.% for slow and 26.3 wt.% for fast pyrolysis with an associated HHV of 35.1 and 32.1 MJ/kg respectively. This was ~17 MJ/kg higher than that produced from the slow and fast pyrolysis of the untreated waste stream.

The last part of this study assessed the economic viability of implementing pyrolysis in a waste to energy perspective at a paper mill as an alternative to waste disposal by landfilling, and resulted in a minimum fuel selling price (MFSP) of between 1.12 to 1.48 \$/kg which was 2 to 3 times greater than the target value of 0.65 \$/kg at current waste production rates. A study on scale revealed that an increase in size from current waste production rates of between 540 to 1378 kg/hr up to 8700 kg/hr greatly reduced the MFSP to between 0.27 \$/kg to 0.73 \$/kg, which was comparable to the targeted value of 0.65 \$/kg. The additional waste required could be achieved by combining the waste streams produced at a mill and by acquiring the waste produced by similar paper mills in the vicinity.

The study has shown that pyrolysis of paper mill waste contaminated with plastic can be a viable alternative to landfilling with fuel products being produced that have a similar calorific value to traditional fuels. It is recommended that the study be scaled up to pilot scale along with testing of the combustion behaviour of the products from pyrolysis with traditional waste fuels. Were possible the waste streams from neighbouring industrial facilities can be combined in order to reach the required scale for economic viability.

## Opsomming

Die onlangse beweging na 'n volhoubare groen ekonomie, tesame met omgewingswetgewing wat verander om afvalbesoedeling te bestry, het die soeke na alternatiewe wegdoeningstegnieke verskerp. Van belang in hierdie studie, is die termochemiese prosesseringsroete, genaamd pirolise, en 'n sekwensiële prosesseringsroete waar die afvalvoerstof eers blootgestel is aan fermentasie om bioetanol te vervaardig, gevolg deur pirolise. Die primêre doelwit van hierdie studie was die assessering van verskillende valoriseringstegnieke (pirolise en fermentasie-pirolise) vir die wegdoening van industriële afvalstrome, wat bestaan uit lignosellulosiese veselstof en plastiek, om brandstofprodukte te vervaardig as 'n alternatief tot opvullingsterreine.

Die eerste deel van die studie het die onafhanklike pirolise (vinnig of stadig) vir die valorisering van drie verskillende papiermeul afval, geklassifiseer as uitskot, in ag geneem. Stadige pirolise van papiermeulafval het 'n energie-digte verkooltsel gelewer met 'n HHV en massa-opbrengs van tot 32.9 MJ/kg en 77.3 wt.%, onderskeidelik, by 'n omsettingstemperatuur van so laag as 300 °C. Die vinnige pirolise het 'n beduidende opbrengs van energie-digte kondenseerbare (vloeistof) fase (HHV van tot 41.7 MJ/kg) tot gevolg gehad, met 'n massa-opbrengs van tot 53.6 % wat behaal is by 'n omsettingstemperatuur van 550 °C. Dit was ~ 21 wt.% hoër as die opbrengs verkry met stadige pirolise. Die verhoging in omsettingstemperatuur na 550 °C vir beide stadige en vinnige pirolise, het 'n nadelige effek op die kwaliteit van die verkoolselproduk tot gevolg gehad, met die HHV van verkooltsel geproduseer wat tot tussen 16.9 en 21.7 MJ/kg vir beide pirolise prosesse afgeneem het.

Die tweede deel handel oor die omsetting van die lignosellulosiese veselagtige komponent in die afval na bioetanol deur middel van fermentasie. Die fermentasie van die drie afvalstrome het tot gevolg gehad dat slegs een gekies is vir vergrote skaal produksie.

Omdat die afvalstrome (W2 en W3) wat beduidende hoeveelhede plastiek bevat het die verklompings van plastiek tydens die voerbondel fermentasie tot gevolg gehad het, het dit die daaropvolgende substraat toevoere verhoed om die fermentasiesop te bereik. Die afvalstroom W1 wat die grootste persentasie glukose (56.9 wt.%) bevat het, en die kleinste hoeveelheid plastiek < 5 wt.%, het bevredigende resultate getoon, met etanolkonsentrasie van 39.8 g/l wat verkry is. Pirolise prosessering van die fermentasie reste, het tot die produksie van 'n kondenseerbare (vloeistof/was) energie-digte fase tot gevolg gehad, met opbrengste van tot 13.2 wt.% vir stadige en 26.3 wt.% vir vinnige pirolise met 'n geassosieerde HHV van 35.1 en 32.1 MJ/kg, onderskeidelik. Dit was ~17 MJ/kg hoër as dit wat geproduseer is deur stadige en vinnige pirolise van die onbehandelde afvalstroom.

Die laaste deel van die studie het die ekonomiese lewensvatbaarheid van die implementering van pirolise van 'n afval tot energie perspektief by 'n papiermeul as alternatief tot afvalwegdoening by die opvullingsterrein, geassesseer. Dit het 'n minimum brandstof verkoopsprys (MFSP) van tussen 1.12 tot 1.48 \$/kg tot gevolg gehad, wat twee tot drie keer groter is as die teikenwaarde van 0.65 \$/kg teen huidige afval produksie koerse. 'n Studie op skaal het gewys dat 'n toename in grootte van huidige afval produksie koerse van tussen 540 en 1378 kg/hr tot 8700 kg/hr die MFSP grootliks verminder tot tussen 0.27 \$/kg en 0.73 \$/kg, wat vergelykbaar is met die teikenwaarde van 0.65 \$/kg. Die addisionele afval benodig kan bereik word deur die kombinasie van afvalstrome vervaardig deur 'n meule en deur die afval vervaardig deur soortgelyke papiermeule in die omgewing te bekom.

Die studie het gewys dat pirolise van papiermeulafval gekontamineer met plastiek, 'n lewensvatbare alternatief tot opvullingsterreine kan wees, met brandstofprodukte wat vervaardig word met 'n soortgelyke hittewaarde as tradisionele brandstowwe. Dit word aanbeveel dat, waar moontlik, die afvalstrome van nabygeleë industriële fasiliteite

gekombineer word om die skaal te bereik wat voldoende is vir ekonomiese lewensvatbaarheid.

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# Chapter 1: Introduction

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## 1.1 Contextual Background

The energy demands of both developed and developing nations are expected to grow by approximately 50 % by 2040 [1]. The current supply of energy is dominated by the use of non-renewable energy (coal, oil, gas and nuclear), which accounts for approximately 86 % of the world's energy demands [1] with the remaining 14 % being comprised of renewable and sustainable energy resources [1]. Concerns over global warming and the decreasing supply of fossil fuels has prompted the search for sustainable forms of energy and the optimal use of the current available resources. One abundant source of energy that is poorly exploited is industrial waste that is comprised of a combination of either organic waste, plastic or a variety of other contaminants. The continuous generation of waste by households and industrial processes is becoming an ever increasing problem in both developed and industrialized countries [2–4] as the disposal of this waste by landfilling is undesirable due to the negative environmental effects and the impact on global warming that the disposal of this waste at landfill sites has [5–7].

The paper recycling industry in South Africa produces large quantities of waste (3264-4827 tons/month per industrial site) that is currently disposed of by landfill and which can be grouped into two main categories, paper waste sludge (PWS) and rejects [4,8]. PWS is comprised predominately of lignocellulosic fibres that have been discarded in the manufacturing of paper due to short fibre length and poor fibre quality [9,10]. Rejects originate from the pre-sorting activities that occur before the paper machine as a result of using recycled fibres as feedstock and are comprised mainly of lignocellulosic fibres and plastics along with small amounts of other contaminants [3,4,9]. Due to increasing costs and

the negative environmental impacts associated with landfilling [3,11], an alternative disposal technique is required.

Low energy dense industrial waste represents a substantial source of energy that can be converted into valuable chemicals or an energy dense fuel product (liquid or solid) via either thermochemical or biological processing [12–14]. Fermentation a type of biological processing, utilises biological catalysts (enzymes, microbes) to convert the polysaccharide fraction of the biomass component of industrial waste into fermentable sugars to produce ethanol [15–17]. Thermochemical conversion covers a wide range of processes such as combustion, gasification and pyrolysis. Pyrolysis involves the thermal degrading of waste in the absence of oxygen to produce energy dense products (oil/wax, char and gas) [18–20]. The conversion of PWS fibres via hydrolysis-fermentation has been shown to be a promising option for bioethanol production as the fibres are mainly comprised of cellulose [17]. Such conversion of PWS produces a fermentation residue that contains significantly less cellulose and is enriched in lignin and plastic[11,21,22], making it an improved feedstock for further conversion via pyrolysis. The presence of plastic in the starting feedstock for pyrolysis is likely to improve the quality of the final fuel products, as plastic is hydrocarbon in nature, it is likely to decompose into a stable, energy dense majority hydrocarbon product.

The distribution of products from pyrolysis is largely dependent on the feedstock properties, type of pyrolysis process (slow or fast) and the final temperature of conversion [23]. An advantage of pyrolysis is its ability to convert both the lignocellulosic fibre and plastic components into useable products in a single process. Fast pyrolysis utilises rapid heating rates ( $> 250\text{ }^{\circ}\text{C}/\text{min}$ ) and short vapour residence times ( $< 30\text{ s}$ ) to promote the formation of a condensable product (oil/wax) [24], whereas slow pyrolysis utilises slow heating rates ( $< 30\text{ }^{\circ}\text{C}/\text{min}$ ) and long vapour residence times (up to 60 min) for the promotion of equal amounts of products from lignocellulosic biomass (char, oil/wax and gas) [23]. The

oil and char products obtained from biomass have calorific values of between 17 -23 MJ/kg (oil) and 18 - 30 MJ/kg (char) [10,25]. The pyrolysis of plastic typically generates limited amounts of char. The oil/wax produced from plastic pyrolysis has a calorific value of between 30 - 45 MJ/kg, depending on the type or mixture of plastic waste under investigation [26]. The char and oil products from pyrolysis can be used for electricity generation or as a means to provide process heat at industrial plants via co-combustion with existing fuel sources [27,28]. The gas produced is usually used onsite to provide the process energy needed for processing activities associated with pyrolysis (heat for drying and pyrolysis, etc.) [23,29–31]. The utilisation of industrial waste to produce energy products via pyrolysis or a sequential fermentation-pyrolysis approach, where the residue from fermentation is used as the feedstock for pyrolysis conversion, has the potential to be a viable form of waste mitigation.

Literature about pyrolysis of fibre plastic mixtures has predominately been studied as mixtures of lignocellulosic biomass or pure cellulose with a known amount of a single pure plastic polymer. These studies have shown that it is possible to improve the total liquid yield when compared to the stand alone pyrolysis of biomass or pure cellulose polymer with increases in the total liquid yield of between 10 to 30 wt.%, depending largely on the predetermined mixture under investigation [32–38]. Further more the addition of a pure plastic polymer has resulted in the increase in the quality of the condensable product with the energy density increasing by up to 25 MJ/kg [33-35]. Studies on the application of pyrolysis for the conversion of real world industrial waste streams containing a mixture of fibre-plastic in unknown proportions is limited along with the fermentation of industrial waste composed of fibre and plastic waste to bioethanol. This study will focus on the conversion of real industrial waste streams containing unknown amounts of lignocellulosic and plastic waste that are produced from the various sorting and pulping operations at a paper mill that utilises

recycled fibre as a feedstock and that are currently disposed off at landfill sites, with the aim of producing fuel products via pyrolysis (fast or slow) or sequential processing (fermentation-pyrolysis), where fermentation is used to produce bioethanol from the lignocellulosic component of the waste stream followed by pyrolysis (fast or slow pyrolysis) for the generation of energy products that can be used by a paper recycling mill to produce process energy thereby reducing their dependence on fossil fuel resources. After which a techno-economic evaluation of the different processes will be conducted to evaluate the economic viability of the process scenarios.

## 1.2 Overall Aim

The overall goal of this project is to assess the potential of using pyrolysis or a sequential processing route (fermentation-pyrolysis) as a means of converting various paper mill residues, that contain an unknown mixture of fibre and plastic, into valuable energy products that can be used by a paper mill to produce process energy. The performances in terms of product yields, product qualities and energy yields as well as the economic benefits of the different processing routes will be investigated for the ultimate conversion of the industrial waste feedstock to provide a useful alternative to disposal by landfilling. The objectives of this study are presented in detail in Chapter 3

## 1.3 Thesis Outline

This dissertation is organised into 8 chapters, **Chapter 2** presents the origin and composition of paper waste sludge and rejects, and discusses the potential of pyrolysis and fermentation processes for their conversion. **Chapter 3** details the main objectives addressed in this study. **Chapter 4** presents the results obtained from the slow pyrolysis of the waste streams used in this study as well as the energy conversion assessment. **Chapter 5** details the results from

fast pyrolysis of the waste streams and the potential use of the respective pyrolysis products.

**Chapter 6** presents the results from the sequential processing of waste streams via fermentation-pyrolysis and the mechanisms affecting the process route. **Chapter 7** presents the results from the techno-economic study, comparing some promising processing routes identified in this dissertation and the industrial viability of each. **Chapter 8** provides the main conclusions and recommendations.

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## Chapter 2: Literature Review

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In this section, after a description of rejects the type of feedstock considered in this work, an overview of the literature on pyrolysis of paper waste sludge and plastic is provided. The origin, physico-chemical characterisation and pyrolysis behaviour, along with the applicability of pyrolysis to convert said waste into fuel products, is discussed.

### 2.1 Waste Feedstocks from Pulp and Paper Mills

In South Africa, the pulp and paper industry contributed approximately 0.5 % to the South African Gross Domestic Product (GDP) for 2014 [1] and can be divided into two main categories based on the nature of the raw feedstock: virgin pulp (typically pulp from the harvesting of trees) and recycled fibre (pulp from the recovery of paper and other items from various recycling activities) [2].

Pulp and paper mills make use of either virgin pulp or recycled fibre for the production of a wide variety of products (tissue, board, paper) and other cellulose based products. After initial pulping, before the raw material reaches the paper machine, it undergoes a wide variety of processing (sorting, de-inking, bleaching etc) which is largely dependent on the type of end product (Figure 2-1). Sorting is done to remove poor unsuitable fibre and unwanted contaminants (plastics, metals, etc. present during recycling) from the pulped streams. Pulp and paper mills produce two types of main waste namely paper waste sludge and rejects. The first, paper waste sludge (PWS), is collected from the primary clarifier. PWS is comprised predominately of short degraded fibres that are unsuitable as a raw material for paper making as well as a variety of other contaminants (inks, glues, clays and inorganics) that may be used in the recovery process [3].

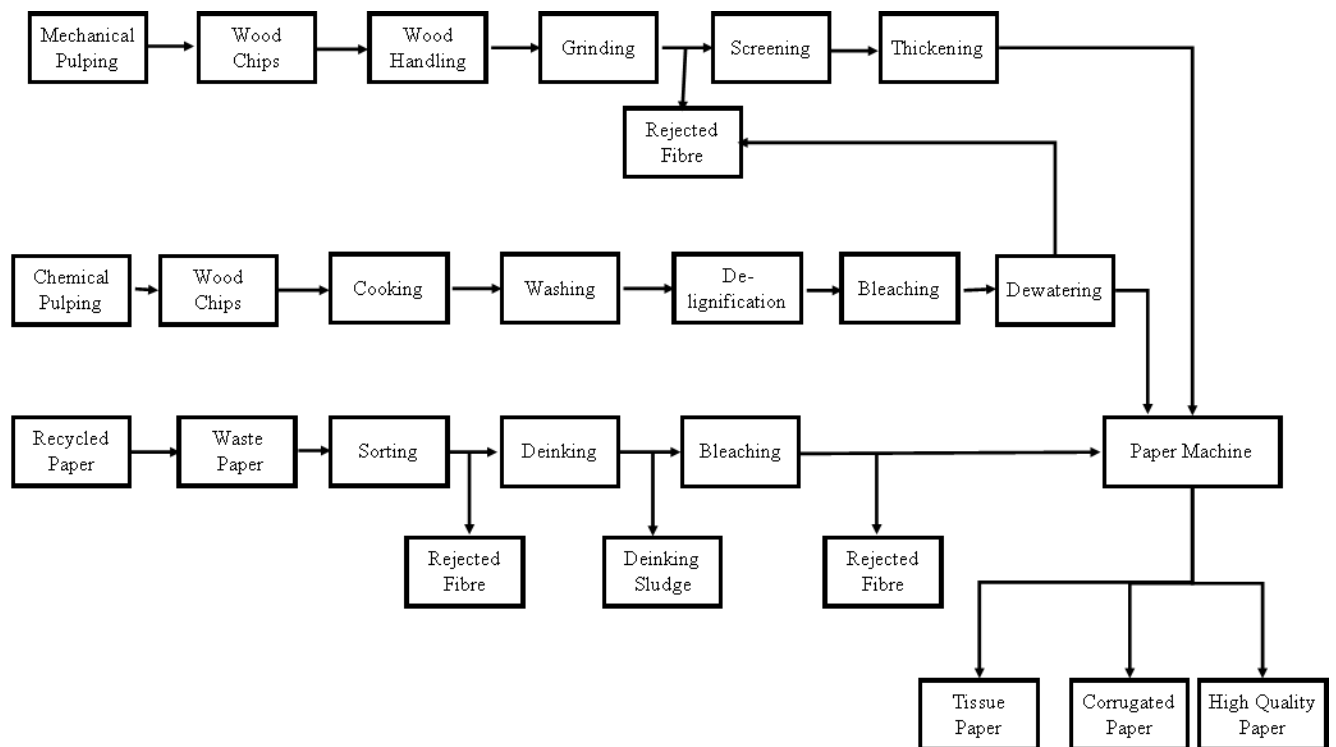


Figure 2-1: Process flow of common paper manufacturing processes (adapted from Gottumukkala et al. [2])

The second is a group of waste streams that can be classified as rejects. Rejects originate from paper mills that make use of recycled fibre (Figure 2-2) as feedstock and originate from the various processing activities that occur before the paper machine.



Figure 2-2: Feedstock used at a fibre recycling mill

Processing residues like PWS are discarded in the paper making process due to the poor quality of the fibre and due to the various contaminants such as plastic that is found in the

waste stream. Rejects, which can be seen in Figure 2-3, are currently disposed of by landfilling as the primary disposal technique [3,4].

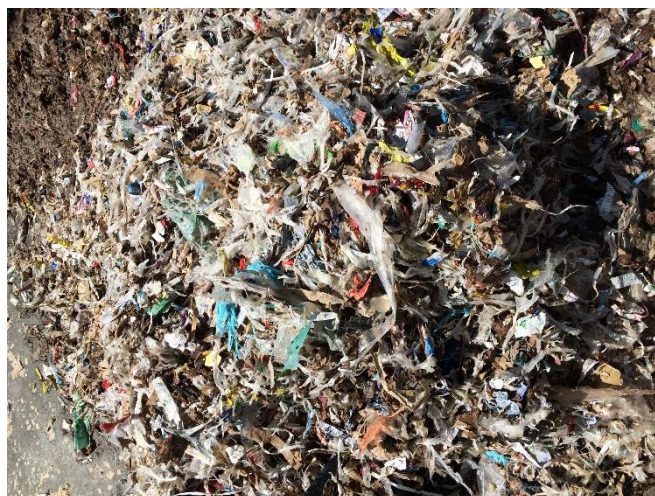


Figure 2-3: Rejects from a paper recycling mill making use of recycled fibre as feedstock

## **2.2 Waste from Fermentation of Lignocellulosic Material Process**

Residues from the hydrolysis-fermentation of lignocellulose can be considered a waste by product and is primarily comprised of lignin, unconverted sugars, ash and any other contaminants such as plastic, found in the industrial lignocellulosic waste streams [5,6]. To extract the maximum amount of value out of waste based feedstocks such as PWS and rejects, the utilization of fermentation residues as a starting material for pyrolysis combines two processing routes namely fermentation and pyrolysis to extract as much value from the waste feedstock.

## **2.3 Components of Paper Waste Sludge and Rejects**

Rejects from a paper recycling mill, as can be seen in Figure 2-3, are readily available wastes and can be considered as second generation feedstocks for energy production which are comprised predominantly of lignocellulosic fibres and a wide variety of plastic waste [3].

This section describes the chemical and physico chemical composition of the main components identified in the waste stream and are presented in Table 2-1 and Table 2-2.

### 2.3.1 Lignocellulosic Waste

Lignocellulose waste can be described as waste that contains fibres that originate from a biomass source and are composed predominately of cellulose, hemicellulose and lignin. As rejects, along with PWS are produced as a sludge from the manufacturing of different types of paper grades from recycled fibre, their fibres are expected to be similar in structure. As the literature of PWS is more readily available, it is referred to in the discussion of the fibre component of rejects.

#### 2.3.1.1 Cellulose

The main structural component of a plant is a polymer constructed from oxygen containing polymers called cellulose [7,8]. It typically comprises between 40 to 50 wt.% of biomass (Table 2-1). Cellulose is a glucose linear polymer that is linked by  $\beta$  – (1-4) glycoside bonds with polymerisation ranging from 500 to 15 000 glucose molecules (Figure 2-4). Strong intra and inter molecular hydrogen bonding connect hydroxyl groups together to form micro-fibril sheets consisting of groups of cellulose polymers to form highly ordered complex patterns that provide a plant cell wall with its crystalline structure [8,9].

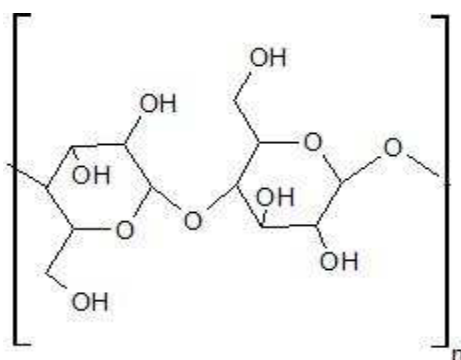


Figure 2-4: Cellulose polymer structure (Source [10])

### 2.3.1.2 Hemicellulose

Hemicellulose comprises between 10-30 wt.% (Table 2-1) of lignocellulosic biomass with its main function being to bind the cellulose micro-fibril sheets and is found between the cell walls of cellulose [11]. Hemicellulose is composed of a variety of monosaccharides such as D-xylose, D-glucose, D-mannose, D-galactose (Figure 2-5) [9,12], that form highly branched and amorphous molecules with ~ 150 linearly connecting monosaccharide units [12] through alpha and beta bonds between the various units.

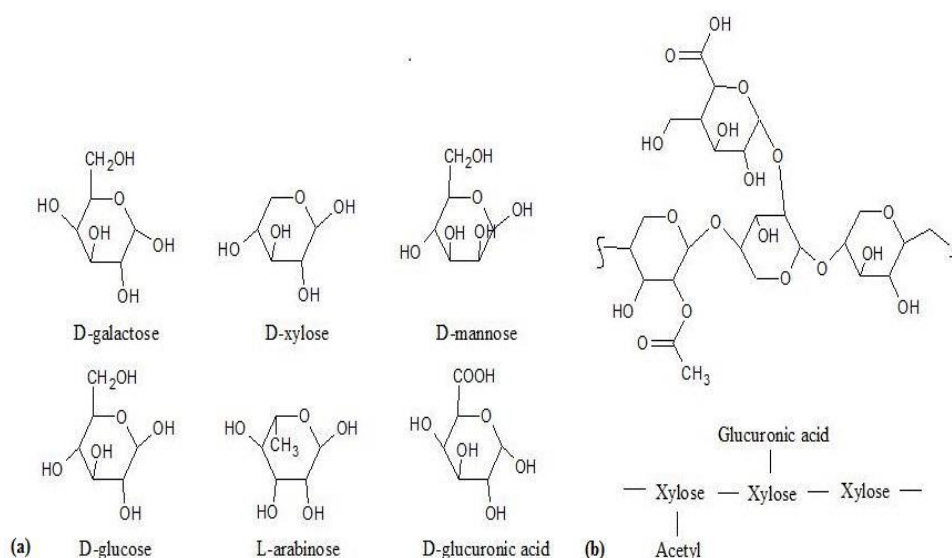


Figure 2-5: Example of structural arrangement of a) hemicellulose monomers and b) the partial structure of xylan (Source [10])

### 2.3.1.3 Lignin

Lignin is generally found in the cell walls of plants and acts as a resin binding the cellulose fibres together and comprises between 10 to 25 wt.% of biomass (Table 2-1). Lignin is an aromatic heteropolymer with monomers that consists of a three carbon chain attached to a six carbon ring called phenyl-propanes [11]. The specific nature of lignin varies greatly depending on the biomass in question and can be altered after the lignin has been isolated by a wide variety of pre-treatment techniques. The degree of polymerisation of lignin can vary

between 450 to 500 units, which are mainly joined by carbon-carbon or carbon ether bonds (Figure 2-6)[13]

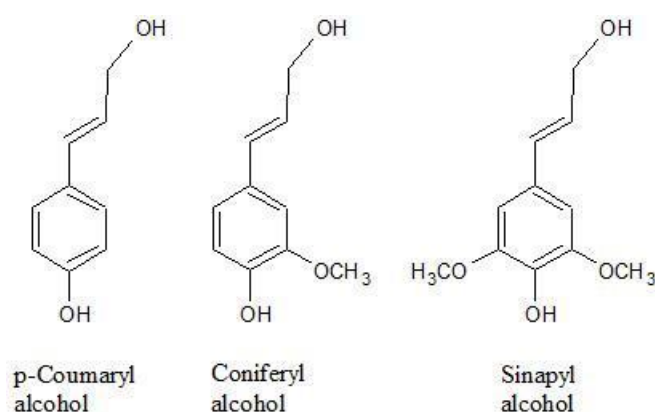


Figure 2-6: Structure of common lignin monomers (Source [10])

Table 2-1: Composition of various biomass-based industrial wastes (db wt.%)

| Biomass                    |            | Cellulose | Hemicellulose | Lignin | Extractives | Reference |
|----------------------------|------------|-----------|---------------|--------|-------------|-----------|
| Corrugated<br>waste sludge | paper      | 47.7      | 16.0          | 11.7   | 7.1         | [10]      |
|                            |            |           |               |        |             |           |
| Virgin<br>waste sludge     | pulp paper | 55.7      | 16.8          | 21.0   | 3.6         | [10]      |
| Sugar cane                 |            | 44.2      | 23.8          | 22.4   | 9.7         | [14]      |
| Corn cobs                  |            | 35.9      | 38.1          | 16.1   | 9.5         | [14]      |



Table 2-2: Physico-chemical characterisation of typical biomass daf wt.%:

|                                     | <b>Volatile</b> | <b>Fixed</b>  | <b>Ash</b> | <b>HHV</b>     | <b>Reference</b> |
|-------------------------------------|-----------------|---------------|------------|----------------|------------------|
|                                     | <b>Matter</b>   | <b>Carbon</b> |            | <b>(MJ/kg)</b> |                  |
| <b>PWS: Virgin Pulp</b>             | 82.3            | 14.6          | 3.5        | 18.8           | [15]             |
| <b>PWS: Recycled fibre high ash</b> | 62.1            | 9.5           | 21.1       | 13.1           | [15]             |
| <b>Sugar Cane</b>                   | 82.2            | 7.5           | 10.4       | 17.6           | [14]             |
| <b>Corn Cobs</b>                    | 83.9            | 14.4          | 1.7        | 17.3           | [14]             |

### 2.3.2 Plastic Waste

A plastic is a polymer comprised of thousands of repeating units called monomers, with polypropylene (PP), polyethylene (PE), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) being the mostly commonly found plastics [16]. PE is a long chain aliphatic hydrocarbon composed of numerous ethylene monomers (Figure 2-7). PE is comprised mainly of volatile matter (VM; >90 wt.%) (Table 2-3) and has a HHV of between 43 to 47 MJ/kg [17–19] (Table 2-3). PP is similar in structure to that of PE (Figure 2-7) with the PP monomer containing a branched methyl group compared to PE and is comprised mainly of VM (>90 wt.%, Table 2-3) with an HHV between 39 to 46 MJ/kg depending on the source of PP waste [17,19,20]. PS is comprised entirely of VM (Table 2-3) and has a HHV between 38 to 41 MJ/kg [20–22]. Unlike PP, PS and PE, PET is not comprised mainly of VM, but rather a combination of VM (86.85 %) and FC (13.15 %) (Table 2-3) [23] and has a corresponding HHV of between 22 to 28 MJ/kg (Table 2-3) [24,25]. The lower HHV of PET is primarily a result of the oxygen molecule found in the PET monomer (Figure 2-7). PVC like PET, consists of a combination of VM (85.90 %) and FC (6.90 %), with a corresponding

HHV of 18- 20 MJ/kg (Table 2-3) and is not readily found in waste as it is primarily used in long term applications.

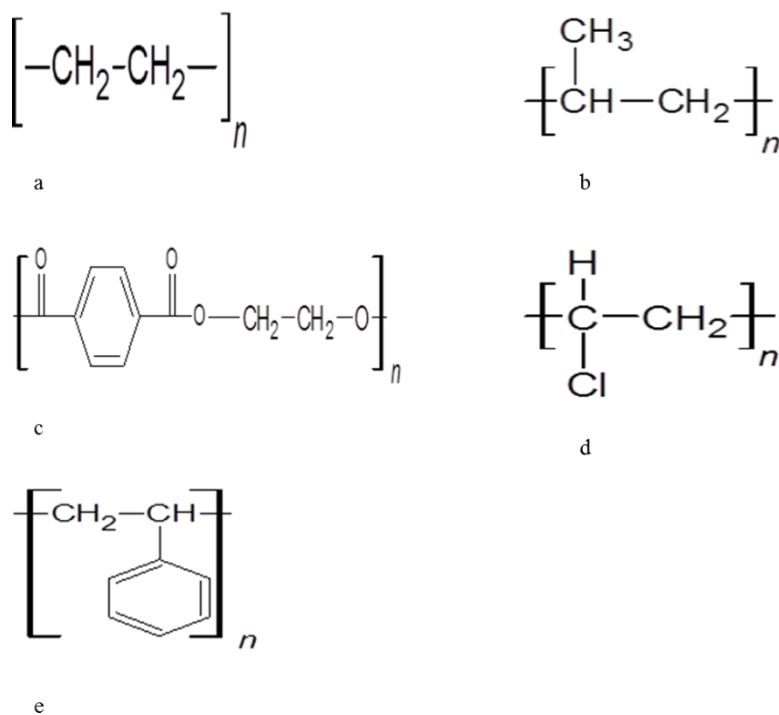


Figure 2-7: Structure of commonly found plastics, a) Polyethylene, b) Polypropylene, c) Polyethylene terephthalate, d) Polyvinyl chloride, e) Polystyrene

Table 2-3: Physico-chemical characterisation of plastic waste [18,19,23]

| Plastic    | VM (wt.%) | FC (wt.%) | ASH (wt.%) | HHV (MJ/kg) |
|------------|-----------|-----------|------------|-------------|
| <b>PS</b>  | 99.80     | 0.00      | 0.20       | 42.0        |
| <b>PE</b>  | 99.70     | 0.10      | 0.20       | 43 - 47     |
| <b>PET</b> | 86.85     | 13.15     | 0.00       | 22 - 24     |
| <b>PP</b>  | 99.19     | 0.11      | 0.70       | 39 - 46     |
| <b>PVC</b> | 85.90     | 6.30      | 7.80       | 18 - 20     |

## 2.4 Biorefinery Concept

Biorefinery can be described as the optimised process route/routes for the conversion of a feedstock from biomass origin, that utilizes various integrated processes and technologies, to extract the maximum possible value from the feedstock, which results in the simultaneous production of a variety of value adding materials, chemicals, and energy products [26,27]. The use of a biorefinery is not a new concept and is attracting significant research, with it mainly being evaluated in terms of product yields, economic viability and environmental impacts [2,28,29]. A number of studies investigating the valorisation of lignocellulosic biomass by fermentation and pyrolysis as well as an integrated approach, have highlighted the practical feasibility of such processing routes as well as the potential of the products to contribute to various market and energy sectors [6,28,30–33]. As rejects are produced in large quantities from a paper recycling mill, an integrated approach to its valorisation could provide a greater benefit to paper recycling mills than standalone technologies.

## 2.5 Energy Conversion Techniques

The conversion of waste material (biomass and plastic) to useful forms of energy can occur via two main processing themes namely thermochemical and biochemical conversion. Thermochemical conversion of waste encompasses three main technologies 1) gasification, 2) combustion and 3) pyrolysis with all three primarily used to produce energy. Biochemical conversion can be grouped into two main categories namely fermentation and anaerobic digestion (Figure 2-8) and is used to produce either fuels for energy application or high value chemicals. Recent studies into the fermentation of the cellulose fraction of paper waste sludge have yielded promising results with ethanol concentrations of >40g/l being obtained[5,6] Thermochemical conversion techniques, such as pyrolysis, can convert a wide variety of low energy dense feedstock into more homogeneous, energy dense products.

Pyrolysis is far more versatile conversion technique than fermentation as it can process both lignocellulosic and plastic wastes [30,34].

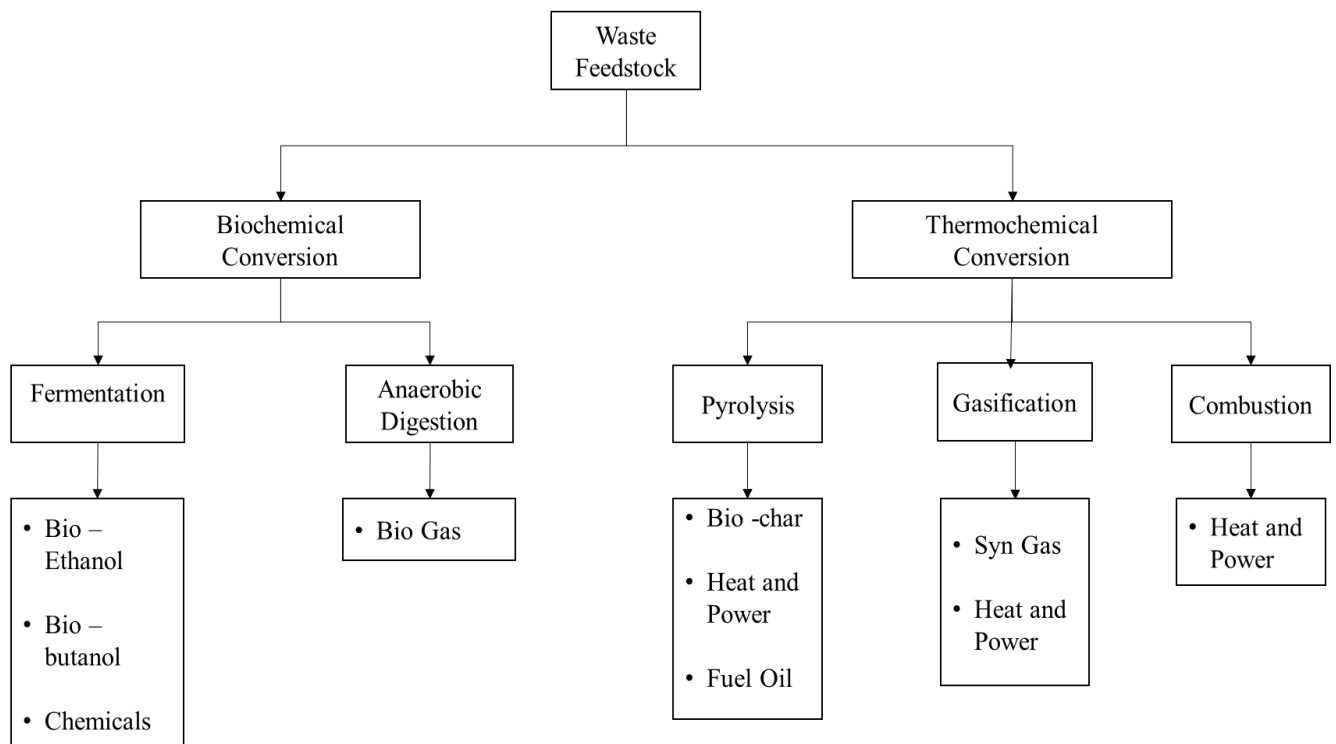


Figure 2-8: Thermochemical and biochemical processing routes of industrial waste (adapted from Menon and Rao [35])

### ***Hydrolysis-Fermentation***

Hydrolysis-fermentation is the breakdown of the cellulose and hemicellulose (carbohydrate) components of biomass into sugars in the presence of enzymes (enzymatic hydrolysis) and the subsequent conversion of the sugars to ethanol by fermentation in the presence of yeast [36]. After fermentation, a residue is obtained containing significantly less carbohydrates and increased amounts of lignin and ash [10]. In the case where the waste stream contains a mixture of fibres and plastic, this residue will be enriched in plastics and lignin, improving its suitability as a source to produce energy products via pyrolysis.

## ***Pyrolysis***

Pyrolysis is the conversion of waste material into condensable volatiles, char and non-condensable gas by the application of heat (400 °C-600 °C) in the absence of oxygen [36,37]. The nature of product qualities and yields from pyrolysis is determined by both the pyrolysis conditions applied and the composition of the waste material as this ultimately affects the thermal degradation behaviour of the feedstock intended for pyrolysis as described in the next section.

## **2.6 Thermal Degradation of Lignocellulosic Biomass and Plastic Polymers**

The thermal degradation (studied under inert atmosphere) of biomass and plastic has distinctly different thermal behaviours which results in different operating regions for pyrolysis.

### **2.6.1 Thermal Degradation of Lignocellulosic Fibre**

The thermal degradation of lignocellulosic waste biomass mostly occurs between 200 °C-500 °C (Figure 2-9), with a maximum mass loss between 350 °C - 400 °C [9,15,38,39]. The degradation of the different constituents of lignocellulose biomass (cellulose, hemicellulose and lignin) occurs within this region and partially overlaps each other [9,11]. Cellulose pyrolysis is known to occur within a temperature range of 300 °C-400 °C, with a maximum mass loss rate between 320 to 350 °C (Figure 2-10) [9,40]. The hemicellulose degradation region (200 °C-290 °C)(Figure 2-10) occurs before that of cellulose with maximum mass loss rate at ~270 °C [9,41], while lignin has a degradation region between 200 °C-500 °C (Figure 2-10) and a maximum mass loss rate between 360 °C - 420 °C [9,41,42]. As the structure of lignin, rich in aromatic rings, is significantly different to that of polysaccharides

(carbohydrates) (Section 2.3.1) the conversion of lignin can result in char yields of up to four times that obtained from both cellulose and hemicellulose [9].

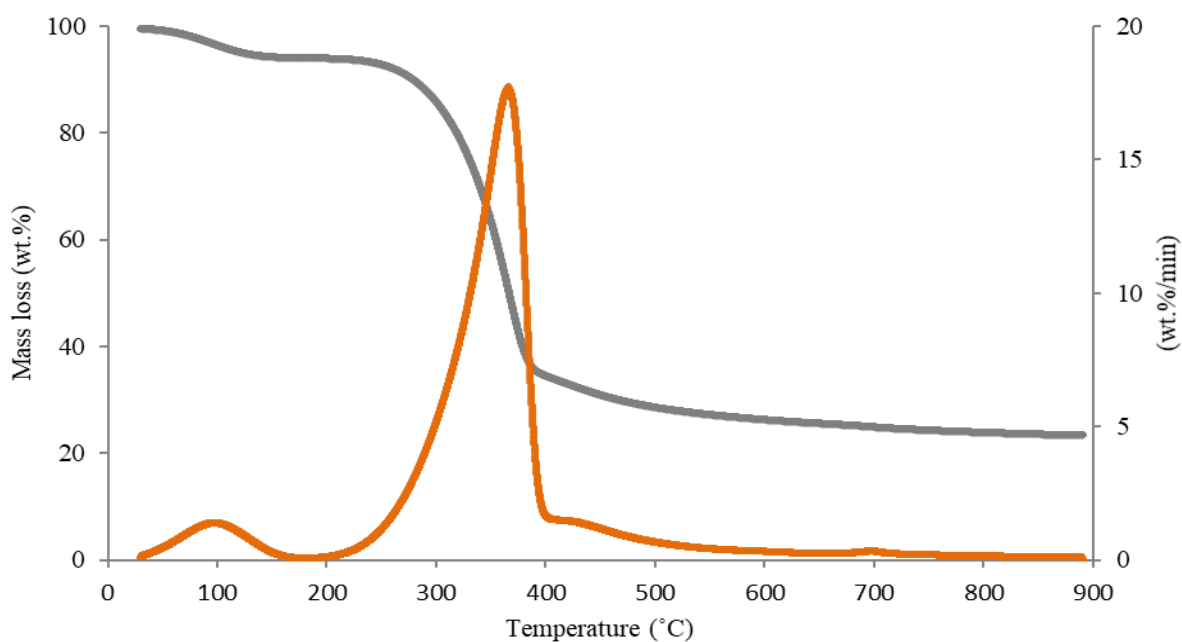


Figure 2-9: Thermal gravimetric curves (TG) and derivative thermal gravimetric curve of low ash paper waste sludge adapted from [15]

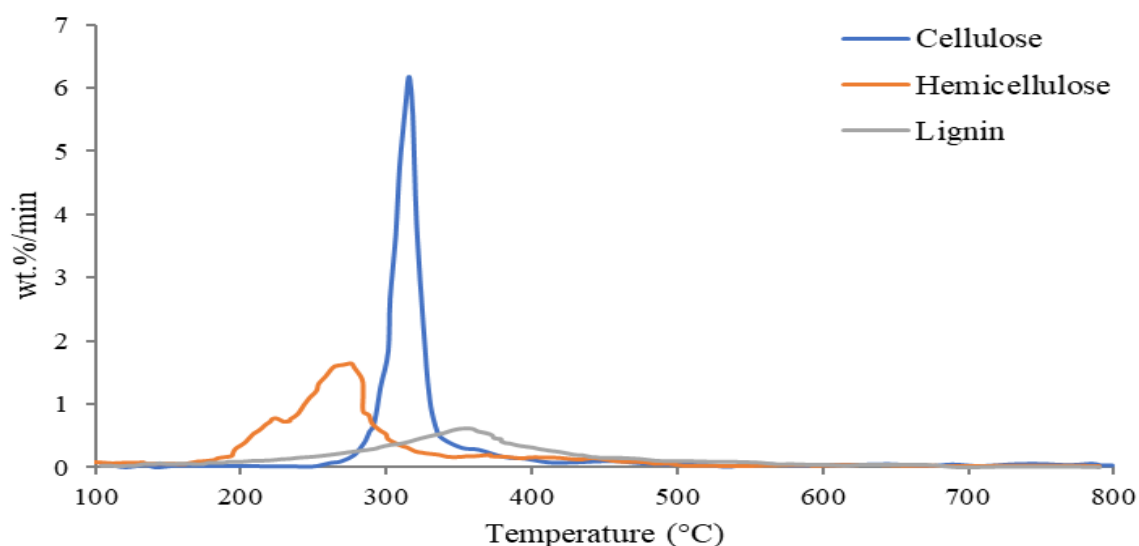


Figure 2-10: The derivative thermogravimetric curve dTG of pure cellulose, hemicellulose and lignin adapted from [9]

### 2.6.2 Thermal Degradation of Plastics

The common plastics found in waste materials are structurally different from one another and exhibit different regions of thermal degradation that cover a wide range of 350 °C-500 °C (Table 2-4) [43–46], except for PVC where thermal degradation starts at a lower temperature of 280 °C (Table 2-4). The degradation ranges of PP and PE overlap one another with both having a maximum mass loss rate above 450 °C (Table 2-4) (Figure 2-11) and decomposing in a single step via random chain scission mechanism [47]. The thermal decomposition of PET occurs via  $\beta$ -hydrogen transfer, de-carboxylation and rearrangement mechanism that occurs in a single step [25,48], with a maximum mass loss rate occurring at ~427 °C (Table 2-4). The thermal decomposition of polystyrene occurs via a free radical mechanism [49], which has a maximum mass loss rate around 440 °C (Table 2-4). The majority of plastics decompose in a single step (Table 2-4) except for PVC, which has two decomposition steps. The first is a result of dehydrochlorination of PVC and occurs below 300 °C. The second occurs at a temperature above 350 °C, with a maximum mass loss rate at 460 °C (Table 2-4) and is a result of the hydrocarbon backbone decomposing.

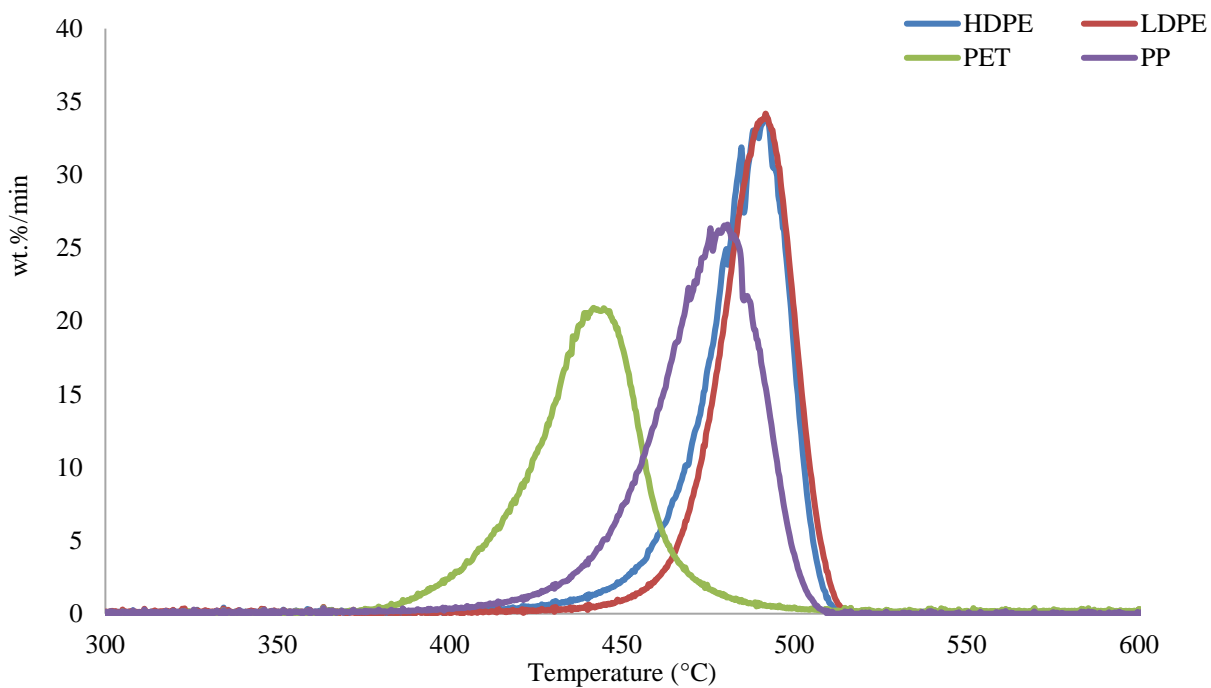


Figure 2-11:dTG of common waste plastics adapted from [48]

Table 2-4: Thermal degradation ranges of waste plastics

| Plastic    | Heating rate<br>(°C/min) | Temperature<br>Range (°C) | Peak Temperature 1 | Peak Temperature 2 | Reference |
|------------|--------------------------|---------------------------|--------------------|--------------------|-----------|
| <b>PE</b>  | 10                       | 410-520                   | 505                | N/A                | [43,44]   |
| <b>PP</b>  | 10                       | 412-462                   | 468                | N/A                | [48,50]   |
| <b>PET</b> | 10                       | 383-477                   | 427                | N/A                | [51]      |
| <b>PS</b>  | 10                       | 350-460                   | 417                | N/A                | [48,52]   |
| <b>PVC</b> | 10                       | 280-520                   | 290                | 460                | [53]      |

N/A- not applicable



## 2.7 Conversion of Waste Components into Fuel Products

This section will discuss the recent studies on the conversion of waste via pyrolysis and fermentation into products.

### 2.7.1 Pyrolysis of Fibres

The thermal degradation of lignocellulosic biomass results in the formation of three main components, a solid char product, a condensable fraction termed bio oil and a non-condensable gas fraction. The composition and fuel properties of these products are detailed in the following sections. There are two main types of pyrolysis techniques:

#### *Fast Pyrolysis*

Fast pyrolysis is mainly used for the production of bio-oil and occurs at rapid heating rates ( $> 100\text{ }^{\circ}\text{C/min}$ ) and short vapour residence times ( $< 30\text{ s}$ ) [30].

#### *Slow Pyrolysis*

Slow pyrolysis employs slow heating rates ( $5\text{ to }25\text{ }^{\circ}\text{C/min}$ ) and long vapour residence times ( $1\text{ to }60\text{ min}$ ) and results in approximately equal distribution of the three products [30].

#### 2.7.1.1 Char

Char obtained from the pyrolysis of lignocellulosic biomass is a solid product that is comprised mainly of fixed carbon, inorganic material (determined as ash during proximate analysis) and a small proportion of volatile matter. With most of the inorganic material (ash) present in the feedstock, remaining in the char after pyrolysis [15]. The organic fraction consists mainly of stable polyaromatic compounds [9,15,54]. Char has the potential to be used as a substitute for coal for the production of electricity or the supply of industrial/domestic heating applications, thus reducing the dependence on fossil fuels [55].

The production of char is favoured at low temperatures, between 200 °C–300 °C, and slow heating rates 5 to 30 °C/min [56–58], with yields in the region of 20 to 50 wt.% [59,60]. The typical energy content of char varies between 18 MJ/kg to 32 MJ/kg, depending on the lignocellulosic biomass feed stock and pyrolysis conditions applied, with higher temperatures favouring the production of better calorific value chars due to the more extensive deoxygenation that occurs [56,59]. In case of high ash PWS (>20 wt.%) (Table 2-2) , a detrimental effect on the char HHV was observed, resulting in values sometimes below 10 MJ/kg [59,61]. Besides their low calorific values, chars with a high ash content (> 50 wt.%) can potentially cause slagging and fouling during combustion in boilers [62], which would make them undesirable as a feedstock for energy generation.

#### **2.7.1.2 Bio-oil**

Bio-oil from the pyrolysis of lignocelluloses is an organic liquid comprised mainly of a complex mixture of oxygenated organic compounds and water [63]. Bio-oil can be used either as an energy source or as a feedstock for the production of valuable chemicals [30,64]. The production of bio-oil is promoted (up to 75 wt.%) by application of rapid heating rates (>100 °C/min) and associated with reactor temperatures of 450-550 °C [14,15,65–67]. The application of higher pyrolysis temperatures typically results in further cracking of the volatile compounds and increased gas yields are observed.

A study on slow pyrolysis of low ash paper waste sludge by Strezov et al. [68] in a temperature range of 300-700 °C resulted in bio-oil yields between 11-36 wt.%, with the highest bio-oil yield of 40 wt.% being reported at 400 °C and 500 °C [68]. In a similar study by Lou et al. [60], PWS was slowly pyrolysed to 800 °C, resulting in a bio-oil yield of 24.4 wt.% [60]. The slow and fast pyrolysis of PWS was compared by Ridout et al. [15,59] in a fixed and fluidised bed reactor respectively, with the highest liquid yield (59.9 wt.%) being

reported for fast pyrolysis compared to 35 wt.% obtained from slow pyrolysis [59]. The difference in yield was attributed to the production of condensable volatiles favoured by rapid heating rates ( $> 100\text{ }^{\circ}\text{C}/\text{min}$ ) and short vapour residence times ( $< 30\text{ s}$ ).

Bio-oil has the potential to be a promising source of bio energy for transportation fuels, electricity and thermal energy [30,69,70]. Pyrolysis bio-oils derived from woody biomass typically have energy contents of between 17 MJ/kg-20 MJ/kg, which represents approximately 50 % of the energy content of conventional (diesel) fuels ( $\sim 40\text{ MJ/kg}$ ) [30]. The energy content of bio-oil produced by slow and fast pyrolysis of PWS has been reported to vary from 10 MJ/kg for slow pyrolysis up to 21 MJ/kg for fast pyrolysis [59]. The poor energy content of the bio-oil derived from slow pyrolysis was attributed to the presence of oxygenated chemical compounds and the large fraction of water ( $> 50\text{ wt.}\%$ ) [59], which is generally observed with slow pyrolysis. Before bio-oil can be used as a substitute for conventional transportation fuels, it would require significant deoxygenation. This can be achieved either by catalytic pyrolysis or hydro treating [30]. A study by Yang et al. [33] showed that bio-oil derived from PWS had sufficient energy to power a diesel engine, however, the presence of solids in the oil from PWS pyrolysis had a negative effect on combustion as a result of clogging of the injection nozzles.

### **2.7.1.3 Gas**

The gas fraction produced via the pyrolysis of lignocellulosic biomass is generally comprised of carbon dioxide, carbon monoxide, hydrogen and methane. Gas phase being composed predominately of CO and CO<sub>2</sub> when pyrolysis temperature is less than  $400\text{ }^{\circ}\text{C}$  producing a gas phase with a low energy content [71]. Increasing the temperature to above  $600\text{ }^{\circ}\text{C}$  promotes the formation of gas phase as secondary cracking reactions predominate at higher temperatures [63,72]. As the temperature of conversion increases, the formation of CH<sub>4</sub> and

H<sub>2</sub> are promoted in the gas phase increasing the HHV up to 12 MJ/m<sup>3</sup> and represents approximately 22% of the energy content of natural gas (37 MJ/m<sup>3</sup>) [63]. The gas phase produced during pyrolysis is primarily combusted to provide the energy needed for process activities (heat for drying and pyrolysis oven, particle size reduction, etc.) [30,32,63].

### **2.7.2 Pyrolysis of Plastic Waste**

The thermal degradation of plastic waste results in two main products, a condensable volatile fraction that can be either an oil, wax or a combination of the two, and a non-condensable gas fraction. The limited yield of a solid char product is due to the majority of waste plastic being comprised of VM, with only PET having a significant amount of FC (> 10 wt.%) that is likely to generate a char product (Table 2-3). As a result, only the oil/wax and gas fractions obtained from plastic pyrolysis are discussed below.

#### **2.7.2.1 Condensable Volatiles from Plastic Pyrolysis**

The condensable volatile fraction from waste plastic pyrolysis consists primarily of aromatic and aliphatic hydrocarbons. Depending on plastic composition and pyrolysis conditions, it can be found either as a liquid or as a wax. The condensed volatile fraction can be used either as a feedstock for energy applications or the production of valuable chemicals, depending largely on the nature of the plastic feedstock. As the condensable fraction obtained from pyrolysis of waste plastic mixtures contains a complex mixture of chemicals in low yields that are difficult to isolate, its use as a fuel product is more favourable [73,74]. The production of condensable (liquid or wax) volatiles from the pyrolysis of individual plastic or a mixture of plastic waste has been effectively shown to be able to obtain a yield of the condensable phase of greater than 80 wt.% in a temperature region of 450 °C to 600 °C, with the condensed fraction having a calorific value of between 28 MJ/kg to 45 MJ/kg [75,76].

The pyrolysis of PP and PE occurs in the region of 400 °C to 550 °C and produces a combination of liquid, gas and wax products, with the sum of liquid and wax yields up to 92 wt.% being reported [21,77–79]. A study by Achilias et al. [77] using PE and PP as feedstock at a temperature of 450 °C produced a combined liquid and wax yield of 84.7 wt.% for PP and up to 96.8 wt.% for PE [77]. Similar studies conducted for both LDPE and HDPE resulted in liquid and wax yields greater than 85 wt.% for conversion temperature in the range of 450 °C to 600 °C [80,81], with the authors noting that the liquid fraction was composed mainly of paraffin and olefinic hydrocarbons [75,76]. As a result, the liquid fraction produced from PE/PP pyrolysis had a calorific value of between 39 to 41 MJ/kg [81,82]. The liquid yields from PET pyrolysis was reported to be in the region of 23 to 40 wt.%, with the oil being comprised mainly of benzoic acid as noted by the review by Sharuddin et al.[81]. The low liquid yield as well as production of large benzoic acid content was attributed to the low volatile matter content of PET and the production of a significant gas yield. Unlike PP and PE, the oil produced from PET has a calorific value of ~ 28 MJ/kg [81,83]. The differences in the calorific values of the oils are attributed to the increase in the oxygen content of PET which is clearly evident from its chemical structure as PET contains an oxygen content of 33 wt.% [23](Figure 2-7). The pyrolysis of PS at temperatures in the region of 400 to 500 °C produced primarily an oil, which consisted mainly of styrene [84,85], and had a calorific value of ~43 MJ/kg [81]. As with PET, the production of a specific chemical was attributed to the stability of the benzene ring of the PS polymer (Section 2.3.2).

#### **2.7.2.2 Gas**

The promotion of gas phase from pyrolysis of plastic is favoured at temperatures greater than 550 °C, with yields between 5 to 20 wt.% [17,81,84] for PE, PP and PS, with PET producing

a gas fraction between 33 to 50 wt. % [21,81]. The composition of the gas phase depends largely on the type of plastic under investigation but is comprised mainly of methane, ethane, ethene, propane, propene, butane and butene for PP, PE and PS with the addition of CO<sub>2</sub> and CO being produced for the pyrolysis of PET [76,81]. As gas produced from plastic pyrolysis is comprised of short chain hydrocarbons, it has the potential to be used as a source of energy for process activities.

### **2.7.3 Co-pyrolysis of Biomass and Plastic Waste**

The co-pyrolysis of lignocellulose with plastic waste has mainly been studied as a means to improve the energy content of the condensable products from biomass pyrolysis [18,86,87].

#### **2.7.3.1 Char**

The co-pyrolysis of lignocellulosic biomass with plastic waste has the potential to improve the energy content of the resulting char fraction, compared to char obtained from lignocellulosic biomass only. Paradela et al. [88] noted improvements in the char from co-pyrolysis of lignocellulosic biomass and plastic waste for conversion temperatures in region of 350 °C to 420 °C, having an energy content of 33 MJ/kg compared to that obtained from lignocellulosic biomass (15 to 22 MJ/kg) [88]. Similar studies reported improvements in the energy content of chars compared to that of lignocellulosic biomass, with an energy content varying between 28 MJ/kg to 35 MJ/kg [89,90]. These chars all have an energy content similar to that of coal that is currently used for power generation (ASTM D 388 coal ranking standard) and as such makes the chars obtained from co-pyrolysis potentially suitable for use in co-firing activities with coal [86].

### 2.7.3.2 Liquid

The liquid produced from the co-pyrolysis of biomass and plastic waste has the potential to be a more suitable fuel than bio-oil produced by the pyrolysis of lignocellulose alone, with improvements in fuel properties for the liquid obtained from lignocellulose-plastic mixtures [86]. The majority of studies on co-pyrolysis with lignocelluloses have dealt with a certain plastic or predefined mixtures of plastics as co-feeds, with the main aim of improving the overall liquid yield from pyrolysis [86,90–92].

Jeon et al. [93], studied the slow co-pyrolysis of predefined mixture of PP and woodchips in 1:1 ratio and achieved a liquid yield of 63.1 wt.%, which represented an increase of 23.8 wt.% compared to the oil obtained from pyrolysis of woodchips alone [93]. A similar study containing a mixture of plastic waste (39 wt. % PE, 12 wt. % PS, 19 wt. % PP) and pine resulted in an increase of the liquid yield by ~21 wt.% compared to pine alone. Similar studies in literature have reported increases in the liquid yield when plastic is mixed with lignocellulose in 1:1 ratios and are summarized in Table 2-5.

Table 2-5: Summary of recent studies on co-pyrolysis of biomass and plastic waste [86]

| Type of material |   | T (°C) | Liquid Yield (wt.%) |         | Energy Content (MJ/kg) |                            |
|------------------|---|--------|---------------------|---------|------------------------|----------------------------|
| Biomass          | Plastic                                       |        | Biomass alone       | Mixture | Biomass                | Mixture (1:1) weight ratio |
| Palm Shell       | PS  | 500    | 46.13               | 61.63   | 11.9                   | 38.01                      |
| Potato Skin      | HDPE  | 500    | 23                  | 39      | 32.0                   | 45.6                       |
| Pine Residue     | Plastic waste<br>PE:56%<br>PS:17 %<br>PP: 27% | 400    | 32                  | 53      | 20.0                   | 45.0                       |

The co-pyrolysis of plastic with lignocellulose has proven to be effective in improving not only the quantity of the liquid product, but also the fuel quality, compared to that obtained from lignocellulose. As discussed in Section 2.7.1, the oil produced from the pyrolysis of lignocellulose has an energy content between 17 MJ/kg to 20 MJ/kg and is a result of the high oxygen and water content of the oil. The improvements in the energy contents of the oils derived from co-pyrolysis of lignocellulose and plastics can clearly be seen in Table 2-5. A remarkable increase in the energy content of the oils, up to ~46 MJ/kg, can be achieved. The improvement in the energy content was mainly attributed to the increase in the hydrocarbon content of the oil, derived from plastics pyrolysis. A recent study by Onal et al. [94] on the co-pyrolysis of almond shell and PE resulted in an increase in the H/C ratio from 1.60 to 2.28 and a corresponding decrease in the O/C ratio of 0.33 to 0.035 of the oil product. The author noted that the increase in the H/C ratio was likely to result in an increase in the energy content of the oil compared to the oil obtained from the pyrolysis of biomass [94] and is in agreement with the results in Table 2-5.

### **2.7.3.3 Gas**

The production of gas in co-pyrolysis of plastic and lignocellulosic biomass, as in the pyrolysis of the individual components is favoured at high temperatures and is typically in the region of 10 wt.% to 23 wt.% [88,95]. The co-pyrolysis of lignocellulose and plastic mixtures resulted in a gas fraction having a higher HHV than that of lignocellulose-derived gas, which was due to the increase in the presence of hydrocarbon in the gas fraction. Sajdak & Muzyka [95] studied the co-pyrolysis of pine wood and PP, which resulted in the gas fraction having an HHV of 24.20 MJ.m<sup>-3</sup> compared to 17.00 MJ.m<sup>-3</sup> for the pyrolysis of pine wood. This gas fraction produced from the pyrolysis of plastics is a much more valuable energy source than that derived from biomass and has the potential to not only be used to



provide the energy needed by pyrolysis and its associated process activities but also to provide heat needed for other process activities at an integrated industrial site.

#### **2.7.4 Fermentation of Paper Waste Sludge**

As the fibre component waste stream described as rejects is similar to that of PWS the fermentation of behaviour of PWS is discussed in the following section. The fermentation of PWS, namely primary clarifier sludge, has found an increasing amount of attention as a potential waste valorisation route. The production of bioethanol via fermentation of such second generation feedstocks is attracting increasing amount of attention as a possible alternative to fossil fuels for transportation [96,97]. Fermentation is the process whereby the cellulose and hemicellulose component of the biomass is broken down in the presence of an enzymatic catalysis to form sugars which can be converted to a variety of fuels or speciality chemicals (Figure 2-8) [98]. The production of bioethanol via fermentation can be achieved by following one of three main processing routes, with the most commonly occurring route being Simultaneous saccharification and fermentation (SSF) described below and represented schematically in Figure 2-12.

***Simultaneous saccharification and fermentation (SSF):*** Is the process whereby cellulose component is hydrolysed to form sugars in the presence of an enzyme and subsequently fermented in the presence of microorganisms to form ethanol in one integrated step [99]. SSF is essentially a two part process occurring simultaneously. The first part involves the hydrolysis of the cellulose component to form glucose. The second is the conversion of the formed glucose into ethanol which occurs immediately upon the formation of glucose from the first step. SSF is said to result in higher yields of ethanol as it has the ability to overcome the inhibitory effects that occur during separate hydrolysis and fermentation (SHF) as a result of glucose accumulation [98,99]

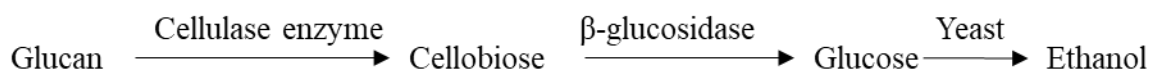


Figure 2-12: Schematic of chemical pathway of simultaneous saccharification and fermentation (SSF) process (redrawn from Lynd et al. [98])

One of the main concerns associated with the fermentation of paper mill waste is the mass and heat transfer limitations that are a result of ineffective mixing, in particular at high solids loading of > 20 wt.% [96,100]. As paper mill waste has a high water holding capacity of between 6.6 to 8.6 g water /g paper mill waste [5,96], there is a need for large agitation speeds (1500 rpm) [5] in order to overcome these limitations. Fed batch fermentation of paper mill waste has been shown to be an effective method compared to batch fermentation to overcome the mass transfer effects associated with water holding capacity of PWS and high solids loading (>20 wt.%) fermentation. As hydrolysis occurs, the cellulose component is converted into sugars which in turn results in more free water being available, thus reducing the viscosity of the fermentation broth. Boshoff et al. [96] studied the fermentation of corrugated recycled paper mill waste at solid loading of 27 wt.% and 11 FPU in feed batch culture with feeding occurring every 12 hours in 3 wt.% intervals and managed to achieve an ethanol concentration of 46 g/l (Table 2-6) which is above the threshold value of 40g/l for economic viability [100]. One of the main advantages of high solids loading fermentation is that the concentrations of substrate and products are increased and can result in more desirable final ethanol concentrations of > 40 g/l. Increasing the ethanol concentration has the potential to lower the associated water and energy input of an industrial facility and furthermore can reduce the capital and production cost as downstream processing operations can be operated in a more efficient manner [101].

Table 2-6: Summary of process parameters for common paper mill waste

| <b>Substrate</b>  | <b>Solids loading</b><br><b>(g/l)</b> | <b>Enzyme dosage</b><br><b>(FPU/g dry</b><br><b>substrate)</b> | <b>Ethanol</b><br><b>concentration</b><br><b>(g/l)</b> | <b>Reference</b> |
|-------------------|---------------------------------------|--|--|------------------|
| <b>Kraft</b>      | 180                                   | 15   | 34   | [96]             |
| <b>Corrugated</b> | 270                                   | 11   | 46   | [96]             |
| <b>Recycled</b>   | 208                                   | 15   | 48   | [6]              |

## 2.8 Implementation of Pyrolysis at a Paper Recycling Mill

Process options need to be assessed to determine a feasible route for the valorisation of paper mill waste, with the ultimate goal of reducing the amount of waste disposed by industries at landfill sites as well as being more profitable by producing a marketable product. Potentially processing options can be assessed by means of a techno-economic analysis whereby a process simulation is first generated using simulation software such as Aspen Plus<sup>®</sup> [102,103]. Some examples using this approach in the context of thermochemical processes can be found in literature. Nsaful et al. [104] studied the pyrolysis and combustion of sugar cane bagasse for energy production at a typical South African sugar mill at a total capacity of 41 dry metric tons/h. Noting that the char produced along with a portion of the oil needed to be used to supply energy demand of the sugar mill and pyrolysis plant, resulting payback period and internal rate of return (IRR) of 17 years and 13.8 % respectively. Similarly Yang et al. [102] and Onarheim et al. [105] simulated an integrated approach of combined heat and power generation, where a different economic evaluation approach was taken to Nsaful et al. [104]. Both Yang et al. [102] and Onarheim et al. [105] set a fixed IRR value in order to

calculate the minimum selling price (MSP) of their chosen marketable product, which was either a combination of heat and power or just power. Both researchers noted that the feasibility of such an integrated process depended largely on plant size and the cost of the biomass feedstock. With Onarheim concluding that the cost of the biomass feedstock needed to exceed 25 €/MWh in order for the plant to be profitable.

Economies of scale is a concept that utilizes scale to make a process more economically profitable (Table 2-7). By applying learning effects and changes in consumable cost, a future MSP for a desirable product can be modelled [106]. Several researchers have concluded that there exists a case for economic viability of producing either a fuel equivalent or combined heat and power scenario utilising pyrolysis by increasing the size of a plant (Table 2-7) along with the application of government incentives and the decrease in capital cost that can be associated with an increase in plant size.

Table 2-7: The economic viability for different uses of pyrolysis process in relation to their plant size

| Process                 | Size (Metric tons/day) | Profitable | Reference |
|-------------------------|------------------------|------------|-----------|
| Combined heat and power | 24                     | Promising  | [102]     |
| Combined heat and power | 438                    | No         | [105]     |
| Fuel product            | 2000                   | Yes        | [107]     |
| Fuel product            | 72                     | No         | [108]     |

## 2.9 Conclusions

The pulp and paper industry currently produces large quantities of waste that are currently disposed of by landfilling. Due to mounting industrial and governmental pressure, alternative

disposal techniques are sought. This study will consider two alternatives to the current disposal technique namely 1) Pyrolysis and 2) Integrated fermentation-pyrolysis approach. These techniques are considered for the conversion of paper mill waste streams that contain both lignocellulosic fibre and plastic (Rejects). Recent research on the pyrolysis of paper waste sludge has proven promising for the production of fuel products, yet limited to little research has dealt with waste streams similar to rejects from paper mills. Indeed, the clear majority of research on fibre plastic mixtures has dealt with predetermined mixtures (with known proportions) of cellulose or a typical biomass and one or more chosen plastic polymers. Furthermore, the fermentation-pyrolysis of fibre plastic mixtures has not yet been studied as a pathway to increase the total waste conversion into fuel products

## 2.10 References

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## Chapter 3: Objectives

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The following research questions were identified:

- Is pyrolysis a suitable technology for converting the waste mixtures of interest into valuable fuel products?
- Which pyrolysis process offers the best fuel properties and highest gross energy yield?
- What effect does fermentation have on the end pyrolysis products and energy yield?
- Which process scenario offers the best option for producing energy products at a paper mill?

The aim and research questions were realised through the following objectives:

- 1) To assess the technical ability of pyrolysis to convert waste mixtures containing biomass and plastic obtained from a paper recycling mill into useful or marketable fuel products*

Three samples were obtained from two different paper recycling mills located in different parts of South Africa, namely Mpact Springs and Mpact Felixton. These waste samples varied in the nature and amount of plastic present (~5 to 50 wt.%) and were subjected to different pyrolysis processes. Several characterisation techniques were used to study the thermal behaviour and fuel properties of the samples. Pyrolysis and the effect of plastic composition on product yields and energy contents were investigated. The literature on co-pyrolysis has predominately looked at improving the condensable (liquid/wax) product quality by the addition of pure plastic polymer such as PP or PE to lignocellulosic fibre. This addition has resulted in the HHV of the condensable (liquid/wax) co-pyrolysis product increasing by ~15 to 25 MJ/kg compared to bio-oil obtained from lignocellulosic fibre which typically has a HHV in the range of 16 to 22 MJ/kg. The increase in the HHV of the

condensable product (liquid/wax) results in it having a similar HHV to that of heavy fuel oil (~40 to 45 MJ/kg) which is commonly used for power generation. The effect this addition of plastic has on the quality of solid char product is rarely reported. This objective specifically looks at producing fuel products from rejects from a paper mill that could be used to reduce mills' dependency on fossil fuels and was achieved using bench scale pyrolysis testing as outlined in **Chapters 4 and 5**.

***2) Quantify the mechanisms between biomass and plastic components during pyrolysis and their impacts on product yields and energy efficiency.***

As rejects from paper mills contain a variety of different components such as lignocellulosic fibre and varying amounts of plastic waste and plastic composition, it is essential to understand how these two components in the waste stream affect the final quality of the pyrolysis product and what their effect on the different pyrolysis processes are in order to obtain a fuel product with an acceptable quality. This objective was addressed in **Chapters 4 and 5**.

***3) To evaluate the capability of each pyrolysis process in an energy context at varying operating conditions and the potential use of the products in an energy context***

The performance of slow and fast pyrolysis was assessed at varying reactor temperatures characteristic of each process to produce a useful fuel product and the potential use of these products from an energy perspective. The energy conversion of PWS for slow or fast pyrolysis has been reported to be in the region of 32 to 41% for char and 17 to 39 % for bio-oil. While this energy conversion for the oil from PWS is particularly low, that obtained from the pyrolysis of lignocellulosic biomass (such as agricultural residues) has been reported to be > 50%. As the pyrolysis of PP/PE plastic produces mostly a fuel product (yields of >70

wt.%) with a HHV similar to that of HFO (~ 40 to 45 MJ/kg), its energy conversion to a condensable fuel product is in the region of 70 to 90 % depending largely on the pyrolysis process conditions. The energy conversion of different pyrolysis processes from industrial waste streams like rejects from a paper mill into useful fuel products (solid/condensable) is the specific focus of this objective and is addressed in **Chapters 4 and 5**.

***4) Assess the ability of a fermentation processing route to convert the lignocellulose component of fibre-plastic mixtures into bioethanol***

Fibre plastic mixtures contain degraded fibre that can be used as a source to produce sugar that can in turn be utilised to make a marketable fuel product in the form of bioethanol via fermentation. After which, the residue left after fermentation is enriched in lignin and plastic which is expected to enhance the fuel properties of pyrolysis product. The fermentation of PWS which has a similar fibre content to that of rejects considered in this study has been extensively studied in literature with ethanol concentration being obtained between 30 to 45 g/l depending largely on the origin and chemical composition of the PWS. This specifically addresses the production of bioethanol on a kilogram scale of certain waste streams described as rejects in this study and is specifically addressed in **Chapter 6**.

***5) Assess the performance of fermentation pre-treatment on final quality of pyrolysis product and its potential use as fuel product***

After fermentation, a residue enriched in lignin, plastic and ash is left that due to the conversion of the cellulose component to ethanol contains a reduced oxygen content potentially making it an improved starting material for pyrolysis. The increase in the plastic

and lignin content is expected to improve the quality of the fuel product and conversion of energy into final useful products and as such the quality of pyrolysis products compared to that from the raw material. Furthermore, the effectiveness of fermentation pre-treatment on the conversion of energy during pyrolysis is also evaluated. Recent studies on fermentation-pyrolysis of PWS has resulted in only slight improvements (+5 MJ/kg) for condensable product and up to +10 MJ/kg for the char product. However, the additional production of ethanol has been able to add up to an additional 32% to the estimated gross energy conversion. This objective specifically looks to address the potential improvement reducing the carbohydrate content from certain waste streams described as rejects and its effect on the quality of the final fuel products. This objective was addressed in **Chapter 6**.

*6) Assess the economic potential of pyrolysis processing scenarios as an alternative waste disposal technique in terms of a pyrolysis plant annexed to a paper mill*

This objective specifically looks at the trade-off between economic and technical viability of annexing a pyrolysis plant to a paper mill as an alternative disposal technique to landfilling and what process parameters are important to overcome, in order to find an economically feasible solution. This objective is specifically addressed in **Chapter 7**

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## Chapter 4: Pyrolysis of Fibre Residues with Plastic Contamination from a Paper Recycling Mill: Energy Recoveries

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**Title** *“Pyrolysis of Fibre Residues with Plastic Contamination from a Paper Recycling Mill: Energy Recoveries”*

**Authors:** Logan Jeremy Brown, François-Xavier Collard, Johann Görgens

### Objective of the Dissertation in this Chapter

This chapter addresses **objectives 1-3** of this PhD study. The aim of this chapter was to assess the technical ability of slow pyrolysis to convert a paper mill waste stream containing a mixture of fibre and plastic into useful fuel products (**objective 1**). Furthermore, the effect that the presence of plastic has on the quality of the final fuel product in relation to the different plastic compositions is discussed (**objective 2**). Lastly, the industrial application of fuel products in an energy perspective is discussed in relation to the final pyrolysis temperature (**objective 3**).

The slow pyrolysis of the three waste streams produced solid fuel product (char) with a calorific value of char up to 32 MJ/kg at pyrolysis conversion temperatures of < 425 °C. The production of condensable phase at temperatures of > 425 °C, resulted in an aqueous phase (comprised mainly of water, >75 wt.%) and an energy dense tarry phase (HHV up to

42 MJ/kg) being produced. As the aqueous phase is made up almost entirely of water its use as a fuel product was not considered as on an industrial plant, waste streams similar in nature to the aqueous phase in this chapter are sent to waste water treatment. The gross energy conversion (EC) to char (>80%) was maximised for all three waste streams at lower temperature of 300 °C. A shift in the EC was observed for increases in temperature to 550 °C, as full conversion of waste stream produced the largest yield of energy dense tarry phase (38.9 wt.%), but decreased the HHV of the resulting char products to between 16.7 to 20.9 MJ/kg and as a result EC of up to 33% for char and 55 % for tarry phase was obtained.



## Candidate declaration

With regards to chapter 4, page numbers 53 to 88 of this dissertation, the nature and scope of my contributions were as follows:

| Nature of contributions   | Extent of contribution (%) |
|---------------------------|----------------------------|
| Experimental planning     | 80                         |
| Executing experiments     | 100                        |
| Interpretation of results | 70                         |
| Writing the chapter       | 100                        |

The flowing co-authors have contributed to chapter 4 page 53 to 88 in the following manner:

| Name                    | Email address  | Nature of contributions     | Extent of contribution (%) |
|-------------------------|--|-----------------------------|----------------------------|
| Francois-Xavier Collard | <a href="mailto:fcollard@sun.ac.za">fcollard@sun.ac.za</a> | • Experimental planning     | 10                         |
|                         |  | • Reviewing chapter         | 80                         |
|                         |  | • Interpretation of results | 20                         |
| Johann Görgens          | <a href="mailto:jgorgens@sun.ac.za">jgorgens@sun.ac.za</a> | • Reviewing chapter         | 20                         |
|                         |  | • Interpretation of Results | 10                         |
|                         |  | • Experimental planning     | 10                         |

Candidate signature:.....

Date:.....

## Declaration by co-authors:

The undersigned hereby confirm that

1. The declaration above accurately reflects the nature and extent of the contributions of the candidate and the co-authors to chapter 4 page numbers 53 to 88 in the dissertation
2. No other authors contributed to chapter 4 page numbers 53 to 88 besides those specified above.
3. Potential conflicts of interest have been revealed to all interested parties and that the necessary arrangements have been made to use the material in chapter 4 page numbers 53 to 88 in the dissertation

| <b>Signature</b> | <b>Institute Affiliation</b> | <b>Date</b> |
|------------------|------------------------------|-------------|
|                  | Stellenbosch University      |             |
|                  | Stellenbosch University      |             |
|                  | Stellenbosch University      |             |

“Declaration and signature is in possession of candidate and supervisor”

# Pyrolysis of Fibre Residues with Plastic Contamination from a Paper Recycling Mill: Energy Recoveries

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## Abstract

Pyrolysis is a promising technology for the production of marketable energy products from waste mixtures, as it decomposes heterogeneous material into homogenous fuel products. This research assessed the ability of slow pyrolysis to convert three waste streams, composed of fibre residues contaminated with different plastic mixtures, into char and tarry phase products at three different temperatures (300, 425 and 550 °C). The products were characterised in terms of mass yield, higher heating value (HHV) and gross energy conversion (EC). Significant amounts of hydrocarbon plastics in the feed materials increased the calorific values of the char (up to 32.9 MJ/kg) and tarry phase (up to 42.8 MJ/kg) products, comparable to high volatile bituminous A coal and diesel respectively. For all three waste streams converted at 300 °C, the majority of the energy in the feedstock was recovered in the char product (> 80 %), while deoxygenation of fibre component resulted in char with increased calorific value (up to 31.6 MJ/kg) being produced. Pyrolysis at 425 °C for two of the waste streams containing significant amounts of plastic produced both a valuable char and tarry phase, which resulted in an EC greater than 74 %. Full conversion of plastic at 550 °C increased the tarry phase yield but dramatically decreased the char HHV. The influence of temperature on product yield and HHV was discussed based on the pyrolysis mechanisms and in relation to the plastic composition of the waste streams.

**Keywords:** Pyrolysis, energy conversion, fibre, plastic, paper recycling mill

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## 4.1 Introduction

The continuous generation of waste from industry is becoming an increasing problem in both developing and industrialized countries [1–3]. The renewed drive towards a sustainable/green economy is promoting the mitigation of waste disposal by reuse and recovery as primary processing routes [4,5]. The paper industry currently produces large quantities of waste, which is commonly disposed of by landfilling. Such waste is unsuitable for use in paper manufacturing due to the poor quality of the fibre and contamination with plastic, metals and other contaminants. The waste streams can be grouped into two main categories: paper waste sludge (PWS) and rejects [1]. Rejects originate from the processing activities that occur before the paper machine, where PWS is the waste that is left over from paper manufacturing using recycled fibres. PWS is composed mainly of fibres that contain a relatively high amount of inorganics [6]. A previous study by Ridout et al. [7] considered the pyrolysis of PWS into fuel products. While it was possible to produce an oil with a HHV of 22 MJ/kg, the HHV of the char product was relatively low (22 MJ/kg) due to its large ash content [7]. Depending on the waste source, rejects consist of waste fibre and varying amounts of different plastics waste that are likely to increase the HHV of the waste stream [1,5]. The valorisation of mixed waste material by pyrolysis is finding increasing application as it has the ability to convert a wide range of mixed organic materials (biomass, plastic and tyres) into marketable energy products by thermally upgrading the raw heterogeneous feedstock into a homogeneous and more energy dense product. The application of pyrolysis to fibre-plastic mixes from fibre recycling operations in the paper and pulp industry is the focus of the present study.

Pyrolysis is a means of thermally degrading a raw material in the absence of oxygen into a solid residue (char) and a volatile fraction. The volatile fraction can be separated into two phases, i.e. a condensable fraction (pyrolysis oil) and permanent gasses. The performance

of pyrolysis for energy production depends largely on the energy content and mass yields of the products. To date, the majority of research has considered the gross energy conversion (EC) as an indication of the efficiency of pyrolysis to convert one energy product (feedstock) into a combination of more useful, higher quality energy products (char, oil or gas) [8,9]. The EC can be calculated based on an overall energy conversion for the process (all products) or based on the EC of target products, allowing one to optimise the product distribution to maximise the EC. The EC from biomass pyrolysis for char and oil ( $EC_{\text{char}} + EC_{\text{oil}}$ ) is in the region of 60 % to 80 % for fast pyrolysis and 33 % to 60 % for slow pyrolysis [7–10]. In the case of fast pyrolysis the oil product contains the majority of the energy content [9] whereas in slow pyrolysis the objective is to increase the energy density of the char [7,10]. A drawback of fast pyrolysis is that it requires extensive pre-processing of the raw material which adds to the overall energy requirements of the process [11]. The gas produced from pyrolysis is generally not targeted as a product because maximising gas yield requires higher conversion temperatures ( $> 600\text{ }^{\circ}\text{C}$ ) compared to those required for char and oil and due to transport issues. As a consequence, gas is used primarily on site to provide process heat [12]. When the process under investigation appears promising, the energy content of the gas needs to be taken into account, along with energy requirements for other process activities (heat needed for drying and pyrolysis, particle size reduction, etc.), to calculate the net energy conversion. The majority of studies about co-pyrolysis of biomass/plastic mixtures have focused on the use of slow pyrolysis [13–15], with the main aim to improve the quality and quantity of the oil product [16,17].

The addition of plastic polymers to biomass has been considered an effective way to increase the total liquid yield and higher heating value (HHV) of the liquid phase by 20 % to 40 %, while decreasing the char and gas yields [18,19]. Liquid yields as high as 69.7 wt.% have been reported from the slow co-pyrolysis of biomass and plastic [14,20–22], which is

significantly higher than that reported in literature for the slow pyrolysis of pure biomass streams [7,23] and is similar to the yields obtained from the fast pyrolysis of biomass [11,24,25].

The purpose of this study was to evaluate the potential of slow pyrolysis for the conversion of fibre residues contaminated with plastic from a paper recycling mill into marketable energy products. Particular attention was given to the fuel properties of the products (char and oil) and to the energy conversion assessment. The relatively high water content of oil obtained from the conversion of biomass has a detrimental effect on the HHV of the pyrolysis oil. By making use of an appropriate condensation train as shown in previous work [7], it is possible to fractionate the pyrolysis oil into two phases, an aqueous phase containing the majority of water produced during pyrolysis and an energy dense tarry phase containing the majority of the organic compounds. In this study, a similar fractionating condensation system was used to improve the quality of the tarry phase product.

## **4.2 Material and Methods**

### **4.2.1 Source and Preparation of Feedstock**

The waste streams used in this study were classified into the group described as rejects and were obtained from two different fibre recycling mills in South Africa. Two of the streams used in this study were sourced from the Mpact Springs mill and the third from Mpact Felixton mill. Rejects are produced as a sludge from the manufacturing of paper and contain significant amounts of water (>50 %). Each waste sample underwent a drying process in a tunnel greenhouse for a period of five days before being milled down to a particle size of 2 mm using a Retsch SM 100 cutting mill. In order to improve packing density inside the fixed bed reactor, the milled feedstock was pelletized. This was done by rehydrating the dried milled material with 40 % water and passing it through ABC HANSEN pellet mill with a dye

size of 6 mm. The pellets were subsequently dried at 60 °C until no further mass loss of the pelletized material occurred. By pelletizing, an increase in packing density by a factor of two was achieved.

#### 4.2.2 Physico-Chemical Characterisation

The moisture content of the as received samples was determined in accordance with TAPPI T264 om -88 standard procedure. A thermogravimetric analyser TGA/DCS 1 Star Systems Mettler Toledo was used for proximate analysis. As observed in other studies [6,24], the fibres obtained from the paper recycling mills contained calcium carbonate (filler). As a result, the proximate analysis of the pelletized recycling residues and char samples was conducted by making a modification to the standard ASTM E1131 testing method as suggested by Ridout et al. [24]. An additional step was added to the standard ASTM E1131 where the sample was held at 650 °C for 5 minutes to drive off all the organic volatiles while avoiding the decomposition of  $\text{CaCO}_3$  which occurred from 700 °C (Eq1). After this, the sample was heated to 900 °C and held there for an additional 5 minutes to ensure the full decomposition of  $\text{CaCO}_3$  occurred before the combustion of the fixed carbon. As  $\text{CaCO}_3$  is an inorganic component unlikely to produce any fuel product, in the proximate analysis results (waste stream and char products) the percentage of  $\text{CaCO}_3$  was included in the ash content.



Ultimate analysis of the raw material was determined using an Elementar Microcube ELIII. This method estimates organic carbon based on the  $\text{CO}_2$  produced by carbon combustion. As combustion occurred at temperatures above 700 °C, the decomposition of  $\text{CaCO}_3$  into  $\text{CO}_2$  was unavoidable. A correction to the organic carbon content had to be made. This was achieved by estimating the  $\text{CO}_2$  produced from the inorganic source by using

the weight percentage of CO<sub>2</sub> produced from CaCO<sub>3</sub> decomposition as measured by the TGA during the relevant step of proximate analysis.

HHVs of the feedstock samples and pyrolysis products were determined in accordance with the ASTM standard D5865-11a, using a Cal2K Eco Calorimeter, which was calibrated using benzoic acid. Fourier transform infrared (FTIR) spectroscopy was performed on the raw materials using a Nicolet iS10 spectrometer operating in ATR mode with a diamond crystal. ThermoScientific OMNIC software was used for collection of data. This enabled the identification of different functional groups present in the sample. Inorganic composition of waste streams was determined via X-ray fluorescence (XRF) analysis using an AXIOS PANalytical.

Thermal behaviour investigation was carried out using a thermogravimetric analyser TGA/DCS 1 Star Systems Mettler Toledo. Experiments were carried out using 20 mg of sample from a temperature 30 °C to 900 °C with a heating rate of 10 °C min<sup>-1</sup>. Nitrogen was used as the inert purged gas at a flow rate of 80 ml min<sup>-1</sup>.

### **4.2.3 Pyrolysis Experiments**

#### **4.2.3.1 Bench Scale Experiments**

Pyrolysis experiments were carried out using a fixed bed reactor depicted in Figure 4-1. The pyrolysis setup consisted of four distinct sections, 1) Pyrolysis oven used to provide heat of reaction, 2) 1m reaction tube made from quartz along with a quartz sample boat that housed 12g of pelletized waste material, 3) A stepwise condensation train that consisted of 5 condensers and 4) Nitrogen gas feeding system. Technical grade nitrogen was fed at a flow rate of 0.5 L min<sup>-1</sup>. Before each experimental run, the reactor was checked for leaks using a vacuum pump and subsequently purged with nitrogen for 10 minutes to maintain an oxygen free environment. The first condenser (C1), kept at room temperature, was where a dark



brown viscous liquid/wax was collected, hereafter referred to as tarry phase. Condensers 2 - 3 (C2 and C3) were cooled using dry ice and were used to collect the aqueous phase. In condensers 4 and 5 (C4 and C5), silica beads were placed to adsorb the aerosols remaining in the gas stream.

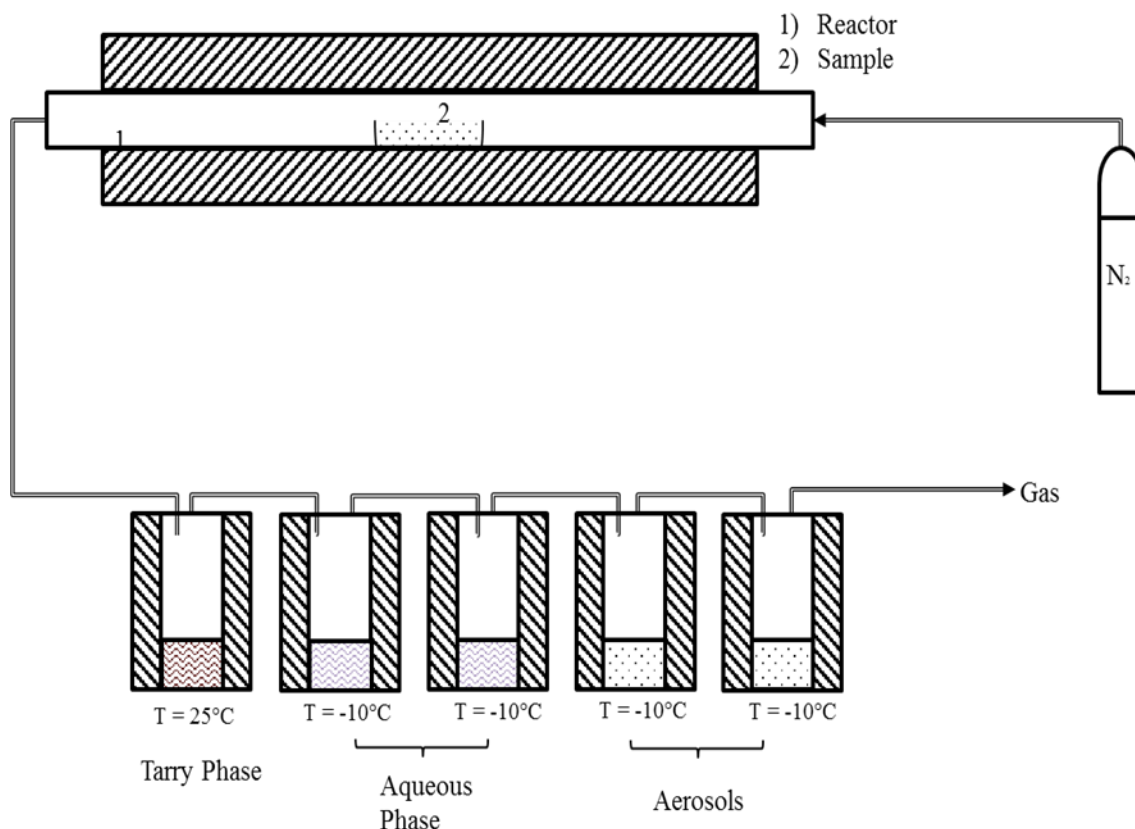


Figure 4-1: Bench scale pyrolysis reactor

Pyrolysis experiments were carried out at 3 distinct temperatures ( $300^\circ\text{C}$ ,  $425^\circ\text{C}$  and  $500^\circ\text{C}$ ) chosen based on the characteristic steps of conversion of the three samples (Section Thermal Behaviour). The experiments were carried out at a heating rate of  $25^\circ\text{C}/\text{min}$  and once the desired temperature was achieved, held there for an additional 60 minutes. Once the experiment was completed, the reactor was cooled to  $90^\circ\text{C}$  before dismantling took place. All experiments were conducted in triplicate to ensure reproducibility of results and resulted in a standard deviation of char and tarry phase product yields of less than 2.5 and 3.3 wt.% respectively.

#### 4.2.3.2 Product Yields

The yields of pyrolysis products were calculated according to Equations 2 – 7 with  $Y_{\text{char}}$  standing for yield of char produced,  $Y_{\text{tarry}}$  standing for the tarry phase produced,  $Y_{\text{aqueous}}$  for the aqueous (watery) phase and  $Y_{\text{aerosols}}$  for aerosols,  $m_{\text{residue}}$  and  $m_{\text{C1}}$  to  $m_{\text{C5}}$  represents the mass of product collected in the sample boat (residue) and at certain points in the condensation system. The water content of the aqueous phases produced from all three streams was determined in accordance with ASTM E203 standard, using a Metrohm 701 Titrino Karl-Fischer Titrator, hydranal composite 5 titrant (Sigma –Aldrich).

$$Y_{\text{char}}(\text{wt.}\%) = \frac{m_{\text{residue}}}{m_{\text{sample}}} \times 100 \quad \text{Eq 4-2}$$

$$Y_{\text{tarry}}(\text{wt.}\%) = \frac{m_{\text{C1}}}{m_{\text{sample}}} \times 100 \quad \text{Eq 4-3}$$

$$Y_{\text{aqueous}}(\text{wt.}\%) = \frac{m_{\text{C2+C3}}}{m_{\text{sample}}} \times 100 \quad \text{Eq 4-4}$$

$$Y_{\text{aerosols}}(\text{wt.}\%) = \frac{m_{\text{C4+C5}}}{m_{\text{sample}}} \times 100 \quad \text{Eq 4-5}$$

$$Y_{\text{oil}}(\text{wt.}\%) = Y_{\text{tarry}} + Y_{\text{aqueous}} + Y_{\text{aerosols}} \quad \text{Eq 4-6}$$

$$Y_{\text{gas}} (\text{wt.}\%) = 100 - (Y_{\text{tarry}} + Y_{\text{aqueous}} + Y_{\text{char}} + Y_{\text{aerosols}}) \quad \text{Eq}$$

4-7

#### 4.2.4 Energy Conversion Assessment

The energy conversion (EC) of the waste feedstock into pyrolysis products (char and tarry phase) was determined by Equation 8,  $m_i$  and  $\text{HHV}_i$  representing the mass and HHV of the respective pyrolysis products and  $m_{\text{sample}}$  and  $\text{HHV}_{\text{sample}}$  representing the mass and HHV of the particular waste stream under investigation with  $\text{EC}_i$  representing the energy conversion of chosen product.

$$\text{EC}_i(\%) = \frac{m_i \times \text{HHV}_i}{m_{\text{sample}} \times \text{HHV}_{\text{sample}}} \times 100 \quad \text{Eq}$$

4-8

### 4.3 Results and Discussion

A preliminary study using several characterisation methods in order to assess the composition of the waste streams was conducted. Thereafter a detailed discussion on the fuel properties of pyrolysis products and a discussion on energy conversion of the pyrolysis experiments are presented.

#### 4.3.1 Waste Stream Characterisation

##### 4.3.1.1 Thermal Behaviour

The waste streams were subjected to a thermogravimetric study to identify the major components present in each sample. As reported in literature [24,26] and observed in Figure 4-2, lignocellulosic biomass and plastic have different devolatilization regions, with biomass decomposing mostly in the region of 200 °C – 400 °C and plastic between 400 °C – 500 °C.

From visual observation of the waste streams, one of the waste streams contained a limited amount of plastic (W1), while the other two contained a significant amount (W2 and W3). The derivative thermogravimetric (dTG) curve of W1 was comprised of one main peak occurring between 200 °C to 400 °C, with a mass loss of 64.43 wt.%, characteristic of the degradation of the fibre component [24,27]. This result confirmed that W1 was composed mainly of lignocellulosic fibres (Figure 4-2). At a temperature greater than 400 °C, a further mass loss of 6.67 wt.% occurred and was attributed to further degradation of fibre and the conversion of the small amount of plastic present in the stream.

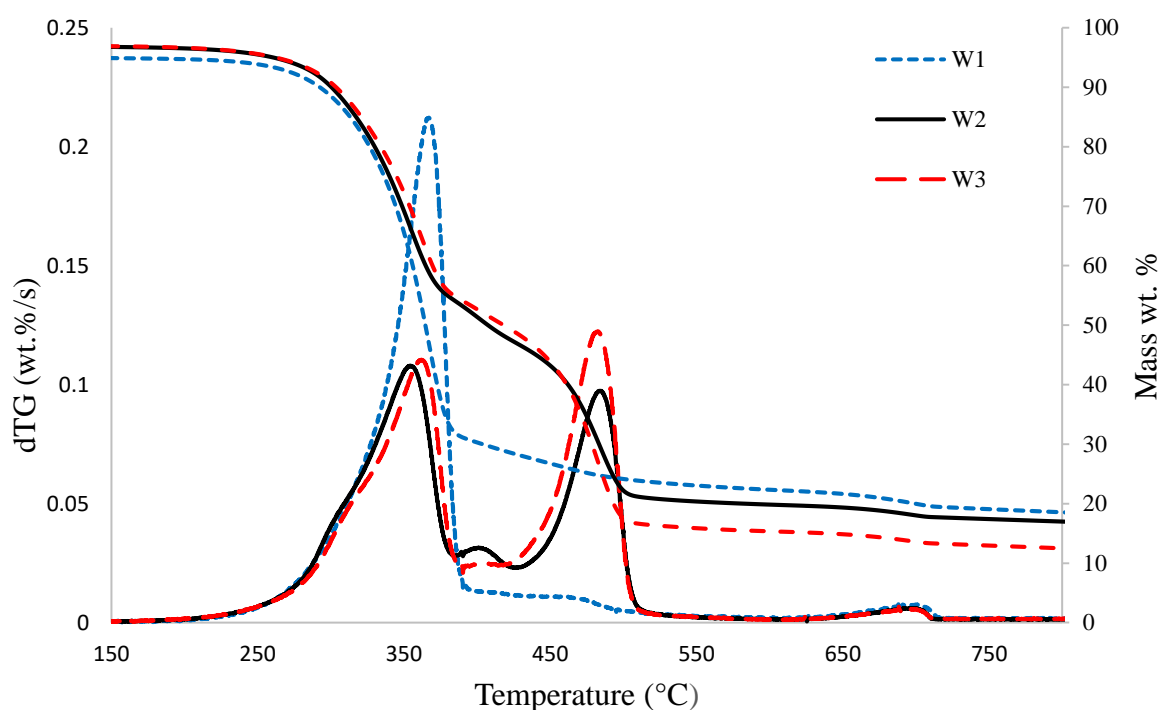


Figure 4-2: Thermogravimetric (TG) and derivative thermogravimetric (dTG) curves of three waste streams

The dTG curves obtained from W2 and W3 were composed of two main peaks. The first peak between 320 °C to 380 °C, characteristic of fibre decomposition, was significantly smaller than that of W1 and had associated mass losses of 45.14 wt.% and 43.64 wt.%, respectively. The second observed peak between 420 °C to 500 °C was attributed to the degradation of the plastic component, corresponded to mass losses of 30.51 wt.% and 36.30

wt.%, respectively. Based on these mass losses and the fact that plastic is known to generate more volatiles during slow pyrolysis than fibres (> 90 wt.% vs 40-75 wt.%) [28,29], it is clear that fibres were the main component of both W2 and W3.

Due to the complex nature of the waste streams, the composition could not be accurately determined. Together with fibres and common plastics found in waste (PP, PE, PET and PS), various other constituents were found to make up the waste sample (rubber, fabric, multilayer plastic, etc.). Due to the various processing steps during recycling, particles were embedded in each other and could not be separated manually as illustrated in Figure A-1 (Appendix A). As such, quantitative characterisation could not be achieved. For both W2 and W3, the temperature of the peak corresponding to the main plastic fraction was 480 °C, which is characteristic of polyethylene (PE) which has a degradation range between 420 °C and 500 °C [30,31] and/ or polypropylene (PP) with a degradation between 400 °C and 480 °C [32,33]. While this peak was higher for W3, a small peak at 410 °C was also observed for W2. Amongst the common plastics, the polymers known to degrade in this temperature region are polystyrene (PS) which has a degradation range between 350 °C and 450 °C [30,34] and polyethylene terephthalate (PET) which has a degradation range between 380 °C and 430 °C [35,36].

FTIR analysis (Figure 4-3) of the waste samples was conducted to identify characteristic functional groups and consider any differences between the plastics make-up of the samples. The strong bands between 2900 cm<sup>-1</sup> to 2800 cm<sup>-1</sup> are attributable to stretching of aliphatic C-H bonds as a result of the presences of CH<sub>2</sub> and CH<sub>3</sub> groups and were a result of the waste sample containing either PP and/or PE [37,38]. The weak C-H peak of W1 in this region was consistent with the fact that the sample was comprised mainly of fibre residues as suggested by dTG (Figure 4-2). The C-H peak in W2 and W3 was more prominent than that of W1 as a result of the sample having more CH<sub>2</sub> and CH<sub>3</sub> groups

confirming the significant presence of PE/PP, with the greater intensity for W3 confirming, as suggested by dTG analysis (Figure 4-2), that W3 was composed of more PE and/or PP than W2. The band visible in W2 and W3 between  $1750\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$  corresponded to that of a carbonyl group ( $\text{C}=\text{O}$ ) and is characteristic of the band observed from PET [38]. The difference in intensity of this peak between W2 and W3 together with the dTG curve of W2 where a peak was observed at  $410\text{ }^{\circ}\text{C}$  indicated that W2 contained more PET than W3.

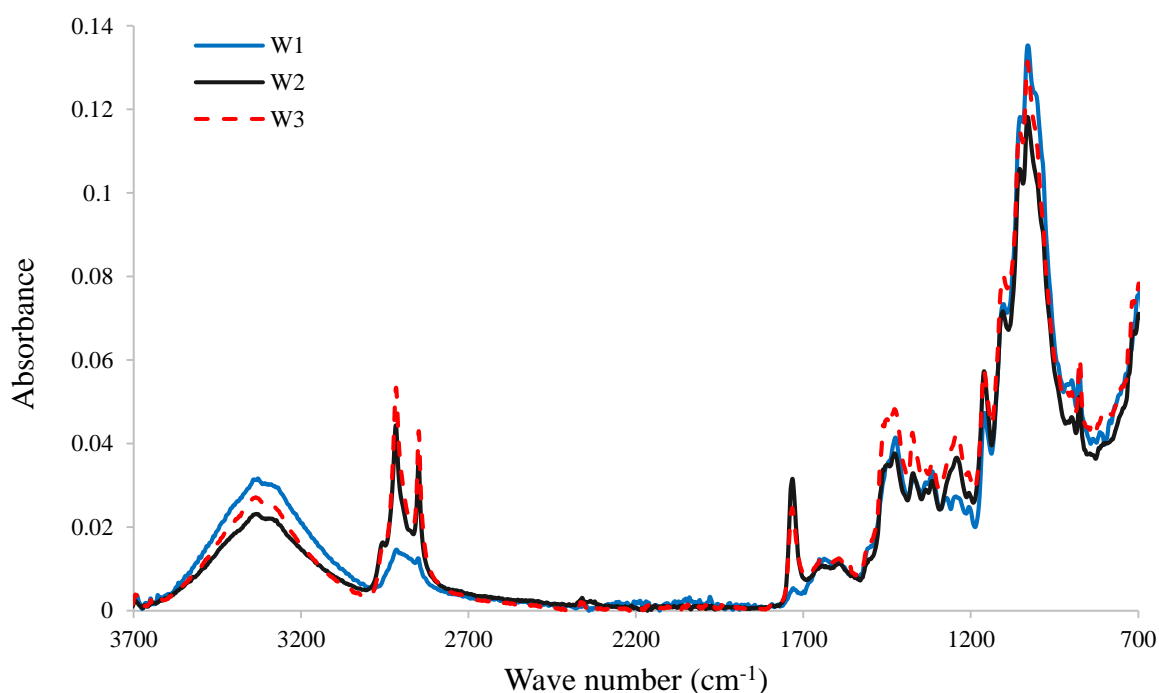


Figure 4-3: Fourier transform infrared spectroscopy spectra of waste streams

$\text{CaCO}_3$  was known to be present in the fibres of waste streams from the manufacturing of paper as it is generally used as a filler and a pigment to whiten paper [24]. For the three waste streams, the small peak present in the range of  $650\text{ }^{\circ}\text{C}$  to  $720\text{ }^{\circ}\text{C}$  of the dTG curve (Figure 4-2) was characteristic of the degradation of  $\text{CaCO}_3$  into  $\text{CaO}$  [24] (Eq 1). The presence of  $\text{CaCO}_3$  in the waste samples was confirmed during inorganic analysis by the detection of  $\text{CaO}$  (obtained by  $\text{CaCO}_3$  conversion, as explained in Section 2.2) as detailed in Section 3.1.2. While the large amount of  $\text{CaCO}_3$  in some paper waste fibres ( $> 40\text{ dry wt.}\%$ )

[6] compromises its use as an energy resource, its content in the waste streams studied in this work (< 5.2 wt.% based on CaO analysis) is acceptable.

#### **4.3.1.2 Physico-Chemical Composition**

The results of the elemental, HHV and proximate characterisation of the three waste streams are presented in Table 4-1, Table 4-2 and Figure 4-4 respectively. The proximate analysis results of W1 resembled those of certain PWS, with volatile matter (VM) (74.52 wt.%) and fixed carbon (FC) (10.80 wt.%) slightly lower than those usually reported for biomasses [24,26,39,40] and a higher ash content resulting in a relatively low HHV value of 16.3 MJ/kg (Table 4-2 and Figure 4-4). W2 and W3 had a greater VM (79.29 wt.% and 85.08 wt.%) content compared to W1 (Figure 4-4), which was a result of the significant proportion of plastic present in the sample and more particularly of PE/PP, which are known to be comprised mainly of VM (> 95 wt.%) [41]. The C/O ratio of W1 (Table 4-1), close to 1, was typical of fibre with high polysaccharide content [24]. The C/O value of 3.1 for W3 was further evidence of the significant amount of hydrocarbon plastic in this waste stream. The intermediate C/O ratio of 2.1 for W2 was influenced by the increase in PET content of W2 (C/O=1.9).

Table 4-1: Chemical characterisation of waste streams

|  | W1    | W2    | W3    |
|--|-------|-------|-------|
| <b>Ultimate Analysis wt % (dry ash free basis)</b> |       |       |       |
| C  | 47.47 | 60.62 | 66.98 |
| H  | 6.74  | 9.97  | 11.16 |
| N  | 0.09  | 0.11  | 0.17  |
| S  | 0.13  | 0.17  | 0.13  |
| O <sup>a</sup>                                     | 45.57 | 29.13 | 21.56 |
| <b>Inorganic Content wt. %</b>                     |       |       |       |
| CaO  | 2.90  | 2.26  | 2.20  |
| Al <sub>2</sub> O <sub>3</sub>                     | 1.50  | 1.36  | 0.90  |
| SiO <sub>2</sub>                                   | 3.19  | 3.83  | 1.06  |

a determined by difference

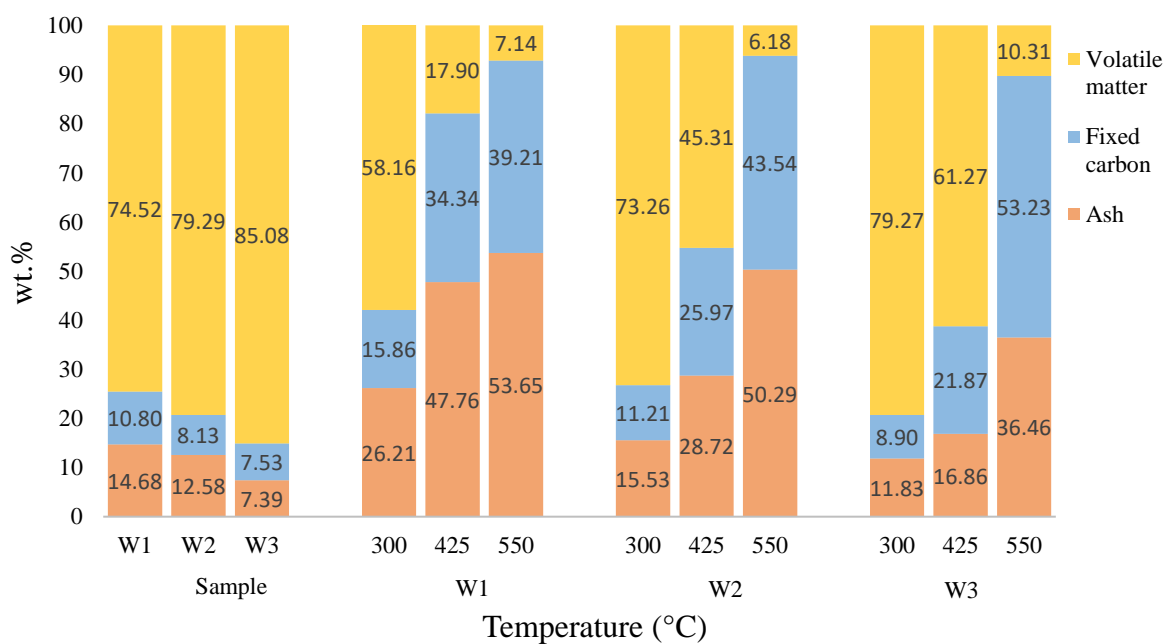




Figure 4-4: Proximate analysis of the three different waste streams and the char products obtained from pyrolysis at different temperatures

The HHV results observed for W2 and W3 (Table 4-2) were consistent with the above interpretations. Based on the HHV of hydrocarbon plastic PE (43 MJ/kg) and PET (24 MJ/kg) [42], the higher HHV of 28.8 MJ/kg obtained for W3 compared to 22.5 MJ/kg for W2 was expected.

### **4.3.2 Pyrolysis Experiments**

The mass yields of pyrolysis products from the three different waste streams at different final conversion temperatures are presented in Figure 4-5, along with the corresponding product HHVs in Table 4-2. The mass yields of the char and liquid products were determined in accordance with Equations 2 to 7, as described in Section Product Yields.

#### **4.3.2.1 Char Yield and Characterisation**

The highest yield for conversion of W1 to char (73.7 wt.%) was observed at 300 °C, where the waste stream was only partially pyrolysed. The increased HHV of the char product (17.9 MJ/kg) compared to the feedstock (16.3 MJ/kg) was attributed to deoxygenation through dehydration reactions that predominated for the fibre component in a temperature range of 200 °C to 300 °C [43]. An increase in pyrolysis temperature at 425 °C and 550 °C resulted in more extensive conversion of W1 into volatile compounds (Section Liquid Yield and Characterisation) resulting in a decrease in char yield to 35.7 wt.% and 30.5 wt.% respectively (Figure 4-5), which was consistent with biomass samples that have a high ash content [44]. The increase in conversion temperature (425 °C and 550 °C) was expected to increase the C/O ratio of the char product and increase the resulting char HHV. However, a decrease in HHV to below 17 MJ/kg was observed for both temperatures.

Table 4-2: HHV of waste feedstock and pyrolysis products (MJ/kg)

|                         | W1          |                    | W2          |                    | W3          |                    |
|-------------------------|-------------|--------------------|-------------|--------------------|-------------|--------------------|
| <b>Waste Material</b>   | 16.3±0.1    |                    | 22.5±0.7    |                    | 28.8±0.5    |                    |
| <b>Temperature (°C)</b> | <b>Char</b> | <b>Tarry Phase</b> | <b>Char</b> | <b>Tarry Phase</b> | <b>Char</b> | <b>Tarry Phase</b> |
| <b>300</b>              | 17.9±0.2    | -                  | 27.1±0.1    | -                  | 31.6±0.1    | -                  |
| <b>425</b>              | 16.8±0.4    | 13.5±2.0           | 26.6±0.2    | 25.8±0.2           | 32.9±0.1    | 42.8±0.1           |
| <b>550</b>              | 16.7±0.2    | 16.8±1.0           | 18.6±0.1    | 30.9±2.3           | 20.9±0.7    | 40.4±1.6           |

This trend, which was already reported for the pyrolysis of paper sludge with intermediate ash content [7], was mainly attributed to the large ash content of the char product 47.76 wt.% and 53.65 wt.% respectively (Figure 4-4).

A higher char yield was also observed during pyrolysis of W2 and W3 at 300 °C, compared to higher temperatures, similar to the trend for W1, as was a result of the feedstock being partially pyrolysed (Figure 4-5). The increased HHVs of the char products at 300 °C for W2 (27.1 MJ/kg) and W3 (31.6 MJ/kg), compared to their respective feedstocks, was attributed to deoxygenation through dehydration reactions associated with the fibre component [43]. As evidenced by the thermal behaviour study (Figure 4-2), the conversion of the plastic component was limited at 300 °C, resulting in a char product still containing a substantial amount of VM greater than 70 wt.% (Figure 4-4). A further increase in temperature to 425 °C significantly reduced the char yield (Figure 4-5). The additional mass loss was due to the further decomposition of the fibre and partial decomposition of the plastic component, as confirmed by the tarry phase yield and HHV (presented in Section Liquid Yield and Characterisation). The char yield decrease between 300 °C and 425 °C was more pronounced for W2 (-38.6 wt.%) than for W3 (-34.9 wt.%). Moreover, it is worth noting that

the higher ash content of W2 compared to W3 always resulted in a higher char yield for W2, except at 425 °C. This result was certainly due to the difference in the plastic composition between W2 and W3 (as detailed in Section Thermal Behaviour). The higher content of less stable plastic (PET and PS) in W2 resulted in a higher degree of conversion at 425 °C than for W3.

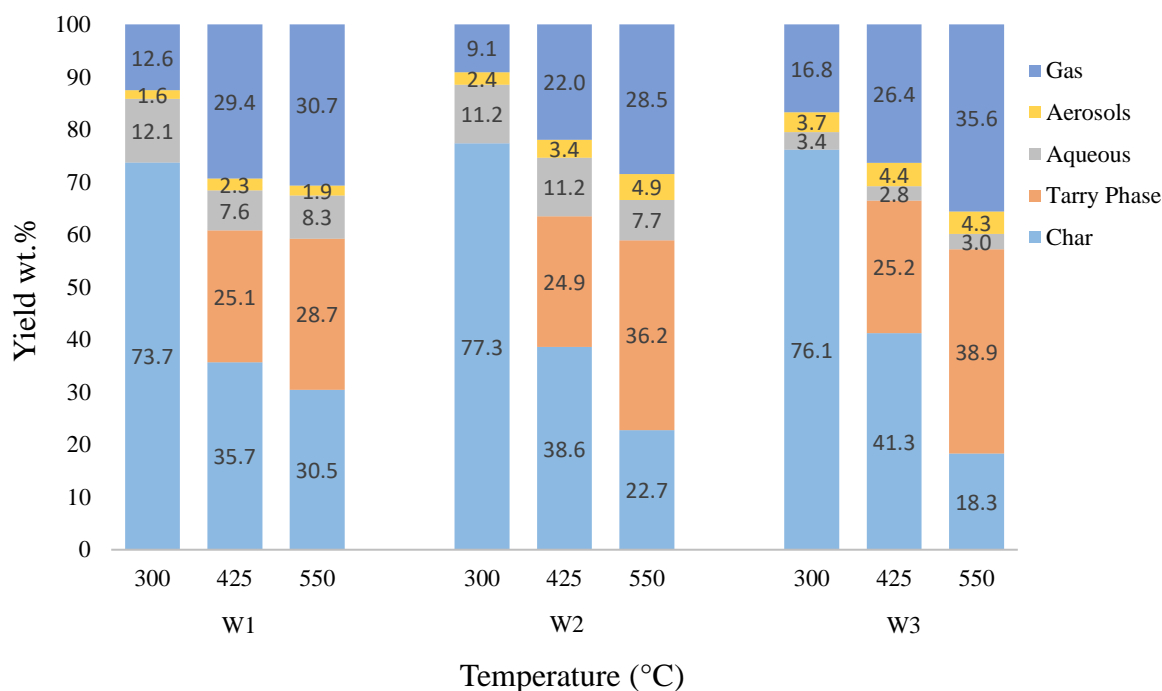


Figure 4-5: Product yields and product distribution of slow pyrolysis of waste streams

The larger amount of unconverted plastic in the char product of W3 was confirmed by the higher VM content (61.27 wt.% for W3 vs 45.31 wt.% for W2). For both W2 and W3, the HHV of the char product remained relatively constant as the temperature was increased from 300 °C to 425 °C. As the more extensive fibre deoxygenation and the increase in ash content had a positive and negative influence respectively, on the HHV, the influence of plastic was more difficult to predict, due to its partial conversion. The higher degree of plastic conversion for W2 could explain the fact that the char HHV slightly decreased for this sample, while it increased for W3 due to the higher content of hydrocarbon plastic remaining

in the char. A large decrease in the HHV of the char prepared at 550 °C were observed for both W2 and W3, with energy contents of 18.6 MJ/kg and 20.9 MJ/kg respectively. This was a result of the full conversion of the hydrocarbon plastic component of the sample leaving behind a char containing a small amount of VM (6.18 wt.% -10.31 wt.%) and a large ash content (36.46 wt.% – 50.29 wt.%) (Figure 4-4).

#### **4.3.2.2 Liquid Yield and Characterisation**

The condensable volatile fraction collected during pyrolysis experiments using the fractionation condensation system (detailed in Section Product Yields) resulted in two main products, tarry phase and aqueous phase. The conversion of W1, W2 and W3 at 300 °C was mainly dominated by the dehydration of the fibre component and produced a single aqueous phase comprised mainly of water (> 75 wt.%) with the highest yield obtained for W1 (12.1 wt.%), the sample with the highest fibre content. When the pyrolysis temperature was increased to 425 °C and 550 °C, depolymerisation mechanisms and the production of organic compounds were promoted. As a consequence a significant amount of tarry phase product was produced for W1 (25.1 wt.%) at 425 °C and (28.7 wt.%) 550 °C. The small increase in the yield between 425 °C and 550 °C was due to the further degradation of the fibre residue and small amounts of plastic present in W1. The HHV of the tarry phase of W1 represented that of typical bio-oil produced by slow pyrolysis [7], with a HHV of 13.5 MJ/kg at 425 °C and 16.8 MJ/kg at 550 °C.

A significant tarry phase yield was obtained for W2 (24.9 wt.%) and W3 (25.2 wt.%) at the temperature of 425 °C. This was due to the substantial conversion of the fibre component and partial conversion of plastic component (Figure 4-2). As the temperature was increased to 550 °C, further degradation of the plastic component occurred, resulting in tarry phase yields of 36.2 wt.% and 38.9 wt.% for W2 and W3 respectively.

The HHVs of the tarry phase obtained at 425 °C for W2 and W3 were 25.8 MJ/kg and 42.8 MJ/kg respectively (Table 4-2). The differences in the HHV of the tarry phase were attributed to the difference in the elemental composition of the waste streams (Table 4-1). The higher content of oxygen in W2 (Table 4-1) was likely to result in a tarry phase containing more oxygen than for W3 and thus a lower HHV. The higher content of PET in W2 certainly contributed to this trend [41]. As the temperature was increased to 550 °C, the additional tarry phase was mostly produced from the full conversion of the PP/PE component, as the conversion of the fibre component of the waste stream was expected to be limited above temperature of 390 °C as usually reported in literature [43] and observed from the dTG curve of W1 (Figure 4-2). As a consequence, a further increase in the HHV of W2 (30.9 MJ/kg) was observed, while that of W3 remained relatively high (Table 4-2). According to literature, the HHV of pyrolysis oil produced from PP and PE is usually higher than 40 MJ/kg [45] .

As the aqueous phases collected in the fractionation condensation system at 300 °C, 425 °C and 550 °C were comprised mainly of water >75 wt.%, it could not be considered for fuel application and only the tarry phase was considered for the EC study discussed in the next section.

#### **4.3.3 Energy Conversion Assessment**

The results of gross EC of streams W1, W2 and W3 are presented in Figure 4-6. In this work as discussed in Section Energy Conversion Assessment, gross EC assesses the ability of pyrolysis to convert the stored energy in the raw material to either a solid (char) or an oil (tarry phase). With regards to the gas fraction (not analysed in this study), it is usually combusted to provide the heat required for the pyrolysis process [11] and therefore not

included in the calculation of EC. There are various scenarios for gross EC in which either a trade-off between char production or tarry phase production has to be considered.

The EC profile obtained for W1 was comparable with previous results reported for the slow pyrolysis of PWS [7]. For the highest char yield at 300 °C, an EC of 81.2 % was obtained. The upgrading of the raw material into a more energy dense char product was limited and resulted in char HHV of 17.9 MJ/kg comparable with lignite A coal (according to ASTM D 388 coal ranking standard). The increase in conversion temperature to 425 °C and 550 °C did not improve the fuel quality of the char obtained (HHV of 16.8 MJ/kg and 16.7 MJ/kg respectively) and produced a low quality tarry phase that had a HHV < 17 MJ/kg with associated EC of 20.8 % and 29.7 % respectively. Based on these results and from an energy perspective, the conversion of W1 through slow pyrolysis is not recommended.

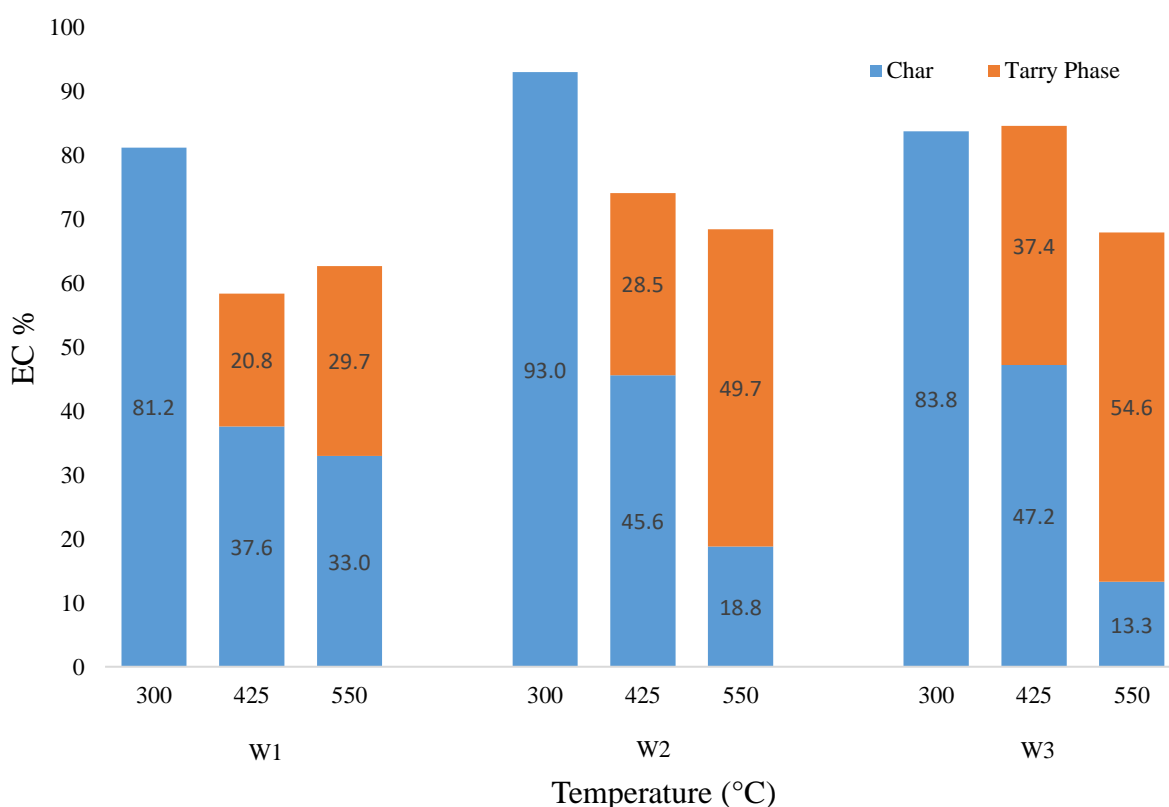


Figure 4-6: Energy conversion (EC) of pyrolysis products

For W2 and W3 the EC analysis resulted in results that are more promising. For pyrolysis at 300 °C, most of the energy content of the sample remained in the char product

(93.1 % for W2 and W3 83.8 % for W3), producing chars with HHVs of 27.1 MJ/kg for W2 and 31.6 MJ/kg for W3. Fuel products with properties comparable to those of commercial coals were produced at a relatively low pyrolysis temperature. The energy content of the waste streams considered in this study represents approximately 10 % of the coal required to produce steam for the paper manufacturing process (personal communication with mill personnel) and as such the co-feeding of the pyrolysis products should have little impact when combusted with existing fuel sources in existing infrastructure at the mill. As noted by Chiaramonti et al. [46], based on the high throughput rates in industrial boilers and blending at less than 10 wt.%, the co-firing of the char produced from W2 and W3 at 300 °C should have little to no effect on stability of the boilers and thus making it possible to utilize existing infrastructure for the co-firing of pyrolysis products [46]. For a pyrolysis temperature of 425 °C, a shift in energy towards the tarry phase (28.5 % for W2 and 37.4 % for W3) occurred, while more than 45 % of the energy in the feedstock remained in the char for both W2 and W3. Moreover, the HHVs of the tarry phases and char products were greater than 25 MJ/kg. In particular, the conversion of W3, the stream with the highest content of hydrocarbon plastic, led to an overall EC of 84.6 %, while producing a char with an HHV of 32.9 MJ/kg and a tarry phase with an HHV of 42.8 MJ/kg. These products are comparable to those of traditional fossil fuels, in particular high volatile bituminous coals (HHV >28 MJ/kg) and diesel (HHV 44 MJ/kg). The increase in pyrolysis temperature to 550 °C led to a further shift in the EC to tarry phase, which contained 49.7 % of the energy content the waste stream for W2 and 54.6 % for W3. However, the increase in the energy content of the tarry phase also lowered the overall EC of W2 and W3 by 5.7 % and 16.7 %, respectively, and substantially decreased the HHVs of the char products (< 21 MJ/kg). The highest EC of liquid products occurred at 550 °C, and has the potential to be utilised in heavy fuel oil (HFO) boilers for the production of steam.

## 4.4 Conclusions

This study assessed the suitability of slow pyrolysis for conversion of fibre residues contaminated with plastic from a paper-recycling mill into valuable energy products. The conversion of the waste stream containing negligible amount of plastic via slow pyrolysis is not recommended, as it produced poor quality fuel products with HHVs < 19 MJ/kg. The conversion of the waste streams containing significant amounts of plastic at 300 °C and 425 °C resulted in char and tarry phase products with remarkably high HHVs up to 26.6 and 32.9 MJ/kg and 30.9 and 42.8 MJ/kg respectively. The energy conversion of all three streams decreased at 550 °C, but favoured the production of tarry phase product at the expense of the quality of the char product (HHV <21 MJ/kg) and as such conversion at 550 °C is not recommended unless a tarry phase product is specifically required for use in heavy fuel oil (HFO) boilers. Final pyrolysis conditions should be chosen in such a way that careful consideration is given to the requirements and existing infrastructure of the facility.

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## Chapter 5: Fast Pyrolysis of Fibre Waste Contaminated with Plastics for use as Fuel Products

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**Title** “*Fast Pyrolysis of Fibre Waste Contaminated with Plastic for use as Fuel Products*”

**Authors:** Logan Jeremy Brown, François-Xavier Collard, Johann Görgens

### Objective of the Dissertation in this Chapter

This chapter addresses **objectives 1-3** of this PhD study. This chapter specifically deals with the production of a condensable fuel product via fast pyrolysis (**objective 1**) and the effect plastic percentage and composition has on the quality of the final condensable fuel product (**objective 2**). The usefulness of pyrolysis products, specifically gas, to meet the energy demand of two of the main energy requirements (feedstock drying and heat for pyrolysis) is discussed. Furthermore, the net energy surplus after the two main energy requirements (heat for pyrolysis and drying) was met and was discussed in relation to the final pyrolysis temperature and waste stream composition (**Objective 3**).

The fast pyrolysis of the three waste streams produced energy dense (HHV up to 42 MJ/kg) condensable fuel products with yields up to 53.6 wt.%, which was significantly higher than the yields obtained for the slow pyrolysis (Chapter 4) of the same waste streams. All three waste streams produced low calorific value chars (HHV of between 18 to 22 MJ/kg) at

the highest conversation temperature. Even those HHV were significantly lower than the ones produced at temperatures  $<550\text{ }^{\circ}\text{C}$ , however, they were still similar to low grade bitumous and lignite coal. The highest estimate yield of surplus energy of between 10 to 26 MJ/(kg dry feedstock) after the energy demand of the pyrolysis process had been met, occurred at temperature  $> 450\text{ }^{\circ}\text{C}$ .



## Candidate declaration

With regards to chapter 5, page numbers 89 to 122 of this dissertation, the nature and scope of my contributions were as follows:

| Name of contributions     | Extent of contribution (%) |
|---------------------------|----------------------------|
| Experimental planning     | 80                         |
| Executing experiments     | 100                        |
| Interpretation of results | 70                         |
| Writing the chapter       | 100                        |

The flowing co-authors have contributed to chapter 5 page 89 to 122 in the following manner:

| Name                    | Email address  | Nature of contributions   | Extent of contribution (%) |
|-------------------------|--|---|----------------------------|
| Francois-Xavier Collard | <a href="mailto:fcollard@sun.ac.za">fcollard@sun.ac.za</a> | <ul style="list-style-type: none"> <li>• Experimental planning</li> <li>• Reviewing chapter</li> <li>• Interpretation of results</li> </ul> | 10<br>80<br>20             |
| Johann Görgens          | <a href="mailto:jgorgens@sun.ac.za">jgorgens@sun.ac.za</a> | <ul style="list-style-type: none"> <li>• Reviewing chapter</li> <li>• Interpretation of results</li> <li>• Experimental planning</li> </ul> | 20<br>10<br>10             |

Candidate signature:.....

Date:.....

## Declaration by co-authors:

The undersigned hereby confirm that

1. The declaration above accurately reflects the nature and extent of the contributions of the candidate and the co-authors to chapter 5 page numbers 89 to 122 in the dissertation
2. No other authors contributed to chapter 5 page numbers 89 to 122 besides those specified above.
3. Potential conflicts of interest have been revealed to all interested parties and that the necessary arrangements have been made to use the material in chapter 5 page numbers 89 to 122 in the dissertation

| <b>Signature</b> | <b>Institute Affiliation</b> | <b>Date</b> |
|------------------|------------------------------|-------------|
|                  | Stellenbosch University      |             |
|                  | Stellenbosch University      |             |
|                  | Stellenbosch University      |             |

“Declaration and signature is in possession of candidate and supervisor

# Fast Pyrolysis of Fibre Waste Contaminated with Plastic for use as Fuel Products

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## Abstract

Pyrolysis is finding increasing application as a tool for the effective management of industrial waste, as it can process a wide variety of heterogeneous feedstock into energy dense products. Inductively heated fast pyrolysis with heating rate of 250 °C/min was applied for conversion into energy products of three industrial waste streams from a fibre recycling mill, contaminated with plastic wastes into energy products. Experiments were carried out at three different temperatures (350, 450 and 550 °C) and the yields and energy contents of the char, oil, wax and gas products were determined. For all three waste streams, conversion at 350 °C, mostly concentrated the energy in the char, resulting in calorific values between 20.9 MJ/kg and 35.1 MJ/kg which is comparable to common bituminous coal used for power generation. Pyrolysis at 450 or 550 °C promoted the formation of condensable volatiles (wax/liquid) with total yields of up to 59 wt.% being obtained at 550 °C, with the calorific value up to 41.7 MJ/kg at temperatures  $\geq 450$  °C comparable to heavy fuel oil. The estimate net energy yield for the three waste streams ranged from 10 to 25 MJ/(kg dry feedstock) with the largest energy yield (25 MJ/(kg dry feedstock)) being obtained at temperatures  $\geq 450$  °C for the stream containing the largest fraction of hydrocarbon plastics.

**Keywords:** Fast Pyrolysis, plastic, energy yield, fibre recycling, fibre

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## 5.1 Introduction

The renewed drive towards a low carbon economy by developing and industrialized economies is promoting the mitigation of waste disposal by reuse or recovery as alternative processing routes to landfilling [1,2]. The South African paper industry currently produces large quantities of waste (600 to 1200 tons/month) from the manufacturing of different grades of paper from recycled fibres, and can be grouped into two main categories namely paper waste sludge (PWS) and rejects. PWS is typically obtained from the waste water treatment facilities of such mills, consists of degraded fibres and appreciable amounts of inorganics [3]. Rejects originate from processing activities that occur before paper machine and are comprised of degraded fibres (similar in nature to PWS) and varying amounts of plastic waste that differ in composition depending on the waste source used as feedstock [4–6].

Thermochemical conversion techniques such as pyrolysis are finding increasing application in the mitigation of waste from industrial processes as they have the ability to convert a heterogeneous waste into a homogenous, energy-dense product [4,7]. A previous comparison of slow, vacuum and fast pyrolysis for the conversion of low ash PWS (below 8.5 wt.%) has shown that fast pyrolysis is the preferred processing option for the production of oil with yields of up to 60 wt.%, as it was possible to obtain fuel product with a higher heating value (HHV) of 22 MJ/kg compared to 10 MJ/kg produced from slow pyrolysis. The char product from slow and fast pyrolysis had an HHV of 20 and 22 MJ/kg respectively [8]. Fast pyrolysis is the process whereby the feedstock is heated rapidly ( $>150$  °C/min) to the pyrolysis temperature and the resulting pyrolysis vapour is rapidly removed from the reaction zone, limiting secondary cracking reactions and promoting the production of liquid fuel. It is well accepted that the maximum yield of bio-oil ( $>75$  wt.%) from lignocellulosic biomass is achieved upon subjecting the feedstock to pyrolysis at elevated heating rates ( $>150$  °C/min)[9], while the slow pyrolysis of biomass promotes the formation of char and/or

gaseous fraction [10,11]. The fast pyrolysis of plastic waste at temperatures  $> 450\text{ }^{\circ}\text{C}$ , like biomass promotes the formation of a condensable product, which is either reported as oil, wax or a combination of both with yields in a range of 68 to 92 wt.% being obtained [12,13]

Addition of a pure plastic polymer to biomass in a 50:50 mass ratio has been shown to improve the mass yields (by 15 - 20 wt.%) and HHVs of liquid products (by 10 – 25 MJ/kg) from slow pyrolysis [14–16], with total liquid yields up to 69.7 wt.% being reported [17,18]. This is significantly higher than what is expected from the slow pyrolysis of lignocellulosic biomass (10-30 wt.%) [10,19] and similar to the yields reported for the fast pyrolysis of lignocellulosic biomass ( $>60\text{ wt.}\%$ ) [20]. Our recent study [6] has shown that it is possible to obtain both viscous liquid and solid fuel product from the slow pyrolysis of fibre contaminated with plastic that have HHVs up to 40 MJ/kg, similar to conventional fuels [6]. However, even the yield of this energy dense oil/wax phase did not exceed 38.9 wt.% during slow pyrolysis. Since fast pyrolysis is known to promote the formation of the condensable volatiles, a higher yield of oil/wax can be expected with these feedstocks, compared to slow pyrolysis. To date, the majority of research on the pyrolysis conversion of mixtures of lignocellulosic biomass and plastic has focused on the slow pyrolysis of synthetic mixtures with known composition [21,22].

This study focused on the fast pyrolysis of industrial fibre-rich waste contaminated with plastic from a fibre recycling mill and determined its performance of the waste conversion into condensable fuel products. The gross energy conversion (EC) has been regarded as a reliable indication of the ability of pyrolysis to transfer the energy in the feedstock into one or more of the pyrolysis products [23,24]. For fast pyrolysis of lignocellulose, the majority of the energy contained in the raw feedstock has been reported to be found in the liquid product ( $> 45\%$ ) [8,23]. The overall EC of char and bio-oil produced from PWS being in the region of 60-70%, which has been observed to be between 20-36%

higher than for slow pyrolysis [8]. The gas fraction produced from pyrolysis is generally not one of the targeted products as obtaining large gas yields requires processing temperatures in excess of 600 °C. Although its composition is often not determined, the gas fraction is generally considered to supply the energy needs for pyrolysis conversion or a variety of other on-site processing activities[25]. The gas produced from co-pyrolysis of biomass-plastic mixtures should be a more valuable source of energy compared to its biomass counterpart. The presence of polypropylene(PP) and polyethylene (PE) plastic in the waste mixtures is likely to produce more short chain hydrocarbons ( $C_2$ - $C_4$ ) [26,27] thereby potentially increasing the calorific value of the gas fraction and the amount of heat that it can provide for the pyrolysis process [20].

This study assessed the ability of the fast pyrolysis process utilising an inductively heated reactor at three distinct temperatures for the conversion of three different fibre-rich waste streams contaminated with plastic from a fibre recycling mill into useful energy products. The main objective was to optimise the yield of the condensable product (organic fraction) while assessing the gross energy conversion, with particular emphasis on the factors affecting the yields and energy content of the pyrolysis products and their potential uses.

## **5.2 Material and Methods**

### **5.2.1 Raw material preparation**

The waste streams used in this study were obtained from two different fibre recycling mills in South Africa. Two of the waste streams were obtained from the Mpact Springs mill and the other from the Mpact Felixton mill and can be classified into the group described as rejects, which comprised of lignocellulosic fibres, a significant amount of plastic waste (10 –50 wt.%) originating mainly from pre and post consumer waste (food cartons, food packaging, plastic bags and cooldrink bottles etc ) and water (>50wt.%). Each waste stream underwent a drying process in a tunnel greenhouse for a period of five days resulting in a moisture content of between 2 to 5 wt.% before being milled down and subsequently pelletized, resulting in a 2-fold increase in the packing density of the feedstock. The physico-chemical characteristics of the feedstock are presented in Table 5-1 and discussed in detailed in Section 5.3.1.

### **5.2.2 Analytical Characterisation Techniques**

The analytical techniques used to characterise the waste feedstock and pyrolysis products are described below. As observed in previous studies with paper waste material [3,4], fibres from the rejects contained significant amounts of calcium carbonate ( $\text{CaCO}_3$ ), which is primarily used as a filler in paper [4]. Calcium carbonate degrades into calcium oxide and  $\text{CO}_2$  (2.1-3.9 wt.% as observed by TGA, see Table 5-1) at temperatures around 700 °C (Eq 5-1) [3,4]. As a result, an adjustment had to be made to the standard proximate analysis testing method (ASTM E1131) as suggested by Ridout et al. (2015). An additional step at 650 °C for 5 min was added to the standard testing method to determine the volatile matter content, while preventing the decomposition of calcium carbonate from occurring.



Ultimate analysis of raw material was conducted using an Elementar Microcube EL III and adjustment to the carbon content had to be made as the carbon content is measured based on the production of CO<sub>2</sub> formed during combustion. Based on the weight percentage of CO<sub>2</sub> produced from CaCO<sub>3</sub> as measured by proximate analysis, a correction was made to take into account the CO<sub>2</sub> released from calcium carbonate during combustion, to determine the content of organic carbon. A Cal2K Eco Calorimeter was used to measure the calorific value of waste feedstock and pyrolysis products (solid and condensed) in accordance with ASTM D5865-11a. The water content of the aqueous phases produced from all three streams was determined in accordance with ASTM E203 standard, using a Metrohm 701 Titrino Karl-Fischer Titrator, hydranal composite 5 titrant (Sigma –Aldrich). In order to study the thermal behaviour of the samples and compare their fibre and plastic proportions, thermal milligram-scale study was carried out using a thermogravimetric analyser TGA/DCS 1 Star Systems Mettler Toledo. Experiments were carried out in triplicates using 20 mg of sample at a heating rate of 10 °C min<sup>-1</sup> from 30 °C to 900 °C using nitrogen as the inert purged gas at a flow rate of 80 ml min<sup>-1</sup>.

### 5.2.3 Fast Pyrolysis Experiments

Pyrolysis experiments were carried out in an inductively heated stainless steel tubular reactor having an outside diameter (OD) of 110mm and a heated reaction zone of 450 mm depicted in Figure 5-1. Infrared (IR) temperature measurement was used to monitor the reactor temperature and was calibrated using a trial and error approach, where the reactor was heated while a metallic thermocouple was placed at the centre. The emissivity of the IR temperature measurement was adjusted until the IR temperature sensor and the metallic thermocouple read the same value. A mass of 30 g of waste feedstock was loaded into the reactor and then



heated rapidly ( $250\text{ }^{\circ}\text{C min}^{-1} \pm 5\text{ }^{\circ}\text{C min}^{-1}$ ) to the desired reaction temperature for all three reaction temperatures (350, 450, 550  $^{\circ}\text{C}$ ).

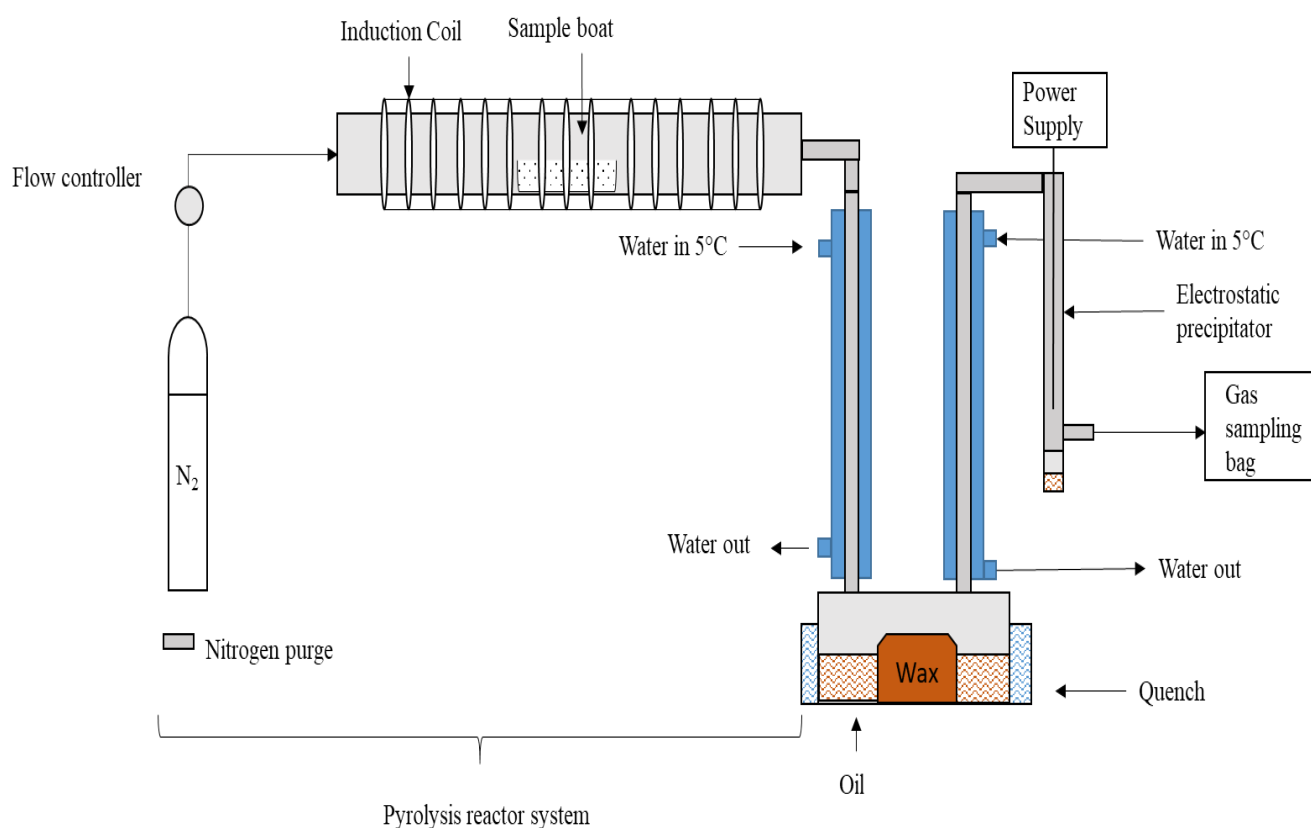


Figure 5-1: Schematic inductively heated pyrolysis setup

The reactor was continuously purged with nitrogen at  $2.5\text{ L min}^{-1}$ . This relatively high flow rate resulted in an average volatile residence time of  $\sim 30\text{ s}$ . The evolved volatiles were swept from the reaction zone to a condensation system that consists of two condensers cooled to a temperature of  $5\text{ }^{\circ}\text{C}$ , a collection pot where a product composed of two phase (oil and wax) was collected (Figure 4-1) and an electrostatic precipitator (ESP) set at  $12\text{ kV}$  where an additional wax product was collected. The oil and wax mixture collected in the condensation pot was separated from each other via decantation, then the oil product was decanted from the pot and filtered to ensure it was free of precipitate after which the wax product (in the pot and filtration residue) was removed and added together with that formed in the ESP. The non-condensable gas fraction was collected continuously for the duration of the experiment using

5L tedlar bags. Sample were collected for a period of two minutes to allow the tedlar bag to fill up before being replaced and subsequently analysed using gas chromatography (G.A.S. CompactGC 4.0) This method allows for the quantification of the main gas compounds produced during the whole experimental run. The instrument was calibrated using standard mixtures of calibration gas (Afrox) to determine the concentration of N<sub>2</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub>. N<sub>2</sub> was used as an internal standard to determine the yield of each gas compound. The HHV (MJ/kg) of the gas phase was calculated by using a weighted summed average of the HHVs of the individual gas species according to Eq 5-2, with X<sub>i</sub> representing the yield of individual gas species in kg, m<sub>total gas</sub> representing the total yield of gas (kg) and HHV<sub>i</sub> (MJ/kg) the HHV of the individual gas specie.

$$HHV_{gas} = \frac{\sum X_i \times HHV_i}{m_{total\ gas}} \quad \text{Eq 5-2}$$

Once an experimental run of 30 min was complete, the reactor was cooled to ambient temperature and the resulting components that comprised the system as depicted in Figure 5-1 were weighed to determine the yield of char and condensed products. For certain conditions, the product collected in the collection pot of the condensation system was composed of two main fractions, a brown liquid oil phase and a brown wax phase. These fractions were separated from each other, weighed and termed oil and wax respectively. The ability of pyrolysis to convert a sample into another form of energy can be assessed in accordance with Eq 5-3.

$$EC_i(\text{MJ}/(\text{kg waste feedstock})) = \frac{m_i \times HHV_i}{m_{\text{sample}}} \times 100 \quad \text{Eq 5-3}$$

Where m<sub>i</sub> and HHV<sub>i</sub> represent the mass and HHV of a specific pyrolysis product and m<sub>sample</sub> represent the mass waste stream of particular interest. EC<sub>i</sub> represents energy content of a pyrolysis product relative to a kg of waste feedstock. The estimate energy surplus estimate

(ES) of pyrolysis can be calculated after the energy required for drying ( $E_{\text{drying}}$ ) and pyrolysis ( $E_{\text{pyrolysis}}$ ) is subtracted from the energy stored in the pyrolysis products and is calculated according to Eq 5-4

$$\text{ES (MJ/kg waste feedstock)} = E_{\text{pyrolysis products}} - E_{\text{drying}} - E_{\text{pyrolysis}} \quad \text{Eq 5-4}$$

Pyrolysis experiments were conducted in duplicates to ensure repeatability of results. For the 3 waste streams, the maximum standard deviation for char, oil, wax and gas was 3.32 wt.%, 3.19 wt.%, 2.76 wt.% and 1.43 wt.% respectively and the resulting mass balance closure between 90 to 96 wt.%.

### 5.3 Results and Discussion

After a description of the raw material characteristics, the subsequent sections detail the results from fast pyrolysis experiments and are discussed in relation to final conversion temperature and plastic composition of the waste streams. After which, applicability of fast pyrolysis to industrial waste streams containing both fibre and plastic from a fibre recycling mill is discussed in terms of the estimate energy yield.

### 5.3.1 Raw material Characterisation

The physico-chemical composition of W1, W2 and W3 is presented in Table 5-1 is described in detail elsewhere [6]. The derivative thermogravimetric (dTG) curve (Figure 5-2) of the three waste samples consisted of two distinct mass loss regions, corresponding to the devolatilization regions associated with lignocellulosic biomass (200 °C – 400 °C) and plastic (400 °C – 500 °C). Though plastic wastes components were identified by visual inspection in all of the 3 waste streams during sample preparation, the dTG of W1 was composed of one main peak (Figure 5-2), corresponding to the degradation of the fibre component, with an associated mass loss of 64.43 wt.%.

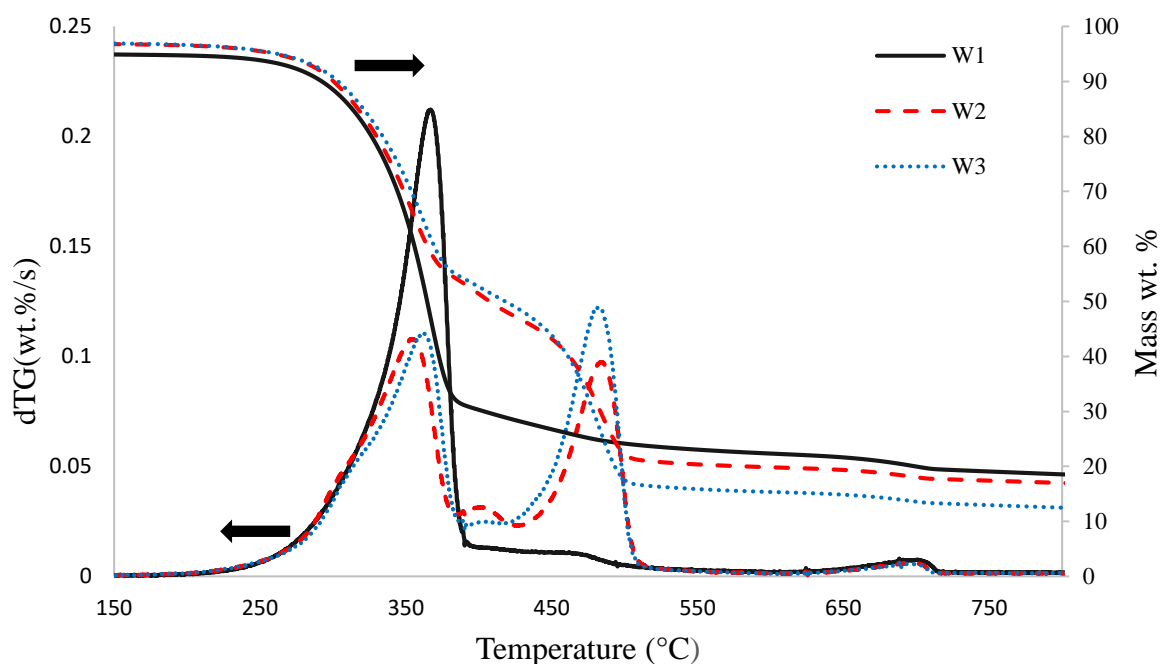


Figure 5-2: Thermogravimetric (TG) and derivative thermogravimetric (dTG) curves of W1, W2 and W3 at a heating rate of 10 °C/min, with arrows pointing to the respective axes

The chemical composition of W1 confirmed the stream was predominantly composed of fibres, with volatile matter (VM) content of 74.52 wt.%, C/O ratio of 1.04 and a relatively low HHV of 16.3 MJ/Kg (Table 5-1), which is similar in composition to low ash paper waste sludge [4,28,29].

Table 5-1: Composition of waste streams from paper recycling mill

|   | W1    | W2    | W3    |
|---|-------|-------|-------|
| <b>Proximate (wt.%)<sup>db</sup></b>          |       |       |       |
| Volatile Matter                               | 74.52 | 79.29 | 85.08 |
| Fixed Carbon                                  | 10.80 | 8.13  | 7.53  |
| <sup>a</sup> CO <sub>2</sub>                  | 3.88  | 2.47  | 2.09  |
| Ash (900 °C)                                  | 10.80 | 10.11 | 5.30  |
| <b>Ultimate Analysis(wt. %)<sup>daf</sup></b> |       |       |       |
| C   | 47.47 | 60.62 | 66.98 |
| H   | 6.74  | 9.97  | 11.16 |
| N   | 0.09  | 0.11  | 0.17  |
| S   | 0.13  | 0.17  | 0.13  |
| O <sup>*</sup>                                | 45.57 | 29.13 | 21.56 |
| C/O   | 1.04  | 2.08  | 3.11  |
| <b>Energy (MJ kg<sup>-1</sup>)</b>            |       |       |       |
| HHV   | 16.3  | 22.5  | 28.8  |

\* Determined by difference, db: dry basis, daf: dry ash free, <sup>a</sup>CO<sub>2</sub> from CaCO<sub>3</sub> decomposition, Total ash =CO<sub>2</sub> + Ash(900°C)

The dTGs of W2 and W3 consisted of two main peaks, the first associated with decomposition of the lignocellulosic component being significantly smaller than for W1 with mass losses of 45.14 wt.% and 43.64 wt.% respectively. The second peak between 420 °C - 500°C corresponded to the degradation of the plastic component [30–32] had associated mass losses of 30.51 wt.% and 36.30 wt% respectively. Due to the complex nature of the waste stream, the exact composition of the plastic fraction could not be accurately determined. The plastic peak occurring at 480 °C was characteristic of polypropylene (PP)/polyethylene (PE) with the peak for W3 being larger than for W2. A small peak at 410 °C was identified for W2

and corresponded to the degradation of polyethylene terephthalate (PET), as identified in our previous work utilising Fourier transform infrared spectroscopy [6]. The higher content of PP and PE in W3 resulted in a larger fraction of VM (85.08 wt.%) compared to W2 (79.29 wt.%). The significant proportion of PET (C/O of 1.9) in W2 explained the C/O ratio of 2.08, much lower than for W3 (3.11). The HHVs of 28.8 MJ/Kg for W3 and 22.5 MJ/kg for W2 were consistent with their plastic compositions, based on the calorific values of the main plastics identified in these waste streams (PE: 39- 45 MJ/kg, PET: 24 MJ/kg [28,33]).

### 5.3.2 Char Yield and Characterisation

The mass yields and HHVs of the char products obtained from pyrolysis of the three waste streams, are presented in Figure 5-3 and Table 5-2 respectively. Pyrolysis of W1, the sample mostly composed of lignocellulosic fibres, resulted in substantial conversion at 350 °C (char yield of 43.02 wt.%) (Figure 5-3) and a significant increase in the HHV of the char product to 20.9 MJ/kg, compared to the W1 feed (16.3 MJ/kg; Table 5-2).

Table 5-2: Higher Heating Value (HHV) of pyrolysis products (MJ/kg)

|                  | W1       |          | W2       |          |          | W3       |          |          |
|------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| Temperature (°C) | Char     | Oil      | Char     | Oil      | Wax      | Char     | Oil      | Wax      |
| 350              | 20.9±0.2 | *n/a     | 29.6±0.4 | 6.2±2.4  | *n/a     | 35.1±0.2 | 5.0±1.4  | *n/a     |
| 450              | 19.5±0.2 | 16.5±0.4 | 30.1±0.1 | 11.2±1.0 | 33.1±1.2 | 33.3±0.1 | 12.2±0.4 | 40.2±0.2 |
| 550              | 18.4±0.3 | 16.4±0.5 | 21.2±0.3 | 13.5±0.9 | 31.3±2.5 | 21.7±0.1 | 15.0±1.0 | 41.7±0.2 |

\*W1 Oil at 350 °C was not determined (it did not combust), W2 and W3 wax component was not formed at 350 °C

This can be attributed to the extensive deoxygenation reactions that predominate in lignocellulosic material between 250 - 350 °C [34]. A further increase in the pyrolysis temperature to 450 °C and 550 °C led to more extensive conversion of the fibre component into volatile compounds (Section 5.3.3 & 5.3.4), resulting in char yields of 32.38 and 26.72 wt.% respectively, which are lower than what was reported for slow pyrolysis of similar streams [6]. This result was expected as the higher heating rate and shorter vapour residence

time inside the reactor limited the formation of secondary reactions, which contribute to char production [35]. Generally an increase in temperature above 350 °C is expected to increase the HHV of char as typically observed with biomass samples [36]. However, the increase in the conversion temperature to 450 °C and 550 °C during fast pyrolysis of W1 resulted in a decrease in the energy quality of the char product to 19.5 MJ/kg and 18.4 MJ/kg respectively (Table 5-2). This trend can be attributed to the increase in the ash content of the char products reaching up to 35.44 wt. % and 39.78 wt.% respectively[3,6]. Similar HHV evolutions were observed from the pyrolysis conversion of fibre mill waste, especially for feedstock with high ash content (> 20 wt.%) [8,29].

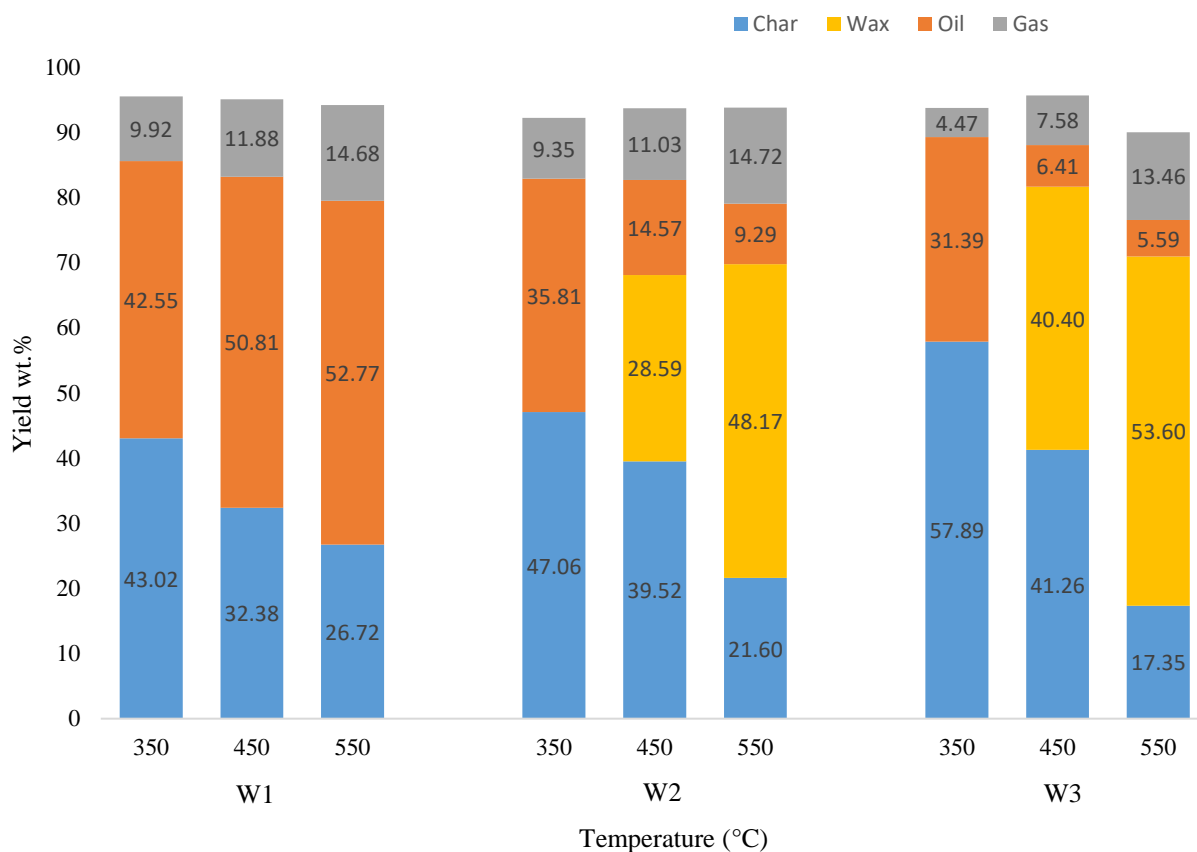


Figure 5-3: Product yields from fast pyrolysis of W1, W2 and W3

Though W2 and W3 were characterised by a higher volatile matter content than W1, the conversion of these streams at 350 °C resulted in char yields of 4.04 wt.% and 14.88 wt.% higher than for W1 respectively. This was attributed to the difference in plastic content of the

waste streams as significant conversion of the plastic fraction only occurs at temperatures higher than 350 °C [30–32], as observed from thermogravimetric analysis (Figure 5-2). The increase in the HHV of the char product for W2 (29.6 MJ/kg) and W3 (35.1 MJ/kg) compared to starting feedstocks (22.5 MJ/kg for W2 and 28.8 MJ/kg for W3, Table 5-1) was attributed mainly to the conversion and deoxygenation of the lignocellulosic fibre component, with limited conversion of the plastic components (Figure 5-2). An increase in pyrolysis temperature to 450 °C decreased the char yields for W2 and W3 by 7.54 wt.% and 16.63 wt.% respectively. This relatively moderate conversion is a result of further degradation of the biomass residue and partial conversion of plastic component. The increase in conversion temperature to 450 °C resulted in the char HHV of W2 and W3 remaining relatively high at 30.1 and 33.3 MJ/kg respectively. A further decrease in the char yield by 17.92 wt.% for W2 and 23.95 wt.% for W3 (Figure 5-3) was observed upon an increase in temperature to 550 °C. This trend was associated with the almost full conversion of the plastic component into volatile fraction, which led to the formation of a char product containing limited amounts of PE/PP residue and increased ash content of 29.54 wt.% for W2 and 33.95 wt.% for W3, ultimately resulting in a significant decrease in the energy content of the char product (21.2 MJ/kg for W2 and 21.7 MJ/kg for W3).

The application of char for use at a paper mill depends largely on the desired application of the product and the infrastructure at the mills. Chars produced from all three waste streams had HHVs ranging from 18 MJ/kg for W1 up to a maximum of 35 MJ/kg for W3 (Table 5-2).. Due to the relatively high ash content of the char product (up to 39.78 wt.%), conversion at 550 °C had a negative effect on char HHV (18 to 22 MJ/kg) (Table 5-2). It must be noted that even though the char produced at 550 °C is of a substantially poorer quality than that produced at lower temperatures, its energy content was comparable to that of lignite/bituminous grade coal (ASTM D 388 Coal ranking standard), which is commonly



used in power generation. As the waste streams used in this study collectively only represent 10 wt.% of the coal requirements for steam and power generation at the fibre recycling mill where the waste stream was sourced, co-firing of the char product should have little to no effect on the operation and stability of the boilers due to the high throughput rate associated with power and steam generation [37].

### **5.3.3 Condensable Product (oil and wax) Yield and Characterisation**

For certain conditions, the condensable volatile fraction collected in the condensation system could be separated into two main products via decantation, namely an aqueous oil phase and a waxy phase of higher density. The conversion of W1 at 350 °C was dominated by the conversion of the fibre component which produced a single oil phase with yield of 42.55 wt.%, comprised of a large proportion of water (~70 wt.%) resulting in a poor quality fuel oil (Table 5-2). An increase in the conversion temperature to 450 °C and 550 °C resulted in further conversion of the fibre residue and degradation of the small plastic component of W1, increasing the liquid yield to 50.81 wt.% and 52.77 wt.% respectively. These results are higher by 10 to 30 wt.% than what was reported for slow pyrolysis of similar waste streams and is attributed to the higher heating rate (250 °C/min) associated with fast pyrolysis compared to 25 °C/min for slow pyrolysis, which promotes condensable volatile formation via depolymerisation mechanisms [6,8]. The energy content of the oil obtained from W1 converted at temperatures  $\geq 450$  °C was similar to that of the waste stream with an HHV of ~16 MJ/kg (Table 5-2) [38].

Due to the lower content of lignocellulosic fibre (Figure 5-2), conversion at 350 °C resulted in oil yields of 35.81 wt.% for W2 and 31.39 wt.% for W3 (Figure 5-3). A poor quality fuel product with HHV of  $< 7$  MJ/kg was obtained. The increase in the conversion temperature to 450 °C and 550 °C decreased the oil yield to  $< 15$  wt.% for W2 and  $< 10$  wt.%

for W3 (Figure 5-3). The substantial decrease in the oil yield (-21.24 to -26.52wt.% for W2 and -24.9 to -25.8 wt.% for W3) (Figure 5-3) can be attributed to the decrease in the production of pyrolytic water as evidenced by the decrease in the water content of the oil from 70 wt.% at 350 °C to between 40-48 wt.% for both W2 and W3. The application of higher heating rates ( $> 250^{\circ}\text{C}/\text{min}$ ) associated with fast pyrolysis is known to limit dehydration reaction and promote depolymerisation mechanisms, which result in higher yields of organic compounds [34]. Consequently, the HHV of the oil phase increased to between 11.2 -15.0 MJ/kg for W2 and W3 (Table 5-2), which is lower than the oil generally produced from the fast pyrolysis of biomass (18 to 22 MJ/kg) [38,39]. This result could be linked to the presence of a wax product, as a result of interactions occurring between the condensable products. It is likely that some of the less polar compounds from fibres were absorbed by the wax compound, due to interactions with the hydrophobic compounds produced from plastic to form part of the viscous wax phase. The yield of viscous wax phase at 450 °C was 28.59 wt.% for W2 and 40.40 wt.% for W3 (Figure 5-3). The HHV of the wax product was found to be particularly high with values of 33.1 MJ/kg for W2 and 40.2 MJ/kg for W3 (Table 5-2). A further increase in pyrolysis temperature to 550 °C resulted in the further conversion of the plastic components and an increase in the yield of the viscous wax phase to 48.2 wt.% for W2 and 53.6 wt.% for W3 (Figure 5-3). This represents an increase of the organic-rich fraction by 12.0 wt.% and 14.7 wt.% respectively, compared to a previous study on the slow pyrolysis of the same waste streams [6], with the HHV remaining relatively high, 31.3 MJ/kg for W2 and 41.7 MJ/kg for W3 (Table 5-2). The difference in the HHV of the two products can be related back to the plastic composition of the feedstock with W2 containing a larger fraction of PET than W3. The conversion of W2 is likely to produce a wax composed of more oxygenated and cyclic condensable compounds, as typical products from the pyrolysis of PET at similar temperatures are benzoic and terephthalic acids [40–42].

The viscous wax produced from W2 is likely to have a lower HHV than non-cyclic hydrocarbons produced from PP/PE [42,43].

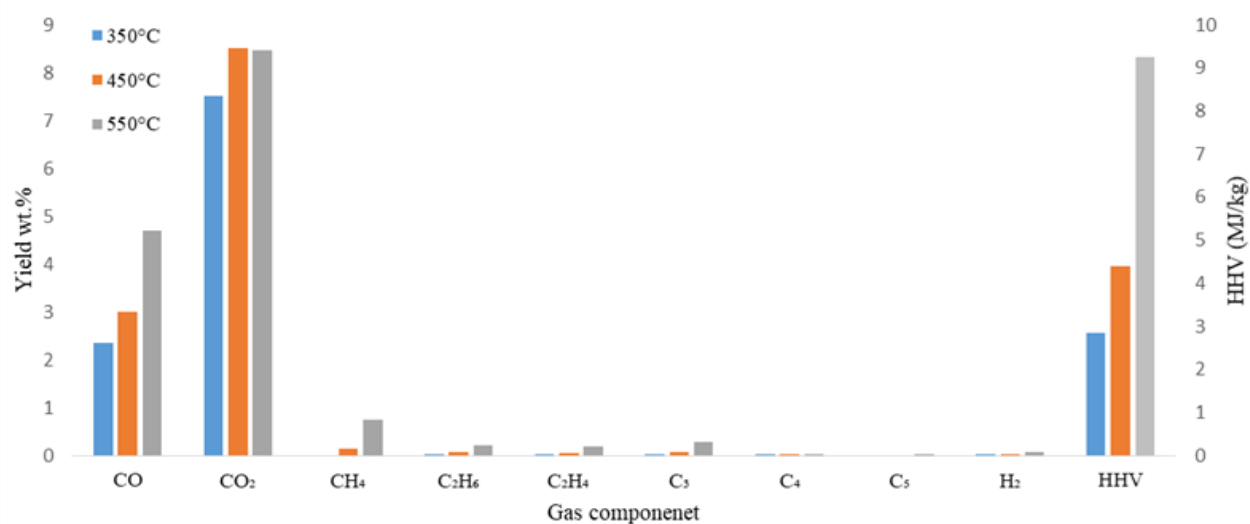
#### 5.3.4 Gas Yield and Characterisation

The gas yields, compositions and HHVs from the fast pyrolysis of three waste streams are depicted in Figure 5-3 and Figure 5-4. The conversion of W1 at 350 °C and 450 °C resulted in gas yields of 9.92 wt.% and 11.88 wt.% respectively. Due to the large presence of CO (2.4-3.0 wt.%) and CO<sub>2</sub> (7.5-8.5 wt.%), typical of lignocellulosic fibre [26], the energy content of the gas phase was rather low with an HHV of 2.8 MJ/kg and 4.4 MJ/kg respectively (Figure 5-4). An increase in conversion temperature to 550 °C promoted the formation of C<sub>1</sub> to C<sub>2</sub> hydrocarbons, usually reported as degradation products of biomass [26], while the presence of C<sub>3</sub> compounds were likely from the degradation of the small plastic component [12,42] (Figure 5-2). Consequently, the HHV of the gas phase increased to 9.3 MJ/kg (Figure 5-4).

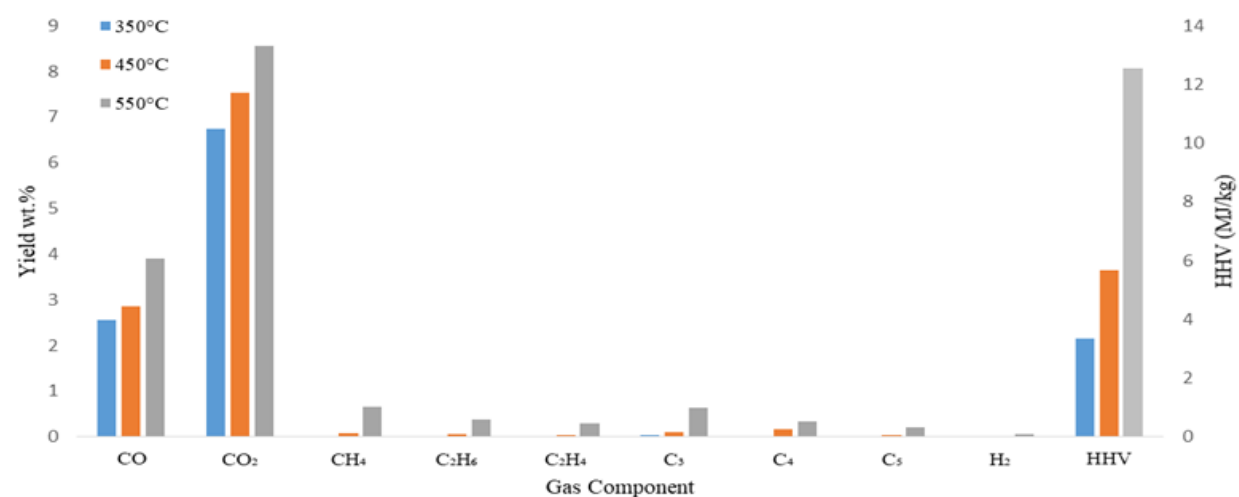
The yield of the gas phase for W2 and W3 at 350 °C was 9.35 wt.% and 4.47 wt.% respectively. As observed for W1, the gas phase was comprised mainly of CO and CO<sub>2</sub>, resulting in the energy content remaining rather low, 2.7 MJ/kg for W2 and 3.3 MJ/kg for W3 (Figure 5-4). An increase in the conversion temperature to 450 °C increased the yield to 11.03 wt. % and 7.58 wt.% for W2 and W3 respectively (Figure 5-3), while the HHV increased to 5.6 MJ/kg and 11.0 MJ/kg for W2 and W3 respectively. The large increase (+7.7 MJ/kg) in the HHV of W3 (Figure 5-4) can be attributed to the presence of C<sub>3</sub> to C<sub>5</sub> hydrocarbons (1.2 wt.%), as a result of the partial degradation of the PP/PE plastic component [12]. A further increase of +3.69 wt.% for W2 and +5.89 wt.% for W3 occurred at a conversion temperature of 550 °C (Figure 5-3) and was attributed to the more extensive

cracking of the plastic component that occurred at higher temperatures with associated increases in the gas HHV of W2 and W3 to 12.5 MJ/kg and 30.8 MJ/kg respectively.

(a) W1



(b) W2



(c) W3

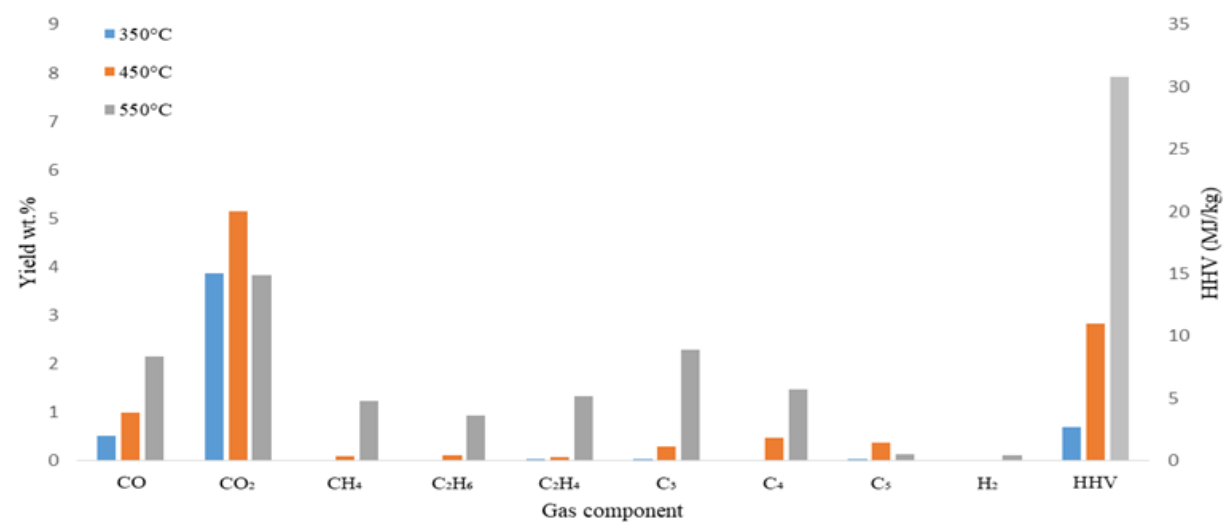


Figure 5-4: Gas yield and higher heating value (HHV) from W1, W2 and W3 as a function of pyrolysis temperature

The large difference in the energy content can be related back to the plastic composition of the waste streams (Section 5.3.1). The presence of PET in W2 was likely to contribute to the production of CO<sub>2</sub> and CO as the main degradation products, due to CO<sub>2</sub> being the main component that occurs in the gas phase from the decomposition of PET during pyrolysis [12,44]. The larger PP/PE component of W3 was likely to produce more C<sub>3</sub> to C<sub>5</sub> hydrocarbons [12,42]. This was confirmed by the composition of the gas phase of W2 and W3, with W2 containing 3.7 wt.% more CO<sub>2</sub> and 1.8 wt.% more CO than W3, and W3 containing 4.1 wt.% more C<sub>3</sub> to C<sub>5</sub> hydrocarbons than W2 (Figure 5-4).

### 5.3.5 Application of Pyrolysis Products

It is often considered that the gas produced during pyrolysis can be used as a source of energy to provide the necessary heat/energy required for pyrolysis or other on site activities [25]. Two of the main energy requirements of pyrolysis are 1) the energy required to dry the as received feedstock to an acceptable moisture content of < 10 wt.% (2.0-3.0 MJ/(kg feedstock) and 2) the heat demand of the pyrolysis process (~1.5-2.5 MJ/(kg dry feedstock)) for lignocelluloses feedstocks [20,25,45]). These typical values of process energy demands were utilised to estimate the energy yield of pyrolysis process considered in this study. In order to meet the heat demand of pyrolysis and drying, utilisation of the entire gas phase (energy content of 0.1 to 0.3 MJ/(kg feedstock), Figure 5-5) with up to 52 % of char product for W1, W2 and W3 at 350 °C would be required and resulted in an energy surplus of 4, 9 and 15 MJ/ (kg dry feedstock) for W1, W2 and W3 respectively (Figure 5-5). Increasing the conversion temperature to 450 °C produced gas products with energy contents of 0.5, 0.6 and 0.8 MJ/(kg feedstock) for W1, W2 and W3. As with conversion at 350 °C, utilisation of up to 71, 37 and 30% of the char product would be required for W1, W2 and W3 respectively to meet the process heat demand of ~ 5 MJ/(kg dry feedstock), ultimately resulting in an

estimate energy surplus of between 10 to 25 MJ/(kg dry feedstock) (Figure 5-5). Increasing the temperature to 550 °C increased the energy content of the gas streams to 1.4 MJ/ (kg dry feedstock) for W1 and 1.8 MJ/ (kg dry feedstock) for W2. Even though the energy content of the gas phase increased for W1 and W2, it was still insufficient to meet the estimated process energy demand (Figure 5-5) with up to 74 % of char or 42 % of the oil being required for W1 and 69 % of char or 21 % of viscous wax for W2.

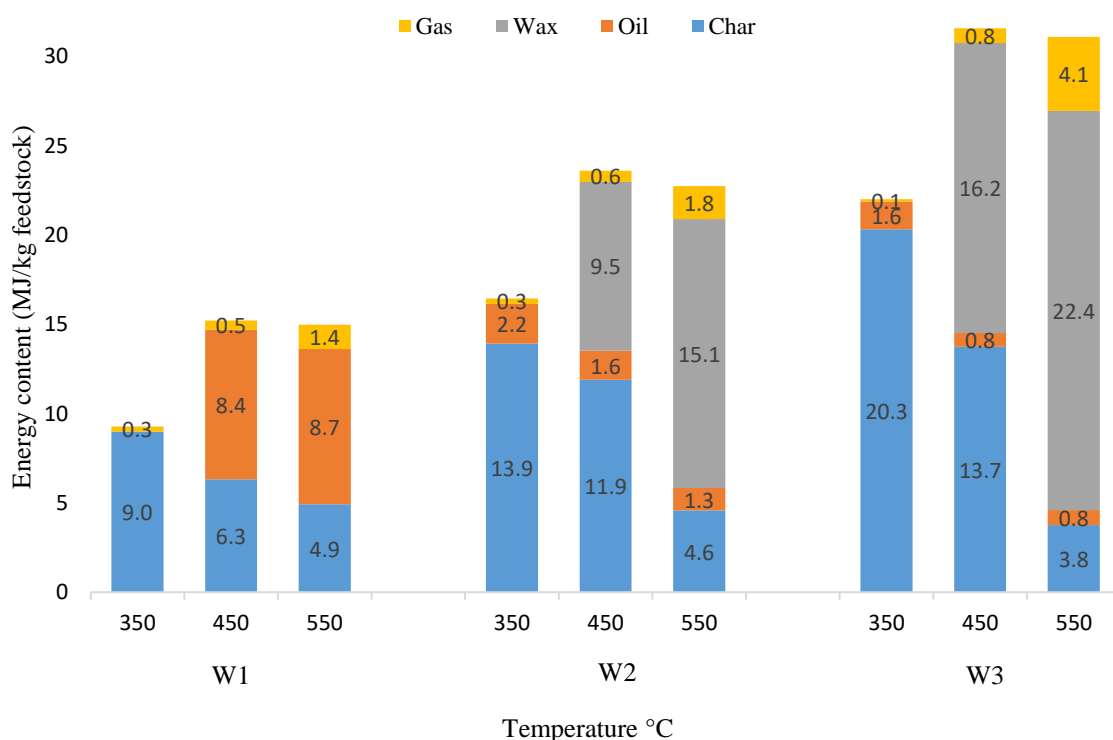


Figure 5-5: Energy transfer to pyrolysis products per kg of feedstock

The large increase in the supplementation of char for W2 can be related back to its HHV (Section 5.3.2) with the HHV of the char decreasing by 8.9 MJ/kg upon an increase in the conversion temperature to 550 °C which can be associated with the increase in the ash content of the char product (Section 3.2). Even though a large portion of the char or condensable product was required to meet the energy demand there was still a surplus of 10 and 17 MJ/(kg dry feedstock) for W1 and W2 respectively which can be used to supply the energy demand for further process activities. The conversion of W3 at 550 °C resulted in a

gas phase with a rather high energy content of 4.1 MJ/(kg dry feedstock) (Figure 5-5) and can be related back to the composition of the waste streams (as discussed in Section 3.4), with W3 being the stream containing the largest fraction of hydrocarbon plastic (PP/PE). As a result, W3 conversion produced a gas stream rich in C<sub>2</sub> to C<sub>5</sub> (6.26 wt.%) hydrocarbons, reducing the amount of either the char or viscous wax that would be needed to be utilised in addition to the gas phase. As a result, an energy surplus of 25 MJ/(kg dry feedstock) was obtained. Estimates of the energy balance indicated that conversion of all three waste streams should occur at temperatures  $\geq 450$  °C as this is where the largest amount of excess energy (between 10 to 26 MJ/(kg dry feedstock)) was generated. The increase in the energy surplus because of an increase in temperature from 350 to 450 °C can be attributed to the production of less pyrolytic water as at lower temperature a portion of the bonds in lignocellulosic fibre are converted to water via dehydration mechanism. Increasing the pyrolysis temperature promoted the formation of the better quality fuel products (gas, viscous wax) which in turn contributed to an increase in the energy yield. However, when choosing a conversion temperature, one needs to consider the end application of the pyrolysis products. If the products are to be used for process energy generation, then the existing infrastructure at the chosen site has to be taken into consideration.



## 5.4 Conclusions

This study assessed the ability of fast pyrolysis to convert fibre waste from a fibre recycling mill contaminated with plastic into valuable fuel products, with the objective to maximise the overall useful net energy yield. The high heating rate  $> 250\text{ }^{\circ}\text{C}/\text{min}$  promoted the formation of condensable volatile fraction with yields of up to 53.60 wt.% being obtained. The conversion of W2 and W3 streams, containing large proportion of plastic waste, yielded a viscous wax product with and HHV up to 41.7 MJ/kg at conversion temperatures  $\geq 450\text{ }^{\circ}\text{C}$ . An increase in conversion temperature to  $550\text{ }^{\circ}\text{C}$  promoted the formation of viscous wax phase at the expense of the quality of the char product (HHV  $< 22\text{ MJ/kg}$ ). The estimate net surplus energy, available after the energy demand of the pyrolysis process had been met, increased with an increase in temperature for all three waste streams. With a net surplus energy of up to 25 MJ/(kg dry feedstock) being obtained at temperatures  $\geq 450\text{ }^{\circ}\text{C}$  for waste streams containing the highest percentage of hydrocarbon plastic. The conversion temperature of pyrolysis should be chosen in such a way that gives due consideration to the requirements and infrastructure of the site as condensable products should only be produced if they are not intended for co-feeding in refinery or for co-combustion in existing heavy fuel oil boilers.

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## 5.5 References

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## Chapter 6: Fermentation-Pyrolysis of Lignocellulosic Paper Mill Waste for the Production of Fuel Products

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**Title** “*Fermentation-Pyrolysis of Lignocellulosic Paper Mill Waste for the Production of Fuel Products*”

**Authors:** Logan Jeremy Brown, François-Xavier Collard, Lalitha Devi Gottumukkala, Johann Görgens

### Objective of the Dissertation in this Chapter

This chapter specifically addresses **objectives 4 and 5**. All three waste streams used in this study were first subjected to fermentation screening to determine if they were a viable source to produce bioethanol (**Objective 4**) upon which only the streams showing potential for bioethanol production were chosen for further investigation (**Objective 5**).

All three of the waste streams were screened for bioethanol production in a shake flask and produced ethanol concentrations of 17.3, 20.9 and 20.5 g/l on gram scale at 15wt.% which corresponds to an glucous conversion to ethanol of ethanol 51, 83 and 87 % for W1, W2 and W3 respectively. However, the streams that contained a large percentage of plastic caused clumping during fed batch fermentation due to the accumulation of the undigested plastic in the shake flask at a relatively high solid loading of 15 wt.% and can be seen in Appendix B. It was thought that this accumulation of plastic could be overcome in a larger scale reactor that provided better agitation. The formation of a plastic layer on top of the



fermentation broth (Appendix B Figure B3) occurred once the solids loading reached 10wt.% which prevented subsequent substrate feeds from reaching the fermentation broth. As a consequence, only waste stream W1, was chosen for upscaling to 20 L fermentation reactors. The large scale fermentation experiment produced an ethanol concentration of 39.8 g/l at a solids loading of 27 wt.% and resulted in a gross energy conversion of 26.9%. Subjecting the fermentation residue to slow and fast pyrolysis produced an energy dense phase (HHV up to 35.1 MJ/kg) with the highest yield up to 26.3 wt.% being obtained for fast pyrolysis process. The gross EC for both SP and FP for the individual pyrolysis products char and wax was the highest at the conversion temperatures that produced the highest yields of the individual products.

## Candidate declaration

With regards to chapter 6, page numbers 123 to 156 of this dissertation, the nature and scope of my contributions were as follows:

| Name of contributions     | Extent of contribution (%) |
|---------------------------|----------------------------|
| Experimental planning     | 70                         |
| Executing experiments     | 100                        |
| Interpretation of results | 70                         |
| Writing the chapter       | 100                        |

The flowing co-authors have contributed to Chapter 6 pages 122 to 156 in the following manner:

| Name                      | Email address  | Nature of contributions   | Extent of contribution (%) |
|---------------------------|--|---|----------------------------|
| Francois-Xavier Collard   | <a href="mailto:fcollard@sun.ac.za">fcollard@sun.ac.za</a>     | <ul style="list-style-type: none"> <li>• Experimental planning</li> <li>• Reviewing chapter</li> <li>• Interpretation of results</li> </ul> | 10<br>70<br>20             |
| Lalitha Devi Gottumukkala | <a href="mailto:lalitha@celignis.com">lalitha@celignis.com</a> | <ul style="list-style-type: none"> <li>• Experimental Planning</li> <li>• Interpretation of results</li> <li>• Reviewing chapter</li> </ul> | 10<br>5<br>5               |
| Johann Görgens            | <a href="mailto:jgorgens@sun.ac.za">jgorgens@sun.ac.za</a>     | <ul style="list-style-type: none"> <li>• Reviewing chapter</li> <li>• Interpretation of results</li> <li>• Experimental planning</li> </ul> | 25<br>5<br>10              |

Candidate signature:.....

Date:.....

## Declaration by co-authors:

The undersigned hereby confirm that

1. The declaration above accurately reflects the nature and extent of the contributions of the candidate and the co-authors to chapter 6 page numbers 123 to 156 in the dissertation
2. No other authors contributed to chapter 6 page numbers 123 to 156 besides those specified above.

3. Potential conflicts of interest have been revealed to all interested parties and that the necessary arrangements have been made to use the material in chapter 6 page numbers 123 to 156 in the dissertation

| <b>Signature</b> | <b>Institute Affiliation</b> | <b>Date</b> |
|------------------|------------------------------|-------------|
|                  | Stellenbosch University      |             |
|                  | Stellenbosch University      |             |
|                  | Celignis Limited             |             |

“Declaration and signature is in possession of candidate and supervisor”

# Fermentation-Pyrolysis of Fibre Waste from a Paper Recycling Mill for the Production of Fuel Products

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## Abstract

The production of different energy fuels (ethanol, char, wax and gas) from fibre waste contaminated with plastic via a fermentation-pyrolysis route was investigated. Fibre was first converted to ethanol by simultaneous saccharification and fermentation (SHF), achieving an ethanol concentration of 39.9 g/L. The residue, enriched in plastics, was subjected to slow and fast pyrolysis. With char yields of 78.8 wt.% for SP and 49.9 wt.% for FP, the gross conversion of energy (EC) to char product (92.3% and 65.8% respectively) was maximised at their respective lowest conversion temperatures. Increasing the conversion temperature promoted the formation of an energy rich organic phase (oil/wax) with a calorific value up to 35.1 and 32.1 MJ/kg and a yield of up to 13.2 wt.% and 26.3 wt.% (based on residue mass) for slow and fast pyrolysis. The EC of the wax, 28.4 % and 51.8% was obtained at 550°C for slow and fast pyrolysis respectively.

**Keywords:** Pyrolysis, fermentation, fibre, paper recycling, energy conversion

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## 6.1 Introduction

The potential of industrial waste to contribute to energy security, while reducing the disposal of waste sent by landfill, has renewed the interest in waste-to-energy technologies as alternatives to disposal at landfill sites [1,2]. The utilisation of industrial waste streams rich in lignocellulosic biomass represents a potential untapped source for the production of fuels, thereby reducing the dependency on fossil resources. Recently it has been demonstrated that the fermentation for the production of bioethanol is a promising route for the valorisation of lignocellulosic waste [1,3]. However, the fermentation of lignocellulosic waste leaves behind a significant amount of fermentation residues (FR) that are rich in organic content [1,4] making it a suitable source for thermochemical conversion into chemical or fuel products[5].

The paper industry currently produces large quantities of waste that can be grouped into two main categories, namely paper waste sludge (PWS) and rejects. PWS is comprised predominately of degraded fibre and is the waste that is generated after the paper machines. Rejects from paper mills that make use of recycled fibre as feedstock originate from the primary processing activities that occur before the paper machine and are composed of degraded fibre, plastic and other contaminants [1,2,6,7]. Paper waste sludge (PWS) has been shown to be an effective feedstock for the production of bioethanol [3,8] as the crystalline structure of the cellulose has been degraded by mechanical and chemical pulping during the manufacturing process, increasing the accessibility of the cellulose for enzymatic hydrolysis into sugar (glucose) [1,3]. Hydrolysis-fermentation can either be performed as simultaneous saccharification and fermentation (SSF) or separate hydrolysis and fermentation (SHF). SHF leads to long process times and high utility costs as separate sterilization of the hydrolysate has to occur, whereas SSF has one integrate step for hydrolysis and fermentation [1,9]. As a result, it decreases the inhibitory effect on cellulose during enzymatic hydrolysis, thus increasing the final ethanol yield [10]. Recent studies on SSF fermentation of PWS have

reported ethanol concentration above the threshold value for economic viability of 40 g/l from low and intermediate ash PWS [1,3] at relatively high solids loading (>20 wt.%). Such conversion results in the formation of a residue with an increased lignin content, that can reach 34 – 39 wt.% (on dry ash free basis) [3].

As with PWS, rejects contain degraded fibres that can no longer be used in the manufacturing of paper board, making it a potential source for the production of bioethanol by SSF of the lignocellulosic fibre component. Based on the rejects composition, such conversion should leave behind a residue rich in lignin and plastics, making it suitable as a feedstock for further thermochemical conversion, such as pyrolysis. Pyrolysis is the means of thermally degrading a feedstock in a single step at temperatures generally in the range of 400-600 °C and under inert atmosphere, into energy dense products (char, oil and gas). Recent studies on the pyrolysis of lignocellulosic fibre and fibre-plastic mixtures (< 10 wt.% plastic) from a paper recycling mill have generated oil products with relatively poor fuel qualities with HHV ranging between 12 MJ/kg to 20 MJ/kg [6,11]. In order to improve the properties of fuel products, a pre-treatment such as the conversion of the cellulose constituent to an additional fuel product (bioethanol) prior to pyrolysis, is expected to be advantageous, through the reduction of the content of polysaccharides rich in oxygen and the increase in the carbon content of the starting feedstock for pyrolysis. Previously, the addition of pure plastic to biomass in a 1:1 ratio was considered an effective way to improve the energy content of the final condensable (oil/wax) and non-condensable (gas) pyrolysis products [12].

This study focussed on the sequential processing of lignocellulosic waste streams contaminated with plastic from a paper recycling mill by first subjecting the feedstock to fermentation to convert a fraction of the polysaccharides to produce ethanol as a commodity/energy product. Thereafter, the residue from fermentation was subjected to different pyrolysis processes to produce usable energy products. Mass yields and energy

contents of the various products were considered, in order to estimate the overall gross energy yield obtained from sequential processes.

## **6.2 Materials and Methods**

### **6.2.1 Source and Preparation of Feedstock**

The rejects waste stream used in this study was obtained from a paper mill utilising recycled fibre as feedstock in South Africa. Rejects are primarily produced as a sludge from the various processing activities (pulp, etc.) that occur before the paper machine and contain significant amounts of water (> 50 wt.%). Samples were dried in a tunnel greenhouse (40 to 45 °C) for a period of 5 days before being milled down to a particle size of 6 mm. The dried and fermentation residue samples are designated as W1 and W1-FR respectively. Sample intended for pyrolysis was further processed to 2 mm before being pelletized to improve the packing density inside the tubular reactors. This was done by rehydrating the sample with 10-30 wt.% water and passing it through an ABC Hansen pellet mill with a die size of 6 mm. The pellets were subsequently dried at 65 °C until no further mass loss of the pelletized material occurred.

### **6.2.2 Physico-Chemical Characterisation**

The moisture content of the as received samples was determined in accordance with TAPPI T264 om -88 standard procedure. The chemical composition of raw waste streams and fermentation residues was determined in accordance with National Renewable Energy Laboratory (NREL) standard procedure (TP-510-42618, 42622 and 42619). A thermogravimetric analyser TGA/DCS 1 Star Systems Mettler Toledo was used for proximate analysis. As observed in other studies [6,7,13], the fibre component of waste streams obtained from paper recycling mills contained a significant fraction of calcium

carbonate, which is primarily used as a filler in paper manufacturing. As a result, the proximate analysis was conducted by making a modification to the standard analytical technique ASTM E1131 testing method, in order to estimate the amount of CO<sub>2</sub> released around 700 °C from calcium carbonate degradation, as described elsewhere [6]. Ultimate analysis of the raw material was determined using an Elementar Microcube analyser. This method estimates organic carbon based on the CO<sub>2</sub> produced by carbon combustion. As combustion occurred at temperatures above 700 °C, the decomposition of CaCO<sub>3</sub> into CO<sub>2</sub> was unavoidable. Based on the determination of the CO<sub>2</sub> produced from the inorganic source by using the weight percentage of CO<sub>2</sub> (3.9 wt.%) [6] produced from CaCO<sub>3</sub> decomposition as measured by the TGA during the relevant step of proximate analysis, a correction was made to determine the organic carbon content.

HHVs of the feedstock, fermentation residue and pyrolysis products were determined in accordance with the ASTM standard D5865-11a testing method, using a Cal2K Eco Calorimeter, calibrated using benzoic acid. Thermal behaviour investigation was carried out using a thermogravimetric analyser TGA/DCS 1 Star Systems Mettler Toledo. Experiments were carried out in triplicates using 20 mg of sample from 30 °C to 900 °C, with a heating rate of 10 °C min<sup>-1</sup>. Nitrogen was used as the inert purge gas at a flow rate of 80 ml min<sup>-1</sup>.

### **6.2.3 Yeast Strain and Enzyme Cocktail**

*Saccharomyces cerevisiae* MH 1000 was stored as glycerol stocks at -85 °C with 30 % (v/v) glycerol as cyroprotectant. Seed cultures for small and large scale fermentation were grown in medium containing per litre, 20 g glucose, 20 g peptone and 10 g yeast extract and incubated in an orbital shaker at 37 °C for 18 hours. Viscamyl flow (Danisco Genencor) was used as the enzyme for SSF experiments.



#### 6.2.4 Fed Batch Fermentation

Ethanol production was first screened on a gram scale in fed batch culture in 250 mL Erlenmeyer flask (100 mL working volume ) at enzyme dosage of 10, 15 and 20 FPU/gdS and final solids loading of 15 wt.% in order to determine a desirable enzyme dosage. The medium for fed batch SSF experiments consisted of 3g/L corn steep liquor and 0.62g/L  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . Initially 6 wt.% dry solids were added to media and autoclaved for 15 min at 121 °C. The fermentation broth was inoculated with 5 % (V/V) *S.cerevisiae* seed culture, after which filter sterilized enzymes were added and incubated at 37 °C and 150 rpm. Subsequent feeds occurred every 12 hours in 3 wt.% intervals until the final solids loading of 15 wt.% was reached.

High solids loading SSF fermentations were carried out at a solids loading of 27 wt.% in 20 L bioreactors (New Brunswick Scientific Edison, N.J, USA) with a final working volume of 10 L. Initial solids loading of 6 wt.%, similar to that in shake flask, was followed with further feedings of 3 wt.% every 12 h until the desired solids loading was reached. The bioreactors were inoculated with 500 mL (5% v/v) of *S. cerevisiae* seed culture together with the specified dosage of filter sterilized enzyme and were incubated for 156 h. The theoretical ethanol yield and concentration were calculated using Eq1 and Eq2:

$$\text{Theoretical maximum ethanol concentration} = \text{Solids fed} \left( \frac{\text{g}}{\text{L}} \right) * \text{Glucose Fraction} * 0.511 \quad \text{Eq1}$$

$$\text{Ethanol Yield (\%)} = \frac{\text{Experimental ethanol concentration} \left( \frac{\text{g}}{\text{L}} \right)}{\text{Theoretical max ethanol concentration} \left( \frac{\text{g}}{\text{L}} \right)} \quad \text{Eq2}$$

## 6.3 Pyrolysis Experiments

### 6.3.1 Slow Pyrolysis

Slow pyrolysis experiments were carried out using a tubular batch reactor depicted in Figure 6-1a. The pyrolysis setup consisted of four distinct sections 1) Pyrolysis oven used to provide heat of reaction 2) 1 m reaction tube made from quartz along with a quartz sample boat that housed 12 g of pelletized waste material 3) A stepwise condensation train that consisted of 5 condensers and 4) nitrogen gas feeding system. Technical grade nitrogen was fed at a flow rate of  $0.5 \text{ L min}^{-1}$ . Before each experimental run, the reactor was checked for leaks using a vacuum pump and subsequently purged with nitrogen for 10 min to maintain an oxygen free environment. The first condenser (C1), kept at room temperature, was where an organic rich phase composed of both liquid and wax was collected, hereafter referred to as wax and oil. Condensers 2 - 3 (C2 and C3) were cooled using dry ice and were used to collect the aqueous phase. In condensers 4 and 5 (C4 and C5), also cooled with dry ice, silica beads were placed to adsorb the aerosols remaining in the gas stream. The non-condensable gas fraction was collected continuously for the duration of the experiment using 5L tedlar bags. Samples were collected for a period of two minutes to allow the tedlar bag to fill up before being replaced and subsequently analysed using gas chromatography (G.A.S. CompactGC 4.0) This method allows for the quantification of the main gas compounds produced during the whole experimental run. The instrument was calibrated using standard mixtures of calibration gas (Afrox) to determine the concentration of  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$ .  $\text{N}_2$  was used as an internal standard to determine the yield of each gas compound.

Slow pyrolysis experiments were carried out at 3 distinct temperatures (300 °C, 425 °C and 550 °C), chosen based on the characteristic steps of conversion of the lignocellulosic

and plastic materials (see dTG curves in Figure 6-2). The experiments were carried out at a heating rate of 25 °C/min and once the desired temperature was achieved, held there for an additional 60 min. All experiments were conducted in triplicates to ensure reproducibility of results and standard deviations of the char, tarry phase and gas product yields of less than 2.0, 1.9 and 1.9wt.% were observed respectively

### **6.3.2 Fast Pyrolysis Experiments**

Fast pyrolysis experiments were carried out using an inductively heated reactor as depicted in Figure 6-1b. The pyrolysis setup consisted of 1) Induction coil used to provide heat of reaction. 2) A 450 mm tubular stainless reactor. 3) Condensation system that consists of two condensers cooled to a temperature of 5 °C and connected to a collection pot where an oil and wax phase was collected simultaneously. An electrostatic precipitator (ESP) set at 12 kV was used to recover the aerosols remaining in the volatile fraction and 4) a nitrogen gas feeding system with a flow of 2.5 L/min. The non-condensable gas fraction was collected continuously after the ESP and analysed using the same method as for slow pyrolysis. Experiments were carried out at three temperatures of 350, 450 and 550 °C at a heating rate of 250 °C/min  $\pm$  5 °C/min and once the targeted temperature was reached, held there for an additional 30 min until only trace amounts of permanent gases were detected. All experiments were conducted in triplicates to ensure reproducibility of results and standard deviations of the char, wax and gas product yields of less than 2.5, 3.3 and 1.8 wt.% were observed respectively

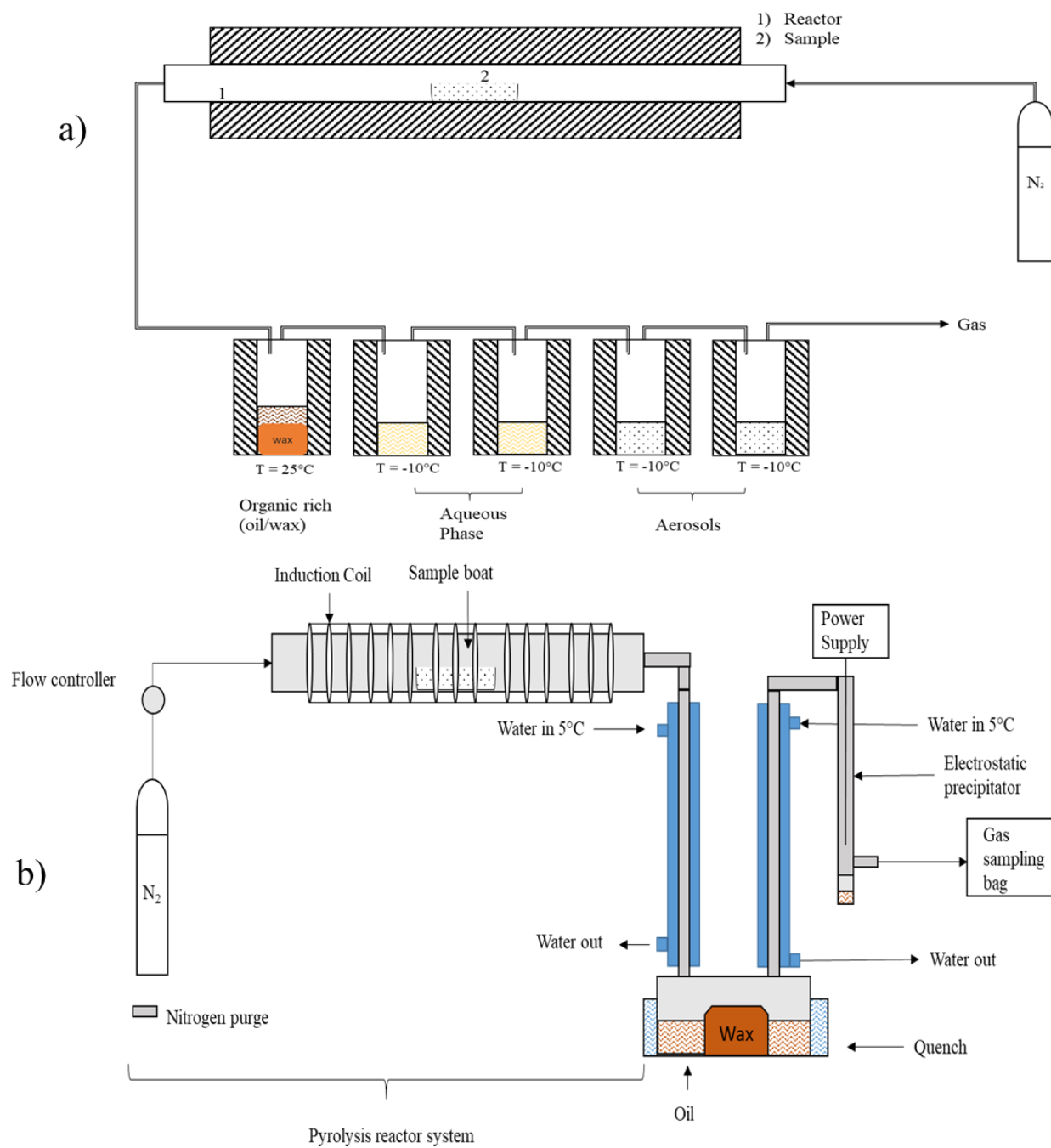


Figure 6-1: Schematic of a) electrically heated slow pyrolysis b) inductively heated fast pyrolysis experimental setups

## 6.4 Results and Discussion

### 6.4.1 Simultaneous Saccharification and Fermentation (SSF)

The comparison of the fibre sample contaminated with plastic, to lignocellulosic PWS from paper recycling mills in South Africa, revealed distinct similarities whereby both exhibited relatively large amounts of cellulose (~50 - 61 daf, wt.%) making it an attractive source for the production of bioethanol

The lignocellulosic waste stream was first screened for ethanol production on a gram scale at a solids loading of 15 wt.%, to determine the desirable enzymatic loading at 10, 15 and 20 FPU/gdS and the results are presented in Table 6-1. The final ethanol concentration varied from 14.6 g/L to 17.3 g/l across the chosen enzyme dosage, with the lowest ethanol concentration of 14.6 g/l being obtained for an enzyme dosage of 10 FPU/gdS (Table 6-1). Increasing the enzyme dosage to 15 and 20 FPU/gdS increased the final ethanol concentration to 17.1 and 17.3 g/l respectively.

Table 6-1: Ethanol results at 15 FPU/gdS for gram and kilogram scale fermentations.

| Parameter                    | Units   | W1- gram scale |      |      | W1 -kg scale |
|------------------------------|---------|----------------|------|------|--------------|
| <b>Enzyme Dosage</b>         | FPU/gdS | 10             | 15   | 20   | 15           |
| <b>Mass dry solids fed</b>   | g       | 15             | 15   | 15   | 2700         |
| <b>Volume Reactor</b>        | L       | 0.2            | 0.2  | 0.2  | 20           |
| <b>Ethanol concentration</b> | g/L     | 14.6           | 17.1 | 17.3 | 39.8         |
| <b>Ethanol Yield</b>         | %       | 42.0           | 49.5 | 50.4 | 69.1         |
| <b>Productivity</b>          | g/(L h) | 0.2            | 0.3  | 0.3  | 0.4          |

The negligible difference between the ethanol concentrations at 15 and 20 FPU/gdS was likely a result of the complete hydrolysis of the available cellulose to glucose, resulting in

similar final ethanol concentrations that were significantly lower than the theoretical determined ethanol concentrations, and was consistent with previous studies on fermentation of PWS produced from the same pulping process [1,3]. The lower experimentally determined ethanol concentrations (solids loading 15 wt.%), resulted in yields of 42.0, 49.5 and 50.4 % at enzyme dosage of 10, 15 and 20 FPU/gds respectively can be attributed to physical properties of the fibre component that affects its digestibility during enzymatic hydrolysis [1,14].

The SSF fermentation was scaled-up in 20L reactors at an enzyme dosage of 15 FPU/gdS and the results are presented in Table 6-1. A final ethanol concentration of  $39.8 \pm 6.5$  g/l was obtained, very similar to what has been reported for the fermentation of PWS produced from the same paper recycling mill (46.1 g/l) [3]. The difference in yield of ethanol between gram scale (0.11 g ethanol/gdS) and kilogram scale (0.15 g ethanol/gdS) can be attributed to the physical properties of the lignocellulosic fibre component, with the fibres produced from a paper recycling mill having an inherently high water holding capacity of between 6-8 g water/g fibre [1,3].

#### **6.4.2 Changes in Composition Before and After Fermentation**

The compositions of the rejects waste stream and its fermentation residue, in terms of proximate analysis and lignocellulosic content, are presented in Table 6-2. Differences in the physico-chemical characterisation of W1 and its fermentation residues were observed, with a decrease in the cellulose content as evidenced by the decrease in glucan content from 56.9 to 32.5 daf, wt.% (Table 6-2).

Table 6-2: Physico-chemical composition of the waste stream and its fermentation residue

| Waste Stream                                | W1    | W1-FR |
|---|-------|-------|
| <b>Proximate Analysis (db wt.%)</b>         |       |       |
| <b>Volatile matter (VM)</b>                 | 74.5  | 67.5  |
| <b>Fixed carbon (FC)</b>                    | 10.8  | 13.4  |
| <b><sup>a</sup>CO<sub>2</sub></b>           | 3.88  | 4.6   |
| <b>Ash (900°C)</b>                          | 10.80 | 14.6  |
| <b>Waste stream composition (daf, wt %)</b> |       |       |
| <b>Glucan</b>                               | 56.9  | 32.5  |
| <b>Xylan</b>                                | 16.7  | 5.9   |
| <b>Extractives</b>                          | 6.7   | 19.5  |
| <b>Lignin + Plastic</b>                     | 19.6  | 42.0  |
| <b>HHV (MJ/kg)</b>                          | 16.3  | 17.1  |

db: dry basis ; daf: dry ash free basis, <sup>a</sup>CO<sub>2</sub> from CaCO<sub>3</sub> decomposition, Total ash = CO<sub>2</sub> + Ash(900°C)

The decrease in the polysaccharide content (indicated by glucan and xylan) is due to its conversion to sugars and subsequently ethanol during enzymatic hydrolysis and fermentation. Consequently plastic/lignin content increased from 19.6 to 42.0 daf, wt.% (Table 6-2). Because of the partial hydrolysis of cellulose and hemicellulose components, an increase in the HHV of W1-FR was expected as lignin and plastic have a higher carbon content than polysaccharides [15,16] . However, as was observed previously for fermentation residue from fibre mill waste [4], an increase in the ash content (19.1 wt.%) (Table 6-2) which is comprised predominately of calcium carbonate [6,7] mitigated the effect the decrease in cellulose content has and as a result the HHV of FR remained relatively constant 17.1 MJ/kg (Table 6-3).

The thermal gravimetric (TG) curves of W1 and its fermentation residue and their respective derivatives (dTG) are presented in Figure 6-2. The thermal decomposition of the polysaccharides present in lignocellulosic fibres under inert atmosphere occurs predominantly in the temperature region of 250– 300 °C for hemicelluloses (amorphous polymer) and 300 – 400 °C for cellulose, while further fibre decomposition (400-500 °C) is mostly due to the conversion of lignin [17].

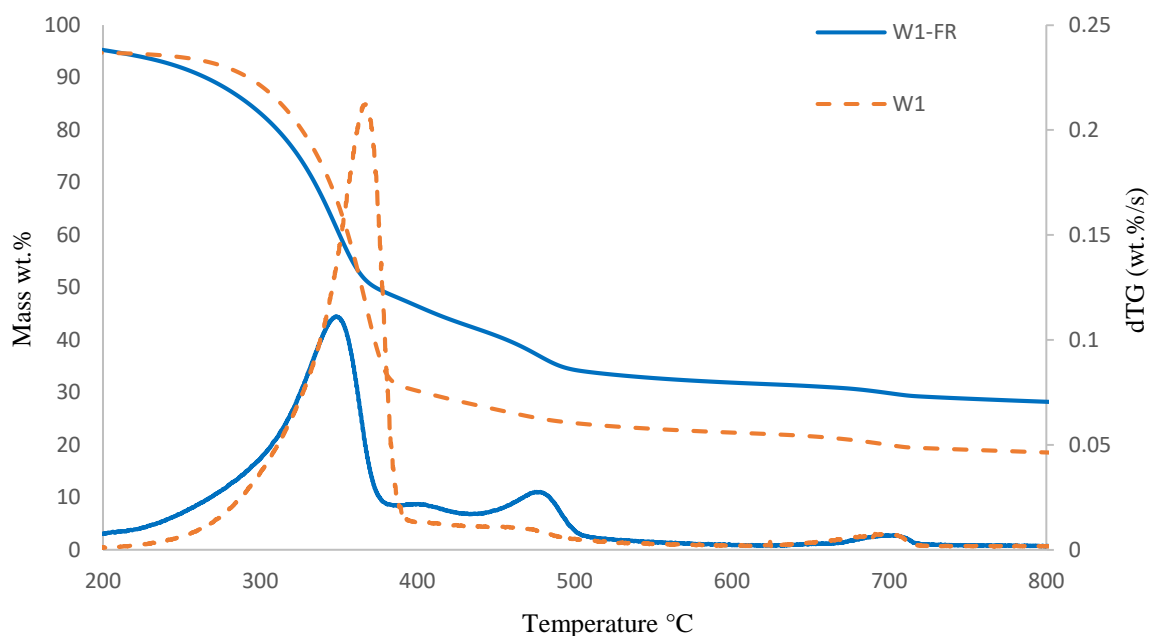


Figure 6-2: Thermogravimetric (TG) and derivative thermogravimetric (dTG) curves of the waste stream and its fermentation residue (FR) at heating rate of 10 °C/min

The plastic component is also expected to decompose at temperatures above 400 °C [16]. The dTG curve of W1 was comprised of one main peak between 250 and 400 °C, corresponding to the degradation of the polysaccharides component with a mass loss of 64.43 wt.% [16,18]. The mass loss of 6.67 wt.% occurring between 400 °C – 500 °C without any clear dTG peak (Figure 6-2), evidenced that plastic content was relatively low. The dTG of W1-FR was comprised of four degradation steps. The intensity of the first peak (250– 400 °C), divided by a factor two and characterised by a reduced mass loss (43.28 wt.%) compared to W1 (Figure



6-2), confirmed the reduction in the amount of polysaccharides in the sample as a result of SSF conversion. The change in the structure of the fibre component as result of the enzymatic hydrolysis step during SSF probably contributed to this phenomenon. Following the reduction in polymer chain lengths of cellulose and hemicellulose, some of the polysaccharide residues becomes soluble and were extracted during the determination of the extractive content (Table 6-2)[4,9], resulting in an underestimation of the polysaccharides content. A partial degradation of the polysaccharides structure (leading to decreases in the thermal stability) due to SSF is also consistent with the difference in degradation rate observed by TGA (Figure 6-2), with higher intensity observed for the fermentation residue at  $T < 300\text{ }^{\circ}\text{C}$ . Lignin degradation peak is generally reported around  $410\text{ }^{\circ}\text{C}$  [17] where the second peak was observed, while the peak at  $480\text{ }^{\circ}\text{C}$  (mass loss of 18 wt.%) was attributed to the plastic component. In particular, polypropylene and polyethylene, two plastics commonly found in waste streams that are known to degrade at similar temperatures [16]. The appearance of more distinct peaks at  $410$  and  $480\text{ }^{\circ}\text{C}$  was a result of their increased content as a consequence of the limited effect of SSF had on these materials. A peak characteristic of calcium carbonate decomposition ( $700\text{ }^{\circ}\text{C}$ ) was observed for both W1 and the fermentation residue

### **6.4.3 Pyrolysis of Fermentation Residue**

The product yields from the slow and fast pyrolysis of fermentation residues at varying temperatures are presented in Figure 6-3 and Figure 6-4 respectively; the energy contents of the products are detailed in Table 6-3. Slow pyrolysis of lignocellulose-rich feedstocks often produces char, oil and gas products in equal proportions, although when the target is to produce an energy dense char product with relatively high yield, temperatures as low as 300 °C are sometimes employed [19–21]. As a consequence, slow pyrolysis experimental runs were implemented at 300, 425 and 550 °C. The use of fast pyrolysis processes is primarily for the conversion of a significant proportion of the lignocellulosic material into condensable volatiles, therefore the minimum fast pyrolysis temperature was set at 350 °C, followed by temperature of 450 and 550 °C.

#### **6.4.3.1 Char Yield and Characterisation**

The pyrolysis of fermentation residue resulted in the highest char yields at the lowest tested temperatures for each process, with yields of 78.8 wt.% and 49.9 wt.% (Figure 6-3) for SP and FP respectively. Conversion at the respective lowest temperatures for SP and FP resulted in an increase in the HHV of the char product by 2.4 MJ/kg and 4.4 MJ/kg (Table 6-3) compared to the fermentation residue and increases of 3.2 MJ/kg and 5.2 MJ/kg compared to W1 (HHV of 16.3 MJ/kg). This increase was attributed to the extensive deoxygenation reactions that predominate in the lignocellulosic material in the temperature region of 250 °C to 350 °C [17]. Increasing the conversion temperature led to more extensive conversion of lignocellulosic fibre component (Figure 6-3) into volatile compounds, resulting in char yields of 43.4 wt.% for SP at 425 °C and 39.9 wt.% for FP at 450 °C. Char yields of 34.4 and 31.9 wt.% were obtained at 550 °C for SP and FP respectively.

Table 6-1: Higher Heating Value (HHV) of products from slow and fast pyrolysis of fermentation residues (the oil and wax products were collected in condenser C<sub>1</sub> for slow pyrolysis and in the collection pot for fast pyrolysis (see Figure 6-1); the HHV of the aqueous fraction collected in condensers C<sub>2</sub> and C<sub>3</sub> for slow pyrolysis could not be determined due to too high water content)

| Slow Pyrolysis |            |           |           |          |
|----------------|------------|-----------|-----------|----------|
|                | Char       | Oil       | Wax       | Gas      |
| <b>300°C</b>   | 19.5± 0.1  | n/a       | n/a       | 1.9±0.6  |
| <b>425°C</b>   | 19.7±0.1   | 4.3±1.0   | 28.1± 1.4 | 5.5±0.1  |
| <b>550°C</b>   | 16.2±1.6   | 8.7±0.8   | 35.1± 2.4 | 10.4±0.5 |
| Fast Pyrolysis |            |           |           |          |
|                | Char       | Oil       | Wax       | Gas      |
| <b>350°C</b>   | 21.5±0.2   | n/a       | n/a       | 3.1±0.6  |
| <b>450°C</b>   | 20.3±0.1   | 6.6 ± 0.1 | 28.2± 1.2 | 6.7±2.6  |
| <b>550°C</b>   | 17.7 ± 0.4 | 7.6± 1.0  | 32.1±2.1  | 9.9±0.4  |

n/a HHV could not be determined due to too high water content

The lower char yields obtained by fast pyrolysis can be attributed to the higher heating rates and short vapour residence times (<10s), which are known to promote volatile formation via depolymerisation mechanisms that limit secondary charring reactions [17]. The increase in the conversion temperature for both SP and FP was expected to increase the C/O ratio of char products, thereby increasing their HHVs, as is typically observed for lignocellulosic biomass [22,23]. However, in comparison with the char generated at lower temperature, the HHV of the char product from SP remained relatively constant at 425 °C, while that from FP decreased by 1.2 MJ/kg at 450 °C. This phenomenon can be attributed to the large ash component (40-50 wt.%) of the char product, offsetting the effect an increase in fixed carbon content had on the product quality [6,24]. Increasing the conversion temperature to 550 °C

resulted in a significant decrease in the HHV of the char product for both pyrolysis processes to below 18 MJ/kg. Similarly, this trend was likely a result of the significant ash accumulation in the char product. The devolatilization of the plastic components (dTG peak at 480 °C), generally characterised by relatively high energy content [12,16], also contributed to this evolution.

#### 6.4.3.2 Condensable Volatile Yield and Characterisation

For certain conditions the condensable organic-rich fraction collected in the condensation system (C<sub>1</sub> for SP and collection pot for FP, see Figure 6-1), used for fast and slow pyrolysis, could be separated into a liquid oil phase and a solid wax phase. Conversion of FR at 300 and 350 °C was predominated largely by the conversion of fibre component, which produced a single oil phase with yields of 6.2 wt.% and 33.7 wt.% for SP and FP respectively, producing a poor quality fuel product comprised mainly of water (>75 wt.%). Indeed, deoxygenation reactions are known to predominate in lignocellulosic fibre in this temperature region [16,17]. An increase in the conversion temperature to 425 °C and 450 °C produced both an oil (17.0 wt.% and 21.0 wt.%) and a wax phase (7.5 wt.% and 23.8 wt.%) for SP and FP respectively.

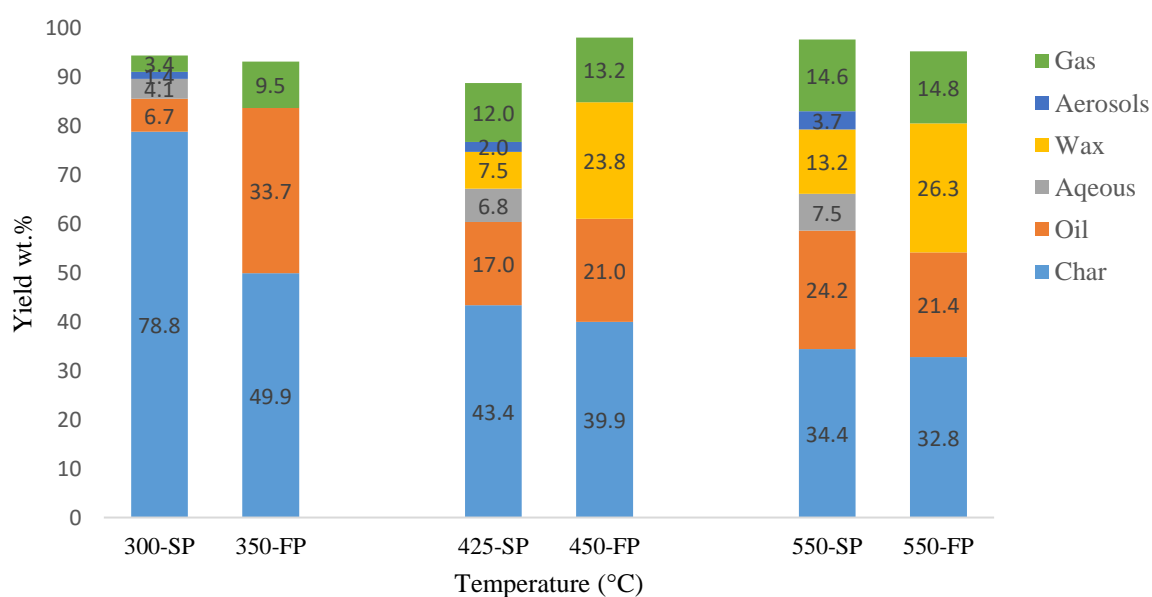


Figure 6-3: Product yields from slow (SP) and fast (FP) pyrolysis of fermentation residues

An increase in the oil yield for SP by 10.3 wt.% occurred, primarily because of significant conversion of the lignocellulosic fibre component (Figure 6-3)[11]. In the case of FP, a significant decrease in the oil yield (-12.7 wt.%) was observed. This decrease can mainly be attributed to the decrease in pyrolytic water yield, as the application of higher pyrolysis temperatures ( $\geq 450$  °C) together with rapid heating rates ( $> 250$  °C/min) is known to limit dehydration reactions and promote volatile formation via depolymerisation mechanisms, ultimately resulting in more organic compounds being formed [17]. The HHV of the oil phase remained low with an HHV of 4.3 MJ/kg and 6.6 MJ/kg (Table 6-3), which is lower than what is typically reported for bio oils (12 -18 MJ/kg) produced from lignocellulosic fibre [25,26]. The presence of a wax product from the pyrolysis of FR is due to the presence of plastic in the FR and the subsequent formation of hydrophobic molecules during pyrolysis. Lignin pyrolysis products are known to be particularly viscous and hydrophobic [27]. In comparison with lignocellulosic biomass, the high content of lignin in the FR explained the formation of a product particularly viscous. Wax has also been described as the main product obtained from the pyrolysis of plastic such as polypropylene and polyethylene [2,28]. The presence of plastic-derived products could have contributed to the precipitation of the lignin – derived products into a wax. It resulted in the formation of an energy dense phase that had an HHV of 28.2 and 28.1 MJ/kg for SP and FP respectively (Table 6-3). A further increase in pyrolysis temperature to 550 °C resulted in an increase in the viscous wax yield to 13.2 wt.% and 26.3 wt.% for SP and FP respectively with a resulting increase in the HHV to 35.1 MJ/kg for SP and 32.1 MJ/kg for FP (Table 6-3). This result was largely attributed to the more extensive degradation of the plastic component of the feedstock that occurred at temperatures between 450 and 550 °C as evidenced by the dTG curves (Figure 6-2).

### 6.4.3.3 Gas Yield and Characterisation

The conversion of FR at temperature  $\leq 450^{\circ}\text{C}$  resulted in gas yields of up to 13.2 wt.% with the gas phase composed mainly of CO (18.2-23.4 gas wt.%) and CO<sub>2</sub> (70.6-81.6 gas wt.%), which arise from the degradation of the remaining lignocellulosic component of the FR [23]. The significant presence of CO<sub>2</sub> in the gas phase negatively affected the calorific values, with the HHV ranging from 1.9 to 3.1 MJ/kg (Figure 6-4) at the lower conversion temperatures up to 6.7 MJ/kg for the intermediate pyrolysis temperature of 425 and 450 °C (Table 6-3). Increasing the conversion temperature to 550 °C increased the gas yield to 14.6 wt.% and 14.8 wt.% for SP and FP respectively, with CO and CO<sub>2</sub> still being the most abundant compounds. However, the formation of short chain hydrocarbons (C<sub>1</sub> – C<sub>4</sub>) from the more extensive degradation of the remaining lignocellulosic fibre component and the plastic component of the waste stream (Figure 6-2) (2.1 wt.% for SP and 2.0 wt.% for FP), resulted in an increase in the HHV of gas product to 10.4 MJ/kg for SP and 9.9 MJ/kg for FP.

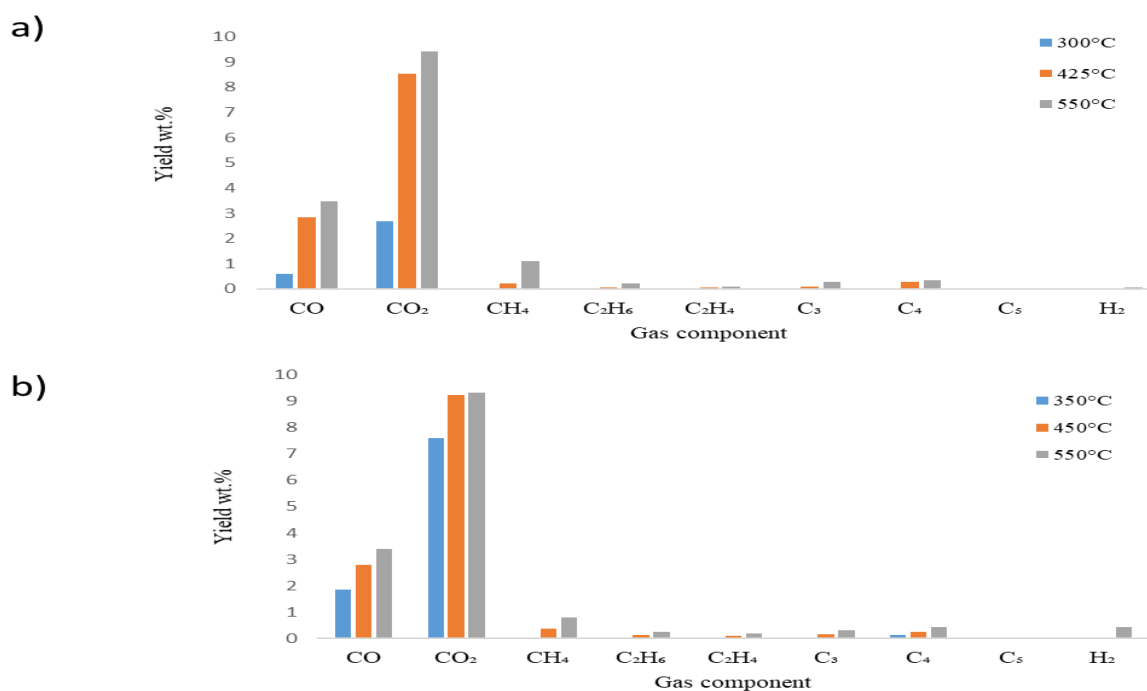


Figure 6-4: Gas yield and compositional distribution from the pyrolysis of fermentation residue, a) Slow pyrolysis and b) Fast pyrolysis

#### 6.4.4 Energy Assessment of Fermentation Residues

The gross energy conversion (EC) from fermentation residue to pyrolysis products is presented in Figure 6-5. Only the solid, liquid/wax and gas products that can be utilised for energy application were considered in the discussion below. As the aqueous phase produced from SP and the oil phase produced from both SP and FP had relatively poor calorific values because of a significant water content, these phases have been excluded from the discussion. On industrial pyrolysis plants oil/liquid products that have poor fuel properties are more likely to be sent to waste water treatment [29,30], if more useful application cannot be identified. In comparison with standalone pyrolysis, the production of an additional fuel in the form of bioethanol, with the concentration and energy conversion of 39.8 g/l and 26.9 % being obtained. The low gross EC for fermentation was attributed to the low conversion of glucan to ethanol of 69.1% (Figure 6-5)

The EC profile obtained for the conversion of fermentation residue at 300 °C and 350 °C for SP and FP respectively resulted in the majority of the energy being converted in the char product (92.3% for SP and 65.8% for FP (Figure 6-5) and was similar to that obtained for the SP and FP of the untreated sample, as reported in a previous work [6,31]. However, the calorific value of the chars were only upgraded by +2.4 MJ/kg to 19.5 MJ/kg for SP and by 4.4 MJ/kg to 21.5 MJ/kg for FP compared to the FR. The energy transfer to the gas phase for both SP and FP was particularly low, not exceeding 1.5% (HHV <3.1 MJ/kg, Figure 6-5) and can be related back to the composition of the gas phase with CO<sub>2</sub> being the main species as decarboxylation mechanisms are known to predominate in this temperature region [17,23].

The intermediate conversion temperature for both SP (425 °C) and FP (450 °C), concentrated the EC in the char product, with values of 53.7% and 49.7% for SP and FP respectively. This resulted, as with the lower conversion temperature, in a char product that had a similar quality to that of low grade subbituminous and lignite coal (ASTM D 388 coal

ranking standard), that is commonly used in power generation [32]. Increasing the conversion temperature for SP (425 °C) and FP (450 °C) along with char product, promoted the formation of an energy dense viscous wax phase (EC of 12.9% for SP and 41.2 % for FP, Figure 6-5) with resulting HHV of ~ 28 MJ/kg for both processes ( Figure 6-5). The difference in the EC of the two processes can be attributed to the conversion temperatures with more extensive conversion of lignin/plastic component occurring for FP.

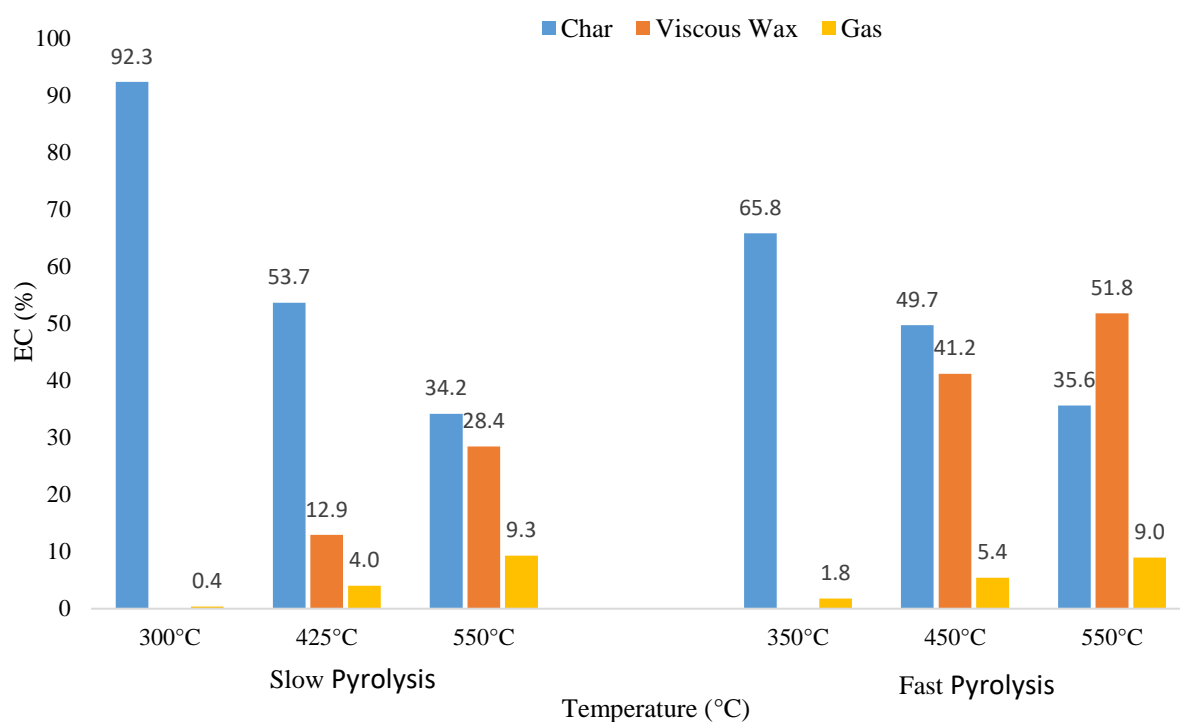


Figure 6-5: Energy conversion assessment of pyrolysis products based on residue mass from fermentation

A further increase in the conversion temperature to 550 °C, resulted in the lowest concentration of energy in the char product (34.2% for SP and 35.6% for FP). The decrease in the EC was a result of the increase in the ash content of the char product up to 48.7 wt.%, resulting in a decrease in the HHV to 16.2 MJ/kg for SP and 17.7 MJ/kg for FP (Table 6-3) and was similar to that of lignite coal (ASTM D 388 coal ranking standard). The increase in conversion temperature to 550 °C promoted the transfer of energy to viscous wax phase



(28.4% for SP and 51.8% for FP, Table 6-3). For both SP and FP, a significant increase of the calorific value of the wax phase by up to 7 MJ/kg was observed and was attributed to the increase of plastic-derived compounds in the wax product, as discussed in Section 6.4.3.2.

In both cases, the HHV (35.1 MJ/kg for SP and 32.1 MJ/kg for FP) is much higher than what was obtained for bio-oil produced from either the slow or fast pyrolysis of untreated lignocellulosic material (~18MJ/kg) [11], making it a more suitable fuel to be blended with conventional liquid fuels (HHV of ~40 MJ/kg). Indeed, submitting lignocellulose to higher heating rates is known to promote the formation of condensable products. This assumption is supported by the higher wax yield obtained by FP (26.3 wt.% vs 13.2 wt.% for SP). Therefore, if the targeted product was wax, FP at 550 °C should be the preferred process as it results in EC of 51.8% (28.4% for SP). Along with the energy dense wax product produced from the pyrolysis of fermentation residue, the ethanol produced in the first fermentation step can also be used for blending with traditional liquid fuels.

## **6.5 Comparison between Pyrolysis and Fermentation Pyrolysis Processing Route**

This section provides an overview of the difference in yield and energy conversion for the standalone pyrolysis and fermentation pyrolysis processing route of W1. The yields from pyrolysis and fermentation pyrolysis along with the energy conversion are presented in Figures 6-6 and 6-7

### **6.5.1 Char Yield**

The highest yield of char for the respective pyrolysis processes of the raw waste feedstock occurred at the respective lowest conversion temperatures of 300 and 350 °C. This can be attributed to the deoxygenation of the fibre component that predominates in this temperature

region [17]. As with the pyrolysis processing route, the fermentation-pyrolysis processing route also yielded the highest char yield of 34.6 wt.% and 21.9 wt.% for the respective pyrolysis processes at 300 and 350 °C (Figure 6-6). Further increasing the conversion temperature for pyrolysis as well as the fermentation pyrolysis processing route resulted in a decrease in the char yields by up to 43.2 wt.% for pyrolysis and 19.5 wt.% for the fermentation-pyrolysis processing route. The lower decrease in the char yield for the fermentation pyrolysis processing route compared to pyrolysis was a result of the increase in the lignin + plastic (Table 6-1) component of the W1 as a result of the conversion of the sugar component by fermentation to produce ethanol, as lignin is known to produce more char than condensable volatiles during pyrolysis [17,19].

### **6.5.2 Condensable Yield**

For certain conditions obtained from the pyrolysis of fermentation residues the condensable product could be separated into an energy dense wax phase and a watery oil phase. Conversion of the W1 and W1-FR at 300 and 350°C was dominated by the conversion of the fibre component of the biomass with an oil yield of up to 42.6 wt.% for pyrolysis and up to 34.6 wt.% for the fermentation-pyrolysis processing route (Figure 6-6), producing a poor quality fuel that had a water content >75wt.%. Increasing the conversion temperature to 425 and 450°C promoted the formation of condensable product for the pyrolysis processing route with yields of 25.1 and 50.8 being obtained with a corresponding HHV of 13.45 and 16.5 MJ/kg for SP and FP respectively. Increasing the conversion temperature for the pyrolysis of the fermentation residue (FR) produced an oil comprised mainly of water with a yield of 1.9 wt.% for SP and 2.9 wt.% for FP and an energy dense wax phase (HHV of 28.1 for SP and FP) with a yield of 12.3 wt.% for SP and 10.5 wt.% for FP (Figure 6-6). A further increase in temperature promoted the formation of the energy dense phase from FR to 15.4 wt.% for SP

and 11.6 wt.% for FP. A further increase in the HHV for both SP and FP to 35.1 and 32.1 MJ/kg (Table 6-3) was observed and is a consequence of the degradation of the remaining plastic and lignin component. This represents an increase +18.3 MJ/kg for SP and +15.7 MJ/kg for FP compared to pyrolysis of untreated waste stream (HHV of up to 16.5 at 550°C).

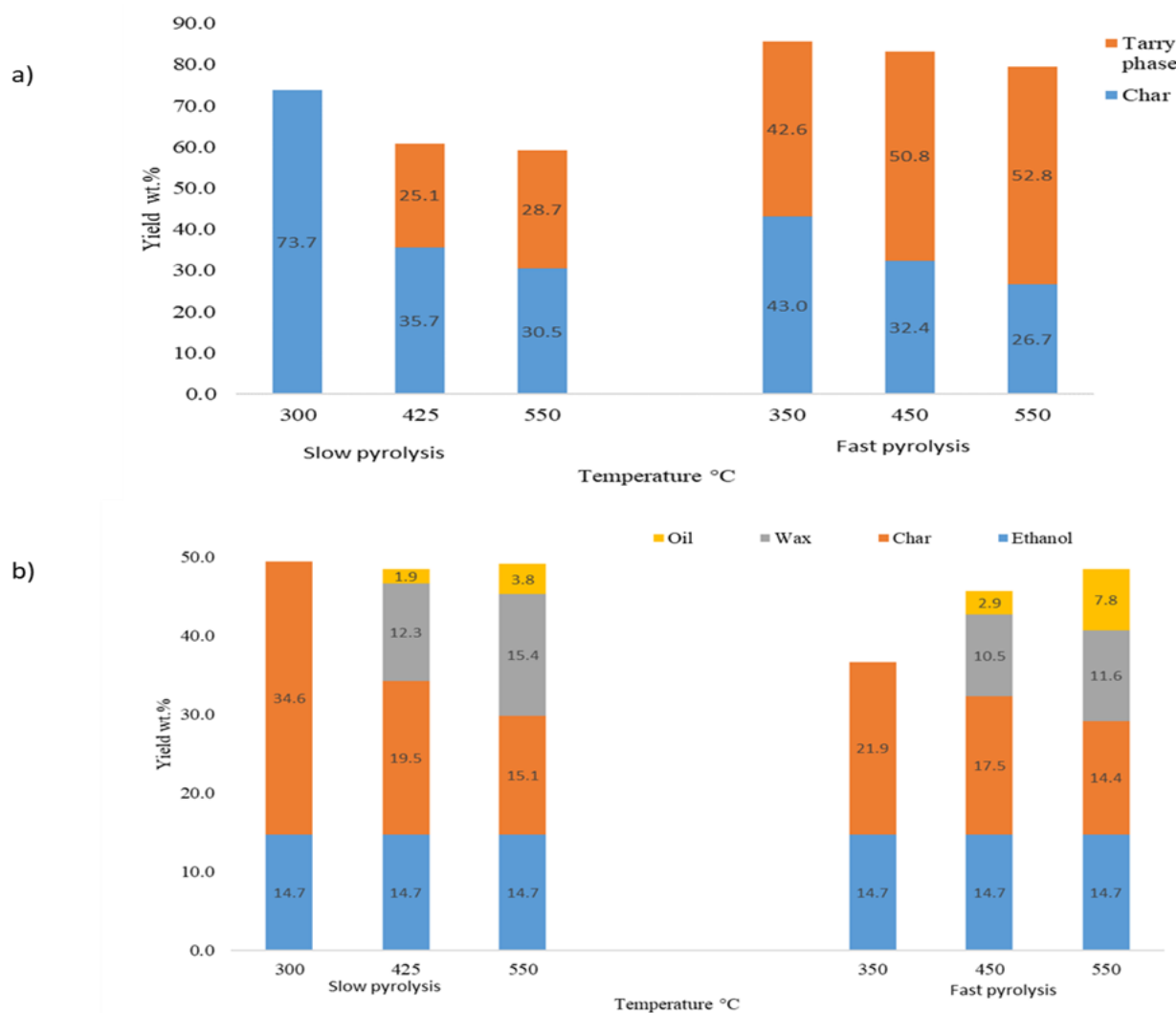


Figure 6-6: Total Yields from a) standalone pyrolysis of W1 and b) the fermentation-pyrolysis of W1

### 6.5.3 Energy Conversion Comparison of different Processing Routes

The gross energy conversion of the pyrolysis and fermentation pyrolysis processing route is presented in Figure 6-7. Only the solid, liquid/wax and ethanol products that can be utilised

for an energy application were considered in the discussion below. The oil phase produced from the pyrolysis of fermentation residue was comprised mainly of water. It is not considered for energy application as on an industrial scale such a stream would be sent to waste water treatment to be disposed of.

The EC obtained for fermentation of waste stream W1 to ethanol was 26.9%. The low EC to ethanol can be attributed to the low conversion of the glucan component of the waste stream to ethanol of 69.1%. This resulted in an ethanol yield by mass of only 14.7 wt.%. The energy conversion profile for the fermentation-pyrolysis processing route resulted in the highest EC to char product of 40.6% and 28.9% at the lowest conversion temperature of 300 and 350°C for FP and SP, similar to that obtained for the EC profile of char obtained from the fast and slow pyrolysis of W1 (Figure 6-7). The fermentation-pyrolysis processing route resulted in a lower EC to char product and improvement in the calorific value of the char product by 2.4 MJ/kg for SP and by 4.4 MJ/kg for FP was observed (Table 6-3). The overall EC from slow pyrolysis 67.5% was lower than that obtained from SP of the W1 (EC of 81.2%) where that from FP was the same.

The intermediate conversion temperature concentrated the EC in the char product for both W1 and W1-FR for SP and FP, with values of 35.7% and 32.4% for W1 and 19.5% and 17.5% W1-FR. This resulted, as with the lowest conversion temperature resulted in a char product that had similar properties to low grade subbituminous coal (ASTM D388 coal ranking standard). The increase in temperature promoted the formation of an energy dense phase for both SP and FP of W1 and W1-FR. This resulted in an EC of 20.8 and 51.3% for SP and FP of W1 and an EC of 5.7% and 18.1% for SP and FP of W1-FR. Even though there is a decrease in the EC of the energy dense condensable phase for W1-FR, the quality of the product improved significantly by +14.8 MJ/kg for SP and +11.7 MJ/kg for FP. The overall

EC for the fermentation-pyrolysis route for SP and FP at 425°C and 450 °C was 57.9% and 69.2%.

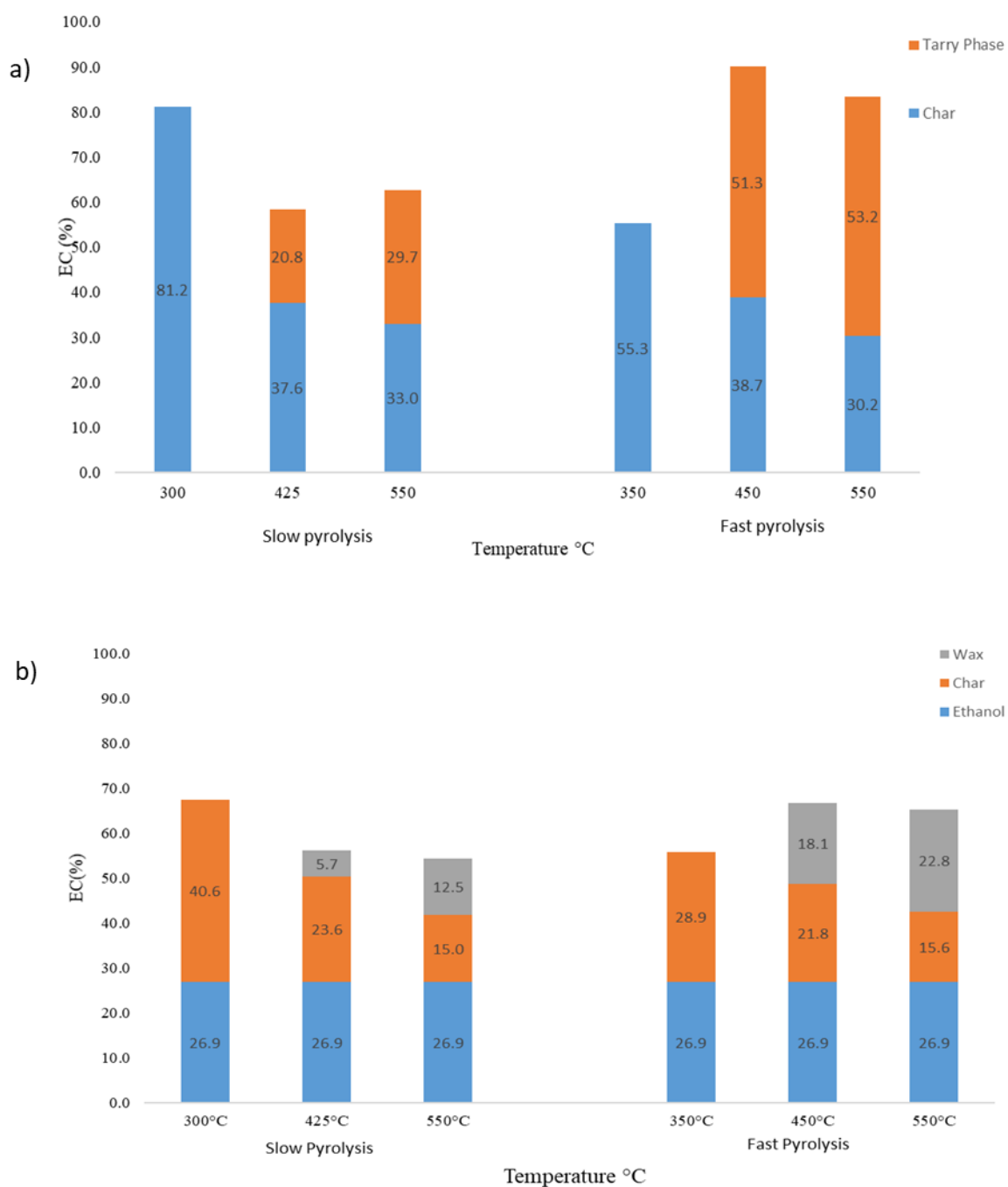


Figure 6-7: Energy conversion profiles of a) pyrolysis of W1 and b) fermentation pyrolysis of W1

A further increase in the conversion temperature to 550 °C resulted in the lowest concentration of energy in the char product for both W1 and W1-FR (Figure 6-7). This

decrease can largely be attributed to the increase in the ash component (up to 53.7wt.%) of chars from W1 and W1-FR, which resulted in a decrease in the HHV of the char product to 16.7 and 18.4 MJ/kg for SP and FP of W1 and 16.2 and 17.7 MJ/kg for SP and FP of W1-FR. The increase in temperature promoted the energy transfer to the condensable phase for both W1 and W1-FR up to 52.8% for W1 and 15.4% for W1-FR. As with the conversion at the intermediate pyrolysis temperature, the fermentation-pyrolysis processing route resulted in a lower EC to condensable phase than pyrolysis. However, there is a significant increase in the quality of the product by up to 15.6 MJ/kg compared to that obtained from the pyrolysis of W1. In both cases the HHV (35.1 MJ/kg for SP and 32.1 for FP) from condensable phase produced from W1-FR was higher than that obtained from either the slow or fast pyrolysis of W1 (HHV ~16 MJ/kg) potentially making it a more suitable fuel to be blended with traditional fossil fuels.

## 6.6 Conclusions

This study assessed a fermentation-pyrolysis processing route for the conversion of an industrial waste stream contaminated with plastic into fuel products. Ethanol concentrations of 39.8 g/l were obtained by SSF. The fast pyrolysis process produced significant amounts (23.8-26.3 wt.%) of wax phase compared to slow pyrolysis (7.5 -13.2 wt.%) at conversion temperature  $\geq 425$  °C, with HHV of the wax phase between 28.2 to 32.1 MJ/kg for both slow and fast pyrolysis. Gross energy yields of up to 51.8 % were obtained. As such if an energy dense wax phase is the desired product, FP at a temperature of 550 °C is recommended. Along with the energy dense wax phase, ethanol produced from the first step (fermentation) can be used for blending with traditional liquid fuels.

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## Chapter 7: Energy Production from Paper Mill Waste Contaminated with Plastic Annexed to a Paper Mill

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This chapter appears as a draft manuscript

**Title** “*Energy Production from Paper Mill Waste Contaminated with Plastic Annexed to a Paper Mill*”

**Authors:** Logan Jeremy Brown, Abdul Petersen, François -Xavier Collard, Johann Görgens

### Objective of the Dissertation in this Chapter

This chapter specifically addresses **objectives 6**. The results obtained from Chapter 5, with only one waste stream being viable for a fermentation-pyrolysis processing route along with preliminary simulation results from fermentation, that resulted in an ethanol selling price of R20/l, that was more than doubled the targeted value of R8/l. As a consequence, only the pyrolysis processing routes discussed in Chapters 4 and 5, were chosen for technoeconomic analysis. The experimental determined pyrolysis resulted yielded a phase that was composed largely of water. As a result, the condensation system used in the technoeconomic model was designed with the main purpose of eliminating most of the water from the condensable product stream. This water stream was first sent to anaerobic digestion to be treated before being disposed off

The different pyrolysis processes produced the largest coal supplement (up to 477 kg/h for SP and 277 kg/h for FP) at their respective lowest conversion temperatures (300 °C (SP) and 350 °C (FP)). Increasing the conversion temperature to 550 °C, promoted the formation of a fuel oil with a yield of up to 41.8 wt.% for SP and 51.4 wt.% for FP. The

increase in temperature to 550°C reduced the minimum fuel selling price (MFSP) from between 18.3 to 48.8 \$/kg to 1.12-1.32 \$/kg. However, this result was still above the targeted value of 0.65 \$/kg for fuel oil. Increasing the size of the pyrolysis plant from a maximum of 1378kg/h to 8700 kg/h decreased the MFSP to below the targeted value of 0.65\$/kg. In order to achieve the scale of 8700 kg/h a centralized pyrolysis facility would have to be built, which process multiple waste streams from different sources.

## Candidate declaration

With regards to chapter 7, page numbers 157 to 191 of this dissertation, the nature and scope of my contributions were as follows:

| Name of contributions     | Extent of contribution (%) |
|---------------------------|----------------------------|
| Simulation planning       | 80                         |
| Simulation Execution      | 100                        |
| Interpretation of results | 90                         |
| Aspen Model Development   | 5                          |
| Writing the chapter       | 95                         |

The following co-authors have contributed to chapter 7 page 157 to 191 in the following manner:

| Name                    | Email address  | Nature of contributions  | Extent of contribution (%) |
|-------------------------|--|--|----------------------------|
| Abdul Petersen          | <a href="mailto:abdulpetersen@gmail.com">abdulpetersen@gmail.com</a> | <ul style="list-style-type: none"> <li>Aspen Model Development</li> <li>Reviewing chapter</li> <li>Simulation planning</li> <li>Interpretation of results</li> <li>Writing of chapter</li> </ul> | 95<br>40<br>10<br>10<br>5  |
| François-Xavier Collard | <a href="mailto:fcollard@sun.ac.za">fcollard@sun.ac.za</a>           | <ul style="list-style-type: none"> <li>Reviewing Chapter</li> <li>Interpretation of results</li> </ul>   | 30<br>5                    |
| Johann Görgens          | <a href="mailto:jgorgens@sun.ac.za">jgorgens@sun.ac.za</a>           | <ul style="list-style-type: none"> <li>Reviewing chapter</li> <li>Interpretation of results</li> </ul>   | 30<br>10                   |

Abdul Petersen was primarily responsible for updating an Aspen plus pyrolysis simulation model built by him for co-current plastic research project in our research group. The model was primarily used as a tool to derive mass and energy balance and economic outcomes for the waste streams use in this study.

Candidate signature:.....

Date:.....

### **Declaration by co-authors:**

The undersigned hereby confirm that

4. The declaration above accurately reflects the nature and extent of the contributions of the candidate and the co-authors to chapter 7 page numbers 157 to 191 in the dissertation
5. No other authors contributed to chapter 7 page numbers 157 to 191 besides those specified above.
6. Potential conflicts of interest have been revealed to all interested parties and that the necessary arrangements have been made to use the material in chapter 7 page numbers 157 to 191 in the dissertation

| <b>Signature</b> | <b>Institute Affiliation</b> | <b>Date</b> |
|------------------|------------------------------|-------------|
|                  | Stellenbosch University      |             |
|                  | Stellenbosch University      |             |
|                  | Stellenbosch University      |             |

“Declaration and signature is in possession of candidate and supervisor”

# **Energy Production from Paper Mill Waste Contaminated with Plastic Annexed to a Paper Mill**

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7602, South Africa*

## **Abstract**

The disposal of paper mill waste at landfill sites is becoming an increasing problem and is seen as a source of sustainable feedstock for combined heat and power generation from a waste to energy facility annexed to a paper mill. To ensure the economic viability of such processing route, an understanding of the trade-off between technical optimum and an investment case must be understood. This work presents the assessment of disposing of three different paper mill waste streams, using a pyrolysis plant annexed to a paper mill.

The pyrolysis plant was simulated using 6 experimentally determined conditions for the waste streams found in literature, with process temperatures ranging from 300°C - 550°C. A minimum fuel selling price (MFSP) in the range of 1.12 to 48.78 \$/kg was obtained. The process condition that produced the most realistic economic scenario occurred at 550 °C. This produced a MFSP of 1.12 to 1.48 \$/kg for the three waste streams and was between 2 to 3 times higher than the targeted value of 0.65\$/kg. Increasing the flow rates of the three waste streams to the pyrolysis plant to 2900 and 8700 kg/h reduced the MFSP to 0.26-0.76 \$/kg.

**Keywords:** Pyrolysis, energy conversion, fibre, plastic, paper recycling mill

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## 7.1 Introduction

The pulp and paper industry in South Africa and around the world produces large quantities of waste (600 to 2000 wet tons/month per industrial site) from the manufacturing of different types of paper grades and products. This waste is currently disposed of primarily by landfilling [1–3]. The pulp and paper mills' waste can be categorised into two main groups namely paper waste sludge (PWS) and rejects [1,2,4]. PWS is produced from the primary clarifiers at a pulp and paper mill and is comprised predominantly of lignocellulosic fibres and inorganic material that are unsuitable for paper manufacturing [1,2]. Rejects originate from the pre-sorting and pulping activities as a result of using recycled fibre as feedstock and are composed of degraded fibre and a wide variety of plastic wastes and other contaminants (inorganics, staples and metal ) [2,4]. Given the rapidly changing situation around disposal of rejects, pulp and paper mills are pressed to find alternative disposal methods that if possible can add sustainable value to their business model [5,6].

Pyrolysis is a thermochemical technique of upgrading low energy dense heterogeneous wastes such as PWS, lignocellulosic biomass and rejects (HHV of 16-22 MJ/kg [1,7]) into homogenous higher energy dense products [8,9] by controlled thermal degradation [5,10]. A recent study by Nsaful et al. [11] investigated the feasibility of annexing a bagasse-based pyrolysis plant to a sugar mill in order to meet the sugar mill's energy demand, as well as that of pyrolysis. As a consequence all of the gas, biochar and up to 61 wt.% of the bio-oil produced had to be consumed to meet the energy demands of the sugar mill and pyrolysis plant. Yang et al. [5] assessed a pyrolysis system as a means of producing electricity and district heating for the local market and noted that the minimum selling prices (MSP) for economic viability was 4 times higher than the targeted price and

that in order to be competitive in the current market further incentives for heat and power generation from renewables needs to be developed [10–12].

Recently the use of pyrolysis to convert paper mill waste has been technically shown to be a potential alternative to disposal at landfill [1,13]. An investigation of the pyrolysis of rejects has shown that it was possible to produce products that have an energy content similar to that of traditional fuels, with char and condensable product having an HHV of up to 35.1 MJ/kg and 41.7 MJ/kg respectively [2,7]. Fast pyrolysis of rejects from paper recycling at temperatures of 550 °C has yielded large quantities (53.6 wt.%) of energy dense (HHV of 41.7 MJ/kg) viscous wax phase [7,12], which is similar in energy content to heavy fuel oil [12]. Slow pyrolysis produced equal quantities of char and energy dense tarry phase [7], with char fraction having an energy content of up to 32.9 MJ/kg at a conversion temperature of 300 °C [2].

The challenges associated with recovering pyrolysis condensable products are related to efficient recovery and product stability. In a previous study, a fractionation condensation system was employed to reduce the water content of the final pyrolysis oil [14,15]. This was achieved by indirectly cooling the vapours according to their boiling point with the heavier fraction condensing in the first condenser followed by the lighter organic fraction and lastly water, which condenses in the last condensation step. This approach results in a pyrolysis oil having a water content of approximately 5 % [16]. An alternative condensation system to reduce the water content of the pyrolysis oil consisted of 1) a primary condenser to remove all the high boiling points compounds, 2) an absorption column that recovered the light products and 3) a liquid-liquid phase separator (decanter) [17]. The resulting water from the decanter was processed using anaerobic digestion [18].

This work seeks to assess the economic viability of valorising paper mill waste contaminated with plastic into energy to be used onsite and saleable fuel oil product through a pyrolysis plant that is integrated with a paper mill. All excess thermal energy generated by the pyrolysis plant is exported back to the paper mill so as to reduce its dependency on fossil fuels.

## **7.2 Material and Methods**

### **7.2.1 Overview of Waste to Energy Plant**

The pyrolysis plant considered in this study will be annexed to a paper mill (PM), located in the Gauteng province of South Africa, and makes use of recycled fibre as feedstock. The waste streams consist of degraded fibre and varying amounts of plastic which are generated during the pulping of recycled fibre and the variety of screening steps that occur before the paper mill [2,7]. The average flow rate of the three waste streams as well as their composition that is used as input into the pyrolysis plant simulation, are presented in Table 7-1

Table 7-1: Waste stream characterisation and flow rates for waste to energy plant [2,7]

|                                      | <b>W1</b>   | <b>W2</b>   | <b>W3</b>   |
|--------------------------------------|-------------|-------------|-------------|
| Flow rate (kg/h, db)                 | 1378        | 540         | 540         |
| Moisture (As received, wt.%)         | 75          | 75          | 75          |
| <b>Proximate analysis (db, wt.%)</b> |             |             |             |
| Volatile matter                      | 74.52       | 79.29       | 85.08       |
| Fixed Carbon                         | 10.80       | 8.13        | 7.53        |
| Ash                                  | 14.68       | 12.58       | 7.39        |
| <b>Ultimate Analysis (daf, wt.%)</b> |             |             |             |
| C                                    | 47.47       | 60.62       | 66.98       |
| H                                    | 6.74        | 9.97        | 11.16       |
| N                                    | 0.09        | 0.11        | 0.17        |
| S                                    | 0.13        | 0.17        | 0.13        |
| Oxygen <sup>a</sup>                  | 45.57       | 29.13       | 21.56       |
| <b>HHV (MJ/kg)</b>                   | <b>16.3</b> | <b>22.5</b> | <b>28.8</b> |

\*db dry basis, daf dry ash free, <sup>a</sup> determined by difference

The overview of the proposed waste to energy plant is depicted in Figure 7-1 and is made up of the following processing units: pre-treatment, pyrolysis, char separation, fuel oil collection system, waste water treatment, and combustion/steam turbine generation. The pyrolysis plant receives the waste streams from the paper mill after pulping and initial sorting activities are carried out. A selected waste stream from the paper mill feeds the pyrolysis plant at the pre-treatment stage where it undergoes drying and particle size reduction. After which, the waste stream is fed to the pyrolysis system, which generates a char and

condensable and non-condensable vapour product. The condensable vapour fraction is recovered in a series of condensation steps and then a portion of the non-condensable fraction is fed back to the pyrolysis system to provide an inert environment inside the pyrolysis reactor. A portion of the non-condensable gas phase along with one or both char/oil that is produced is needed to provide the energy needed for pyrolysis. The remaining thermal energy and char is exported back to the paper mill (PM) to reduce its dependency on fossil fuels (coal or heavy fuel oil (HFO)) while the condensable fuel oil is sold as an energy product.

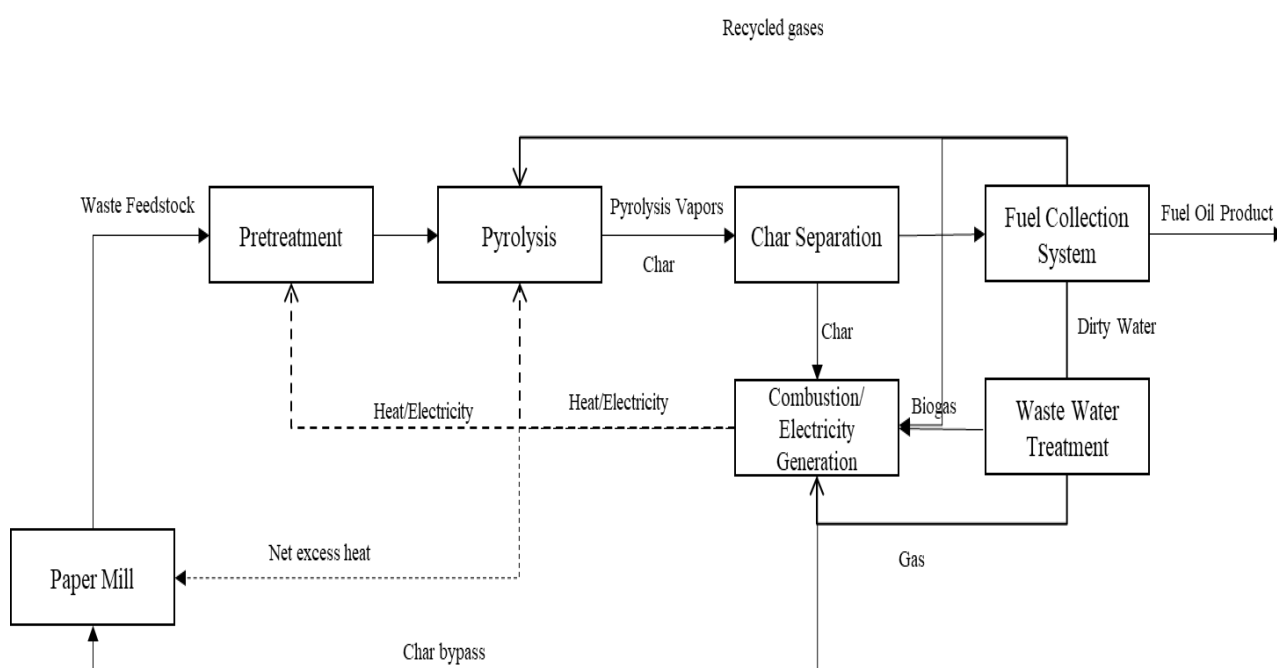


Figure 7-1: Overview of the pyrolysis system used for the production of fuel product

### 7.2.2 Choice of Scenarios

In this study, a total of 3 scenarios were simulated for the pyrolysis plant to convert rejects from a paper mill into valuable energy products as an alternative disposal technique to landfilling. The first scenario (S1) (base case) was simulated at the experimental conditions 300, 425, and 550 °C for slow pyrolysis (SP) and 350, 450 and 550°C for fast pyrolysis (FP) as obtained by Brown et al. [2,7] at the respective average yearly flow rates (Table 7-1) for waste streams W1, W2 and W3. Scenario 2 (S2) assumes that on an industrial scale, in

addition to the 3 waste streams simulated in this study, the flow rate to the pyrolysis plant is a sum of all the waste streams at the paper mill which results in a total flow rate of 2900 kg/h (personal communication with mill personnel) being fed to the pyrolysis plant for each waste stream. The proposed pyrolysis plant annexed to a paper mill in this study is in an industrial area of South Africa that has two additional paper mills similar in size that make use of recycled fibre as feedstock and currently also dispose of their waste at landfill sites. Scenario 3 (S2) proposes that the pyrolysis plant processes the waste from all three paper mills, thereby bringing the total input to 8700 kg/h.

### **7.2.3 Development of Mass and Energy Balance**

Aspen Plus® simulation software was used to derive mass and energy balances for the three process scenarios described in section 7.2.2. All processes were modelled to incorporate the highest level of energy integration to minimize waste energy recovery and improve process efficiency. As a result of the complex nature of the waste mixture and only the ability to qualitatively analyse the waste streams as described by Brown et al.[2], the waste stream could not be accurately described by the Aspen Plus® data base. The waste streams were entered as a non-conventional component into Aspen Plus®, which required the elemental and proximate analysis data (Table 7-1) in order to estimate the thermodynamic properties [12,19].

### **7.2.4 Technical Evaluation**

The performance of the simulated pyrolysis plant in Aspen Plus® was analysed and compared to the following criteria: the amount of coal that can be replaced by steam generated from waste heat integration and in certain instances, the amount of remaining char produced from pyrolysis after the energy demand of the system was met. The equivalent amount of steam that can replace coal was calculated using a steam coal correlation described

by Petersen et al. [20]. The amount of saleable fuel oil product that can be produced. The overall thermal efficiency of the pyrolysis plant was calculated according to the method described by Nsaful et al [11] and detailed by eq 7.1

$$\eta_{\text{overall}} (\%) = \frac{E_{\text{char replacement}} + E_{\text{fuel product exported}}}{E_{\text{th waste fuel}}} \quad \text{Eq 7.1}$$

Where  $E_{\text{char replacement}}$  (MW) is the thermal energy in the amount of char that can be exported to the paper mill,  $E_{\text{fuel product exported}}$  is the amount of energy exported in the saleable fuel oil produced by the pyrolysis and  $E_{\text{th waste fuel}}$  is the thermal energy in the waste feedstock inputted into the pyrolysis plant.

### 7.2.5 Economic Evaluation

The economic performance of the different pyrolysis scenarios described in section 7.2.2 and simulated in this study, will primarily be assessed on the ability of the processes to produce a fuel oil product that can be sold as HFO equivalent based on the determination of the minimum fuel selling price (MFSP). The main inputs to the economic model are summarised in Table 7-2. In all the economic models, the total capital investments (TCI) was calculated from an in house tool using the mass and energy balances obtained from Aspen Plus® and described in detail by Petersen et al. [21]. Included in the TCI cost was capital expenditure cost (CAPEX) which was calculated from parameter cost calculations found in literature. CAPEX considers cost of installation, sundry equipment cost, indirect capital cost and working capital which was calculated as 5% of TCI (Table 7-2).

Table 7-2: Main parameter inputs into the economic model [11,12,25]

| <b>General Investment Parameters</b> |                 |
|--------------------------------------|-----------------|
| Plant Life                           | 20 years        |
| Operating hours                      | 8000 hr/year    |
| Working capital                      | 5 % of TIC [30] |
| Tax rate                             | 28% [30]        |
| Interest rate                        | 9.5 %           |
| <b>Operating Cost Parameters</b>     |                 |
| Disposal cost                        | 0.12 \$/kg      |
| Electricity cost                     | 0.11 \$/kW      |
| Coal cost                            | 120 \$/ton      |
| Targeted fuel selling price          | 0.65 \$/kg      |

Operating cost (OPEX) was calculated as a combination of feedstock cost, disposal cost and other fixed costs. The main costs used in the economic model are summarised in Table 7-2. The feedstock cost considered in this study was assigned a negative value. The waste streams considered in this study are currently disposed of by landfilling and as such, the implementation of a pyrolysis plant as a disposal technique will divert a substantial amount of material being disposed of at landfill sites. Therefore, the cost associated with avoiding landfilling the waste streams can be seen as an additional income to the pyrolysis plant.



## **7.3 Process Description and Model Development.**

### **7.3.1 Pre-treatment**

The pre-treatment section receives the initial waste stream from the paper mill. The material first undergoes a drying cycle, which involves pressing the as-received waste feedstock to a moisture content of approximately 50%. The pressed sludge is then subjected to direct contact drying using spent flue gas (130 °C) recovered from the pyrolysis plant, followed by indirect drying using low pressure steam, to produce a sludge with the required moisture content of < 10 wt.%. The dried feedstock is further processed in a shredder to reduce the particle size to 6 mm before being sent to the pyrolysis reactor. The energy consumption of the shredder is modelled as 20 kWhr/ton of processed waste material [22].

### **7.3.2 Pyrolysis and Char Separation**

After pre-treatment, the material, along with the sweeping gas used to supply the inert environment, is sent to the pyrolysis reactor where it undergoes pyrolysis at the desired conversion temperature. This step produces a char, condensable products and non-condensable gas. The pyrolysis reactor is modelled using a yield reactor, utilising the RYield process block which considers only the direct feed (dried waste stream) as input in Aspen Plus®. Experimental determined yields and gas compositions were used as input into the pyrolysis simulation and were obtained from bench scale data from Brown et al. [2,7]. The char product is separated from the vapour product by means of a cyclone directly after the pyrolysis reactor [11,19]. The entire or a portion of the char product, where necessary, was combusted along with a portion of the non-condensable gas product to meet the energy needs of the pyrolysis plant.

In order to describe the composition of oil produced from the pyrolysis of fibre-plastic mixtures, 17 compounds (Table 7-3) were chosen to represent the fuel oil that is produced. Compounds related to the biomass component were identified from previous work on the pyrolysis of paper waste sludge (PWS) and complemented with data from literature [10,23–25]. The plastic component of the oil was modelled using 3 compounds which covered the boiling range of light, medium and heavy compounds produced from the pyrolysis of plastic wastes (Table 7-3) [12,26].

Table 7-3: Model compounds used to represent the oil fraction obtained from pyrolysis.

| <b>Lignin Compounds</b>       |                    |                         |              |
|-------------------------------|--------------------|-------------------------|--------------|
| 4-vinylguaiacol               | Eugenol            | Apocynin                | Phenol       |
| Guaiacol                      | 2,3-dimethylphenol | 2,6-dimethylphenol      |              |
| <b>Carbohydrate Compounds</b> |                    |                         |              |
| 2-furanmethanol               | Furanone           | 5-hydroxymethylfurfural | Levogluconan |
| Glycol aldehyde               | 2-cyclopente-1-one |                         |              |
| <b>Plastic Compounds</b>      |                    |                         |              |
| n-decane                      | n-hexadecane       | n-octadecane            |              |

### 7.3.3 Condensable Volatile (Oil/Wax) Recovery

In the fuel oil recovery section, the char free hot gas stream that exits the pyrolysis and char separation units are sent to product recovery to give an energy dense fuel product. As had been done in previous Aspen Plus® pyrolysis simulations, the NRLT activity coefficient model was used [11,27] with binary interaction parameters that were not available in the NRLT database estimated using the UNIFAC model.

The condensable volatile fraction from pyrolysis is composed of a mixture of high and low boiling point compounds and water depending on which waste stream is being investigated. The condensation system used in this study was designed to eliminate most of the water produced during pyrolysis. This was achieved by first cooling the hot gas stream to ensure that the high boiling point components produced during pyrolysis are condensed and separated from the remaining vapours in an initial condenser [16] with the temperature of the condenser being set at 60 °C [11,28,29]. The resulting non-condensed products which can be described as a light/medium fraction along with pyrolytic water is first cooled using a series of indirect heat exchangers. This condensation step results in the recovery of waste heat that can be used to produce superheated steam that is either used for drying of the wet waste feedstock in the pre-treatment section or exported to the paper mill. The vapour that exits the first condensation step is cooled to 16 °C, using a combination of process cooling water and refrigeration, before it enters an absorption column. The liquid product of the absorber enters a decanter where the aqueous and organic phases are separated from each other and approximately 95 % of the organic fraction is recycled back to the column via a refrigeration unit that cools it to 10 °C [17]. The recovered light-medium oil fraction is then blended with the heavy oil fraction before being sold as a value adding product.

The aqueous phase generated from the decanter is first heated to 35°C using a proportion of the recovered heat and sent to an anaerobic digester. Approximately 60 % of the organic compounds in the organic phase are removed and the resulting biogas that is generated is sent to the pyrolysis furnace where it is combusted along with other pyrolysis products (gas, char) to supply the heat needed for the pyrolysis furnace.

### **7.3.4 Combustion and Steam, Electricity Generation**

The non-condensable gas fraction that is required to provide the inert environment during pyrolysis is removed before the remaining off gas and other pyrolysis products (provided they are required for the energy needs) are sent to the combustor. The heat generated during combustion is used to supply the energy needs of the pyrolysis reactor. The remaining process heat in the exhaust gas is recovered and used to generate steam at 20 bar along with heat recovered from the condensation of the fuel oil product via a heat transfer medium such as glycol in the heat recovered steam generator (HRSG). The superheated steam is then expanded in a back-pressure turbine to produce electricity and low-pressure steam at 4 bar that is used for biomass drying. The excess electricity and low-pressure steam that is produced are exported back to the paper mill.

## **7.4 Results and Discussion**

### **7.4.1 Technical Evaluation of Base Case Scenarios**

The technical performance of the base case scenarios for the experimentally determined conditions of slow and fast pyrolysis were assessed according to the criteria described in section 7.2.4 and are presented in Figure 7-2, Figure7-3 and Table 7-4.

The largest coal substitute of between 207 to 477 kg/h for SP and 173 to 274 kg/h for FP was produced at the lowest conversion temperature of 300 and 350 °C, the condition that yielded the highest experimentally determined char yield [2,7], for both pyrolysis processes.

Table 7-4: Total char from the pyrolysis system produced that can replace coal (kg/hr)

| W1                                |       |       |       |       |          |          |
|-----------------------------------|-------|-------|-------|-------|----------|----------|
|                                   | 300°C | 350°C | 425°C | 450°C | 550°C SP | 550°C FP |
| Coal Replacement equivalent steam | 16    | 27    | 77    | 26    | 20       | 15       |
| Char (pyrolysis)                  | 461   | 247   | 0     | 0     | 0        | 0        |
| <b>Total coal replaced</b>        | 477   | 274   | 77    | 26    | 20       | 15       |
| W2                                |       |       |       |       |          |          |
| Coal Replacement equivalent steam | 12    | 8     | 22    | 8     | 25       | 15       |
| Char (pyrolysis)                  | 198   | 127   | 0     | 0     | 0        | 0        |
| <b>Total coal replaced</b>        | 210   | 136   | 22    | 8     | 25       | 15       |
| W3                                |       |       |       |       |          |          |
| Coal Replacement equivalent steam | 14    | 9     | 66    | 7     | 63       | 9        |
| Char (pyrolysis)                  | 193   | 164   | 0     | 0     | 0        | 0        |
| <b>Total coal replaced</b>        | 207   | 173   | 66    | 7     | 63       | 9        |

Though the lowest conversion temperature for both SP and FP produced the largest amount of char that could be exported to the paper mill, the yield of this coal supplement was between 34.6 to 38.9 wt.% for SP and 19.8 to 31.9 % for FP. This yield was lower than the experimentally determined values obtained by Brown et al.[2,7] and was a result of the combustion of a portion of the char product in order to supply the process energy needed. The production of a condensable phase was not favoured due to the low conversion temperature (300 °C for SP and 350 °C for FP). As a consequence, a maximum production rate of up to 34.1 kg/h for SP and 108.1 kg/h for FP for all three waste streams was obtained (Figure 7-2). As most of the char that was produced was required to help meet the energy demand of the process, the process thermal energy efficiency of 40.1%, 48.0% and 43.2% for SP and 41.5%, 35.0% and 41.5% for FP was obtained for W1, W2 and W3 respectively (Figure 7-3).

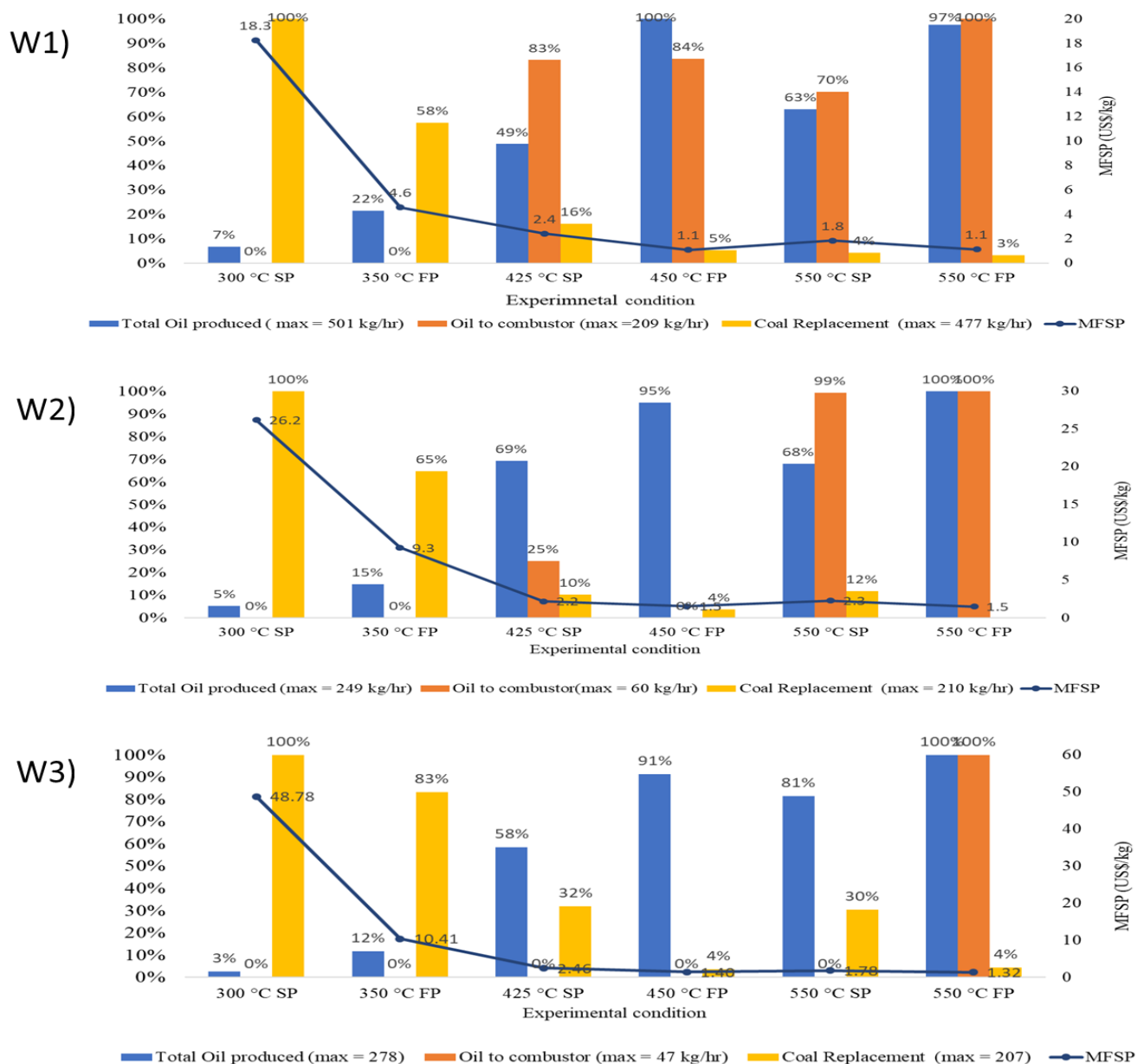
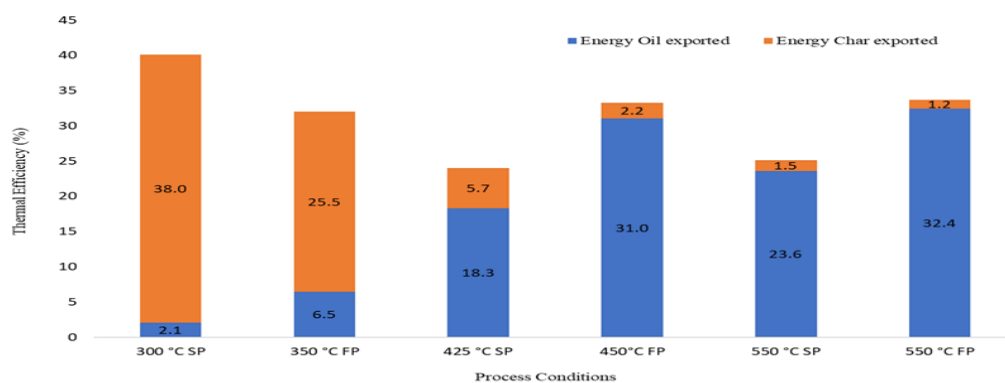


Figure 7-2: Technical outcomes as a function of the minimum fuel selling price (MFSP) of the base case scenario

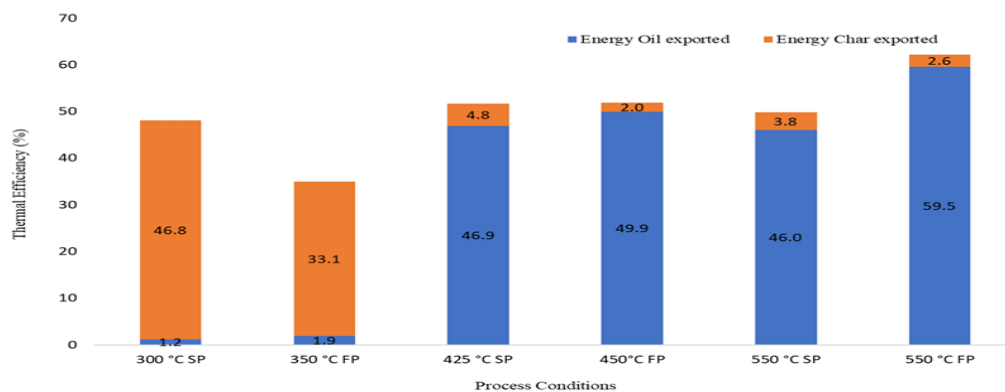
Increasing the conversion temperature to an intermediate pyrolysis temperature for both slow (425 °C) and fast (450 °C) pyrolysis of W1 resulted in a decrease in the production of a coal supplement from 477 to 77 kg/h for SP and 274 to 26 kg/h for FP (Table 7-4). The coal supplement comprised entirely of process heat that was recovered in the form of steam (Table 7-4), as all the pyrolysis char had to be burnt to help meet the energy demand of the process. The thermal energy exported in the form of a coal supplement decreased from 38 to

5.7 % for SP and 25.5 to 2.2 % for FP, upon an increase in the respective pyrolysis process conversion temperatures. The increase in the conversion temperature promotes the formation of fuel oil with a yield of 17.6 wt.% for SP and 36.4 wt.% for FP. The low fuel oil yield was a result of char and gas streams being insufficient to meet the process energy demands, with 174 kg/h for SP and 175 kg/h for FP (Figure 7-2) of the product oil being sent to the combustor along with char and gas products. Therefore, the overall process thermal efficiency was 24.0% for SP and 33.3% for FP (Figure 7-3). Increasing the conversion temperature for W1 up to 550 °C resulted in the lowest char substitute being obtained (20 kg/h for SP and 15 kg/h for FP) (Table 7-4). The decrease in coal substitute was attributed to the increasing energy demand of the pyrolysis system at elevated temperatures as well as the low char yield obtained at a pyrolysis temperature of 550 °C [2]. At a conversion temperature of 550 °C, all the gas and char that is produced with up to 208 kg/h of the final fuel oil must be combusted to meet the energy demand (Figure 7-2). As a consequence, the thermal energy efficiency of the process was 25.1% for SP and 33.7 % for FP (Figure 7-3).

W1



W2



W3

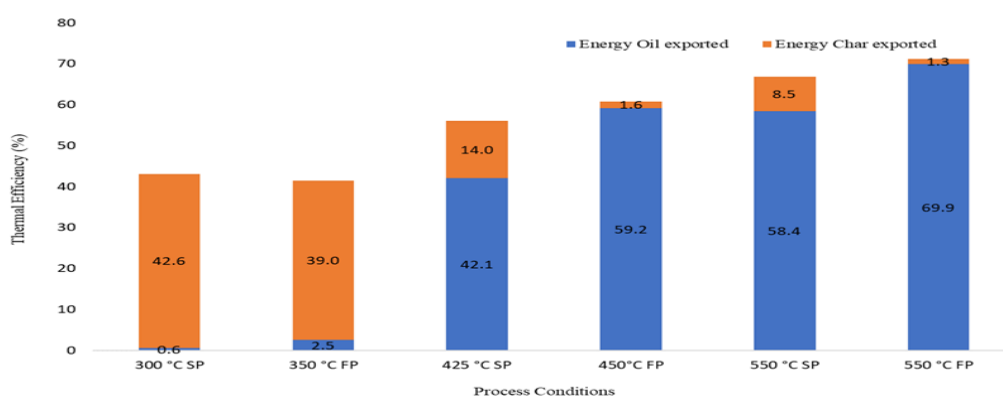


Figure 7-3: Thermal energy efficiency of different process simulations for base case scenario

The simulated conversion of W2 and W3 at intermediate pyrolysis temperature for both slow and fast pyrolysis followed a similar trend as W1, with a subsequent decrease in the amount of char (coal substitute) that could be exported to the paper mill (22 and 8 kg/h for W2 and 66 and 7 kg/h for W3) for SP and FP respectively (Table 7-4). This resulted in the thermal energy transfer of the coal supplement not exceeding 3.9% for W2 and 9.3% for W3 (Figure 7-3). The production of fuel oil increased to 172 kg/h and 235 kg/h for W2 and 162 kg/h and 253 kg/h for slow and fast pyrolysis (Figure 7-2). The increase in temperature



resulted in an increase in the thermal energy transfer to the fuel oil product, 46.9% and 64.3% for W2 and 41.9% and 65.4% for W3 for slow and fast pyrolysis respectively. A further increase in conversion temperature to 550 °C required that up to 60 kg/h for W2 and 47 kg/hr for W3 of the fuel oil product for slow and fast pyrolysis be sent to the combustor to provide heat needed for the process. As a consequence, the final fuel oil yields for slow and fast pyrolysis of 31.3 and 46.0 wt.% for W2 and 41.8 and 51.4 wt.% for W3 were obtained. The smaller amount of the fuel product required for W2 and W3 at a conversion temperature of 550 °C compared to W1 can be related back to the composition of the waste stream as evidenced in our previous work [2]. As W2 and W3 contained a larger percentage of plastic, they produced a gas phase that contained a larger concentration of C<sub>1</sub> to C<sub>5</sub> hydrocarbons resulting in a more energy dense gas phase than that produced from W1 [7]. Consequently, a larger proportion of the energy demand was met by the char and gas phase, thereby reducing the amount of final oil product that was needed to supplement the pyrolysis process. As a result, the thermal energy transfer to the fuel oil for slow and fast pyrolysis process of 46.0 and 67.7% for W2 and 58.4 and 71.7 % for W3 (Figure 7-3) were obtained. The higher thermal efficiency obtained for W2 and W3 was a consequence of the composition of the waste streams. As discussed previously, W2 and W3 had a larger percentage of hydrocarbon plastic that when degraded at evaluated temperature produced a fuel product that has a similar energy content (~40 MJ/kg) to that of heavy fuel oil.

#### **7.4.2 Minimum Fuel Selling Price (MFSP) Analysis of Base Case Scenarios**

The MFSP and total capital investment from the simulation of the base case scenario are presented in Figure 7-2 and Figure 7-4. As discussed in section 7.4.1 the largest amount of char that could be exported to the paper mill was obtained at the lowest conversion temperature for both pyrolysis processes and resulted in the highest MFSP of 18.25 and 4.56

\$/kg for W1, 26.18 and 9.29 \$/kg for W2 and 48.78 and 10.41\$/kg for W3 for SP and FP respectively (Figure 7-2), which resulted in a total capital investment of up to 11.1, 6.8 and 6.9 million \$ for W1, W2 and W3 respectively.

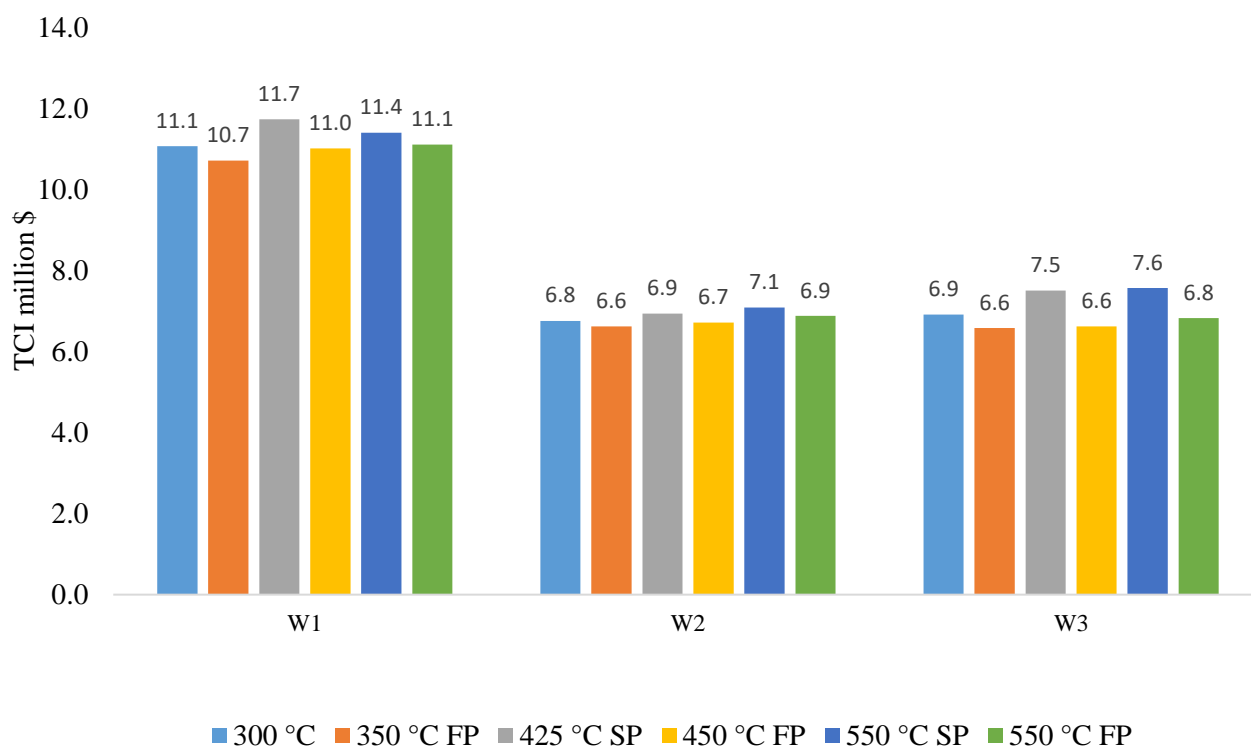


Figure 7-4: Total capital investment (TCI) of the different base case scenarios

The large MFSP obtained at the lowest conversion temperature for both SP and FP can be attributed to the low cost of coal (US\$ 120/ton) that the pyrolysis char was meant to replace, as the cost of coal was 5 times cheaper than the targeted selling price of the pyrolysis oil or equivalent heavy fuel oil (HFO) (Table 7-3) and the low yield of fuel oil obtained at conversion temperatures of 300 and 350°C. A reduction in the MFSP to 2.42 and 1.08 \$/kg for W1, 2.19 and 1.53 \$/kg for W2 and 2.46 and 1.4 \$/kg for W3 for slow and fast pyrolysis was observed at an intermediate pyrolysis temperature of 425 (SP) and 450 °C (FP), while the capital investment remains relatively constant (Figure 7-4). The decrease in the MFSP was largely attributed to the increase in the production of the marketable fuel product (Figure

7-2), however the obtained MFSP was still approximately 2 to 4 times higher than the targeted value of 0.65 \$/kg (Table 7-3). The low cost of coal at \$120/ton (Table 7-3) contributed to the high MFSP as the amount of char that can replace coal was considered as an income. When considering the overall coal consumption of a paper mill (2800 – 4200 tons/month), the coal replacement achieved by the pyrolysis system on the average consumption of a paper mill was at most 10 wt.%. Increasing the conversion temperature to 550 °C for both pyrolysis processes, promoted the formation of fuel oil product (as discussed in Section 7.4.1) and as a result decreased the MFSP to 1.84 and 1.12 \$/kg for W1, 2.29 and 1.48 \$/kg for W2 and 1.78 and 1.32 \$/kg for W3 for slow and fast pyrolysis respectively. The MFSP obtained for both SP and FP was still 2 to 3.5 times higher than the targeted value of 0.65 \$/kg (Table 7-3).

#### **7.4.3 Technical and Economic Analysis of Scenarios 2 and 3**

This section looks at the effect that upscaling of a pyrolysis plant annexed to a paper mill has on the overall economics of the process and is presented in Table 7-5 and Figure 7-5. The larger scale scenarios were simulated at the FP experimental condition of 550 °C. This condition was chosen as it produced the lowest MFSP for all three waste streams and, except for W1, the largest net process thermal efficiency. The first simulated scenario S2 (as described in Section 7.2.2), considered that on an industrial scale one pyrolysis plant will be built to process all waste streams at a respective paper mill. As a consequence, the total daily flow rate is approximately the sum of all the waste streams at a mill, which was estimated to be 2900 kg/h (S2). The second simulated scenario (S3) considered that the paper mill used in this study was located in an industrial area of South Africa that has three similar paper mills within a 20 km radius. A centralized facility will be built to process the waste from the three paper mills and as such, the total input into the pyrolysis plant for S3 is 8700 kg/h.

Total oil production for scenario S2 was 1468, 1659 and 1673 kg/h for W1, W2 and W3 respectively (Table 7-5). In order to meet the energy demands of the process, a portion of the oil (15 wt.% for W1, 11 wt.% for W2 and 7 wt.% for W3, Table 7-5) had to be consumed along with the entire char and gas fractions. This resulted in a final saleable oil yield of 36, 46 and 50 wt.% for W1, W2 and W3 respectively. As a result of the entire char stream being consumed for process energy production, only energy in the form of steam, which is recovered through process integration, can be exported back to the paper mill and results in an equivalent amount of coal of 32, 83 and 63 kg/hr for W1, W2 and W3 respectively. Scenario (S3) followed a similar trend for oil production with a portion of it being required to meet the energy demands of the process (Table 7-5). As a result of the increase in plant capacity size, a slightly larger amount of steam could be recovered and converted to the equivalent amount of coal and as such, a coal supplement of 100, 252 and 195 kg/h was obtained (Table 7-5). The small coal supplement equates to between 1.0 to 2.4 wt.% for S1 and 2.9 to 7.2 wt.% of a single paper mills current coal requirement.

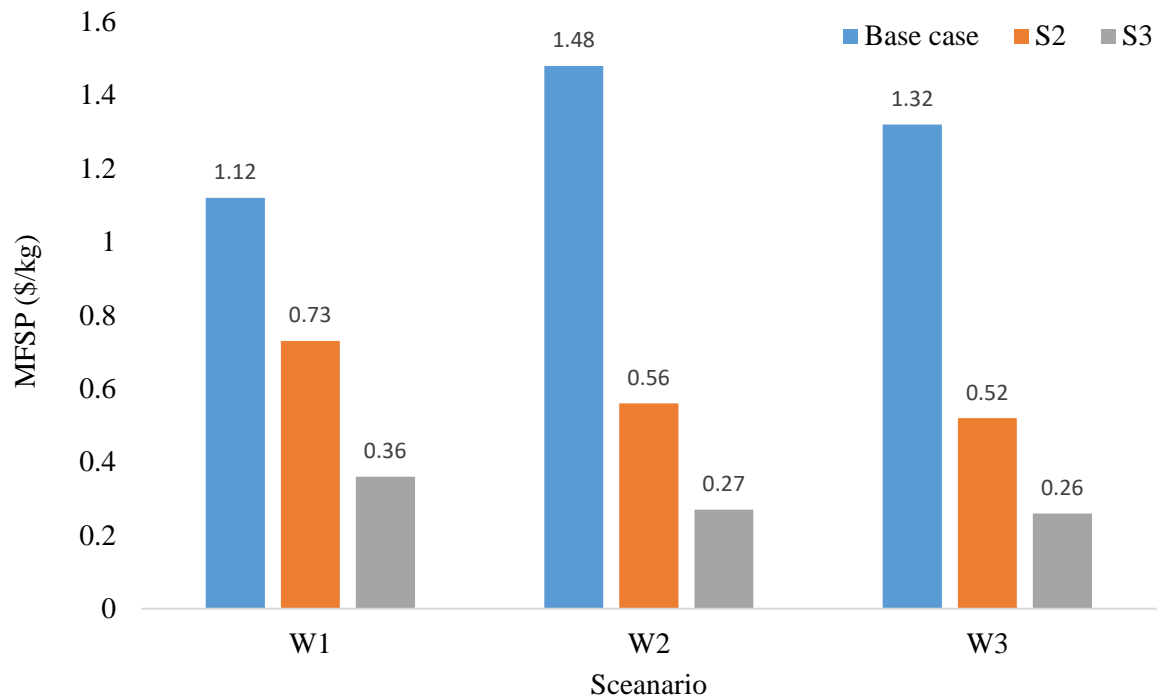


Figure 7-5: Effect of scale on the minimum fuel selling prices (MFSP) for base case scenarios, S2 (2900 kg/hr) and S3 (8700 kg/h)

Table 7-5: Summary of technical and economic outcomes from scenario 2 (S2) and scenario (S3)

|  | <b>W1</b> |           | <b>W2</b> |           | <b>W3</b> |           |
|--|-----------|-----------|-----------|-----------|-----------|-----------|
|  | <b>S2</b> | <b>S3</b> | <b>S2</b> | <b>S3</b> | <b>S2</b> | <b>S3</b> |
| <b>Inputs (kg/hr)</b>                        |           |           |           |           |           |           |
| Plastics                                     | 2900      | 8700      | 2900      | 8700      | 2900      | 8700      |
| <b>Total Oil Produced</b>                    | 1468      | 4405      | 1659      | 4977      | 1673      | 5018      |
| Saleable Product Oil                         | 1030      | 3090      | 1335      | 4005      | 1461      | 4382      |
| Oil to combustor                             | 438       | 1315      | 324       | 972       | 211       | 636       |
| <b>Total coal replaced (kg/hr)</b>           | 32        | 100       | 83        | 252       | 63        | 195       |
| <b>Total Capital Investment (\$ million)</b> | 17.044    | 33.307    | 17.815    | 35.342    | 17.813    | 35.439    |
| <b>Opex (\$ million /year)</b>               | -0.277    | -2.939    | -0.505    | -3.649    | -0.415    | -3.368    |
| <b>MFSP(\$/kg)</b>                           | 0.73      | 0.36      | 0.56      | 0.27      | 0.52      | 0.26      |

Increasing the size of a pyrolysis plant has a significant effect on the TCI and MFSP, with TCI increasing up to a maximum of 17.8 and 35.4 million \$ for S2 and S3 respectively. The MFSP obtained from S2 and S3 reduced significantly compared to the base case scenario (Figure 7-5) with the MFSP reducing to 0.73 and 0.36 \$/kg for W1, 0.56 and 0.27 \$/kg for W2 and 0.52 and 0.26 \$ /kg for W3 for S2 and S3 respectively. The large decrease in the MFSP can be attributed to indirect income received from the migration of waste from landfill

sites. The cost associated with disposal of the waste at landfill sites can be considered as an income for the pyrolysis plant and outweighed the OPEX of the proposed pyrolysis plant (Table 7-5). As a result, the MFSP for simulated scenarios S2 and S3 for waste streams W2 and W3 was below the target value of 0.65 \$/kg. The simulated scenario S2 for W1 produced a MFSP (0.73 \$/kg) only slightly above the targeted value of 0.65 \$/kg (Figure 7-5)

## **7.5 Further Comments**

The local industry in South Africa, regulated by the Paper Manufacturing Association of South Africa (PAMSA), has endeavoured to promote the conversion of paper mill waste either by biological or thermochemical routes as alternatives to landfill. As such, the disposal of paper mill waste at landfill sites is being discouraged with landfill costs in the coming years set to increase by orders of magnitude. Such increases in disposal cost will eventually make the disposal of paper mill waste at landfill sites unviable, increasing the economic attractiveness of small scale pyrolysis plants at current paper mill flow rates.

## **7.6 Conclusions and Recommendations**

This work presents a study of the trade-off between economic and technical optimisation when integrating a pyrolysis plant at a paper mill as an alternative disposal technique to landfilling.

The largest coal/energy supplement from pyrolysis occurred at the lowest conversion temperature for all three waste streams with coal substitution of up to 476 kg/hr being obtained at current paper mill flow rates. This resulted in the highest minimum oil selling price being obtained (up to 49 \$/kg). The lowest minimum fuel selling price occurred at a conversion temperature 550 °C for fast pyrolysis process for all three waste streams. It was associated with the lowest coal substitution being obtained (up to 15 kg/hr) as the entire gas,

char and a portion of the condensable fuel product must be burnt to meet the energy demands of the pyrolysis plant.

The benefits of increased scale on the economic outcome are clearly shown with both scenarios S2 and S3, producing a MFSP (0.36 to 0.73 \$/kg for W1, 0.27 to 0.56 \$/kg for W2 and 0.26 to 0.52 \$/kg for W3) in the range of the targeted value of 0.65 \$/kg. Increasing the size of a pyrolysis plant indirectly generates additional revenue as a result of the avoided cost of disposal at landfill sites. Ongoing legislation evolution and the recent drive away from disposal at landfill sites combine favourably for a pyrolysis plant as an alternative disposal technique to landfilling.

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## Chapter 8: Conclusions and Recommendations

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Industrial waste streams contaminated with plastic from a paper mill, making use of recycled fibre as feedstock, have the potential to be used as a source to produce high calorific value fuels. After using a fraction of the products (especially the gas) for the pyrolysis process to be energy self-sufficient, the char or condensable (oil/wax) product obtained can be used to partially meet the energy demands of a paper mill. The main findings and recommendations for future work on the uses of industrial paper mill waste streams classified as rejects are discussed in this chapter.

### 8.1 Conclusions

The valorisation by pyrolysis of industrial waste described as rejects for fuel product generation showed that the pyrolysis process in question (fast or slow) and conversion temperature had a vital role in influencing the quality and yield of the final pyrolysis product. The production of a char phase with increased energy density (17.9, 27.1 and 31.2 MJ/kg for W1, W2 and W3) from slow pyrolysis was favoured at temperatures as low as 300 °C with associated yield of 73.7, 77.3 and 76.1 wt.% for W1, W2 and W3 respectively. Increasing the slow pyrolysis temperature up to 550 °C produced condensable energy dense tarry phase (combination of oil and wax) with an HHV of up to 42.8 MJ/kg.

The application of fast heating rates ( $> 250$  °C/min) and short vapour residence times ( $< 10$ s) limited the effect of secondary charring reactions and promoted the formation of condensable volatiles. As such, fast pyrolysis resulted in yields of energy dense oil/wax phase of up to 52.8, 48.2 and 53.6 wt.% for W1, W2 and W3, with an HHV of up to 41.7 MJ/kg for the waste stream that contained the largest percentage of hydrocarbon plastic. The increase in

conversion temperature had a detrimental impact on the quality of the char product for both slow and fast pyrolysis with the calorific value of the char product decreasing by as much as 11 MJ/kg.

Attempts to convert the lignocellulosic component of the waste streams for W2 and W3 during fermentation resulted in the accumulation and clumping of the plastic component along with sterilization difficulties. As such these streams were not considered as a viable feedstock for a fermentation-pyrolysis route. The waste stream W1 was successfully fermented on large scale (20 L reactors) and resulted in ethanol concentrations of 39.8 g/L. The residue obtained was subjected to both slow and fast pyrolysis which resulted in an energy dense phase (oil/wax) with a yield up to 13.2 and 26.3 wt.% of a high calorific value (HHV of 35.1 MJ/kg for slow and 32.1 MJ/kg for fast pyrolysis) respectively. The significantly improved quality of the product compared to what was obtained for slow and fast pyrolysis of the untreated waste stream (HHV of 16.8 MJ/kg for slow and 16.5 MJ/kg for fast pyrolysis) was a consequence of the conversion of a large fraction of the polysaccharide fraction present in the fibres.

Assessing the potential of utilising pyrolysis as an alternative disposal technique in the form of a pyrolysis plant annexed to a paper mill at current waste generation flow rates from a mill, produced a minimum fuel selling price of 1.12, 1.48 and 1.32 \$/kg for fast pyrolysis at 550 °C, the temperature identified as the most advantageous (based on techno-economic assessment) for the three waste streams under investigation. The selling price of the fuel was between 2 to 3 times higher than heavy fuel oil equivalent. In order to meet the energy demand of the pyrolysis plant at the process condition that resulted in the best minimum fuel selling prices (550 °C), the entire char and gas products had to be combusted along with a proportion of the saleable condensable (oil/wax) product, with up to 209 kg/hr of

oil/wax being directed to the combustor. As a consequence, a saleable fuel oil yield of 35.5, 46.0 and 51.4 wt.% was obtained for W1, W2 and W3 respectively.

## **8.2 Recommendations**

Based on the findings from this work, further research could be conducted into the following key focus areas.

### **8.2.1 Pelletization of Raw Material for Refused Derived Fuels Combustion**

The pelletization of the raw material for use as a refused derived fuel pellet (RDF). As the starting pelletized waste material used in chapters 4 and 5 had a HHV of between 16 to 28 MJ/kg. They could be used for co-firing directly in the existing boilers. Alternative to directly co-firing the waste feedstock is to pelletize the char product produced at 300°C utilising the small quantity of oil that is produced as a binder to form char pellets that can be co-combusted in the existing coal boilers.

### **8.2.2 Scaling up of Pyrolysis Process**

As the pyrolysis set-up used in this study can be classified as bench scale, the most promising scenarios should be scaled-up to a kilogram scale pyrolysis system. As the main energy dense condensable phase produced from both W2 and W3 was predominately a viscous wax phase, this could present problems in the condensation train during continuous operation due to its viscosity and as such heat tracing along the entire condensation could be recommended. The performance of the pyrolysis system at bench scale (mass yields) can be used to update the technoeconomic model.

### **8.2.3 Combustion Testing of the Pyrolysis Products**

The combustion behaviour of the products obtained during pyrolysis should be assessed and compared to that of traditional fuels. The effect of the blending ratios on the combustion behaviour with traditional fuel sources should be determined as it can have a significant influence on the boiler performance as the addition of too much pyrolysis oil or char can lead to boiler instability.

### **8.2.4 Updating the Economic Model**

The economic model in this study utilised the input from gram scale pyrolysis experiments. Updating the economic model with data obtained from a pilot plant and detailed compositional data of the pyrolysis condensable product will allow for a more accurate comparison with traditional fossil fuels. Along with data obtained from the combustion testing and from lesson learnt from the operation of the pilot scale pyrolysis system, could provide a more accurate estimate of the economic viability of the process



## Appendix A: Additional Information for Chapter 4

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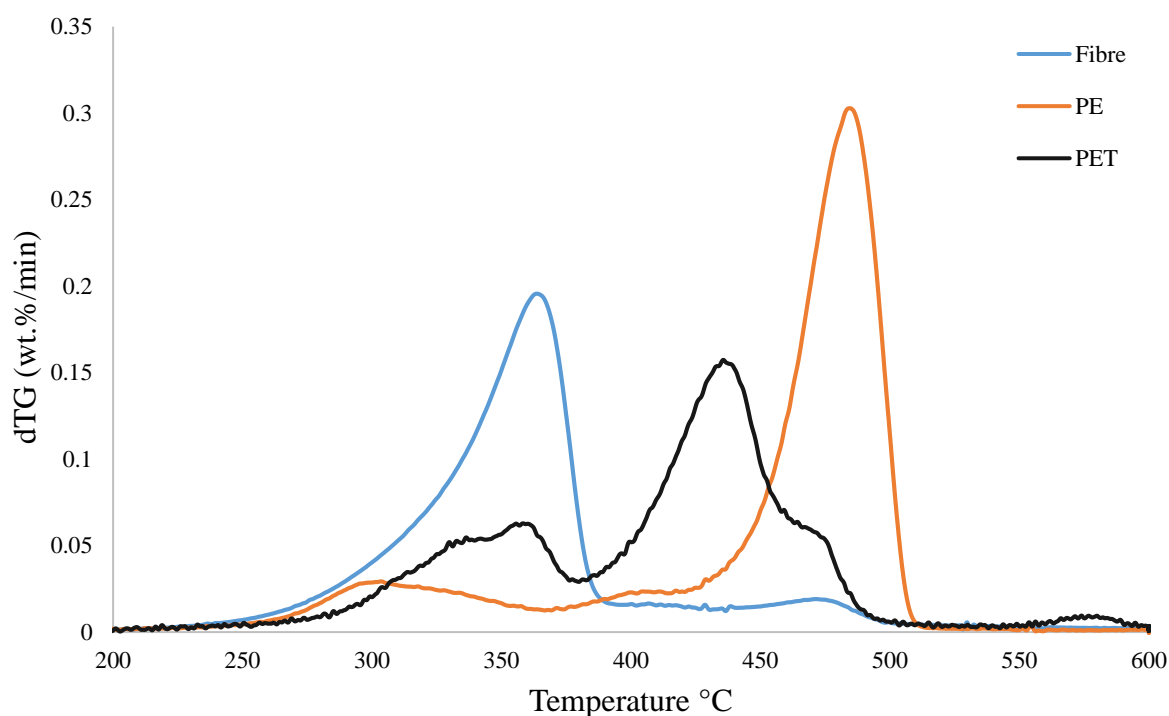


Figure A-1: dTG (derivative thermogravimetric) curves of some tentatively sorted components from waste streams representing characteristic peaks of PET, PE and fibre. Contamination of fibre component can be observed between 450 and 500 °C, PET and PE contamination (probably due to fibre) can be seen between 280 and 400 °C.

## Appendix B: Additional Information for Chapter 5

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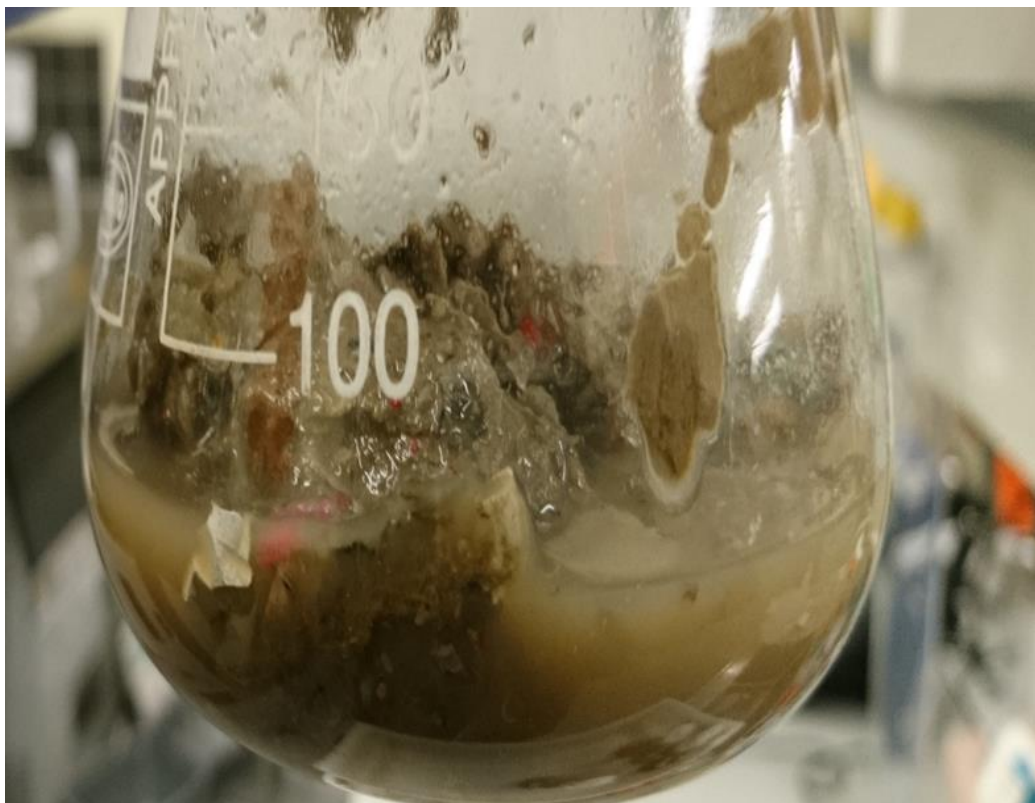


Figure B-1: Picture of shake flask experiments of waste streams W3, showing the clumping of plastic waste that occurred during fermentation.

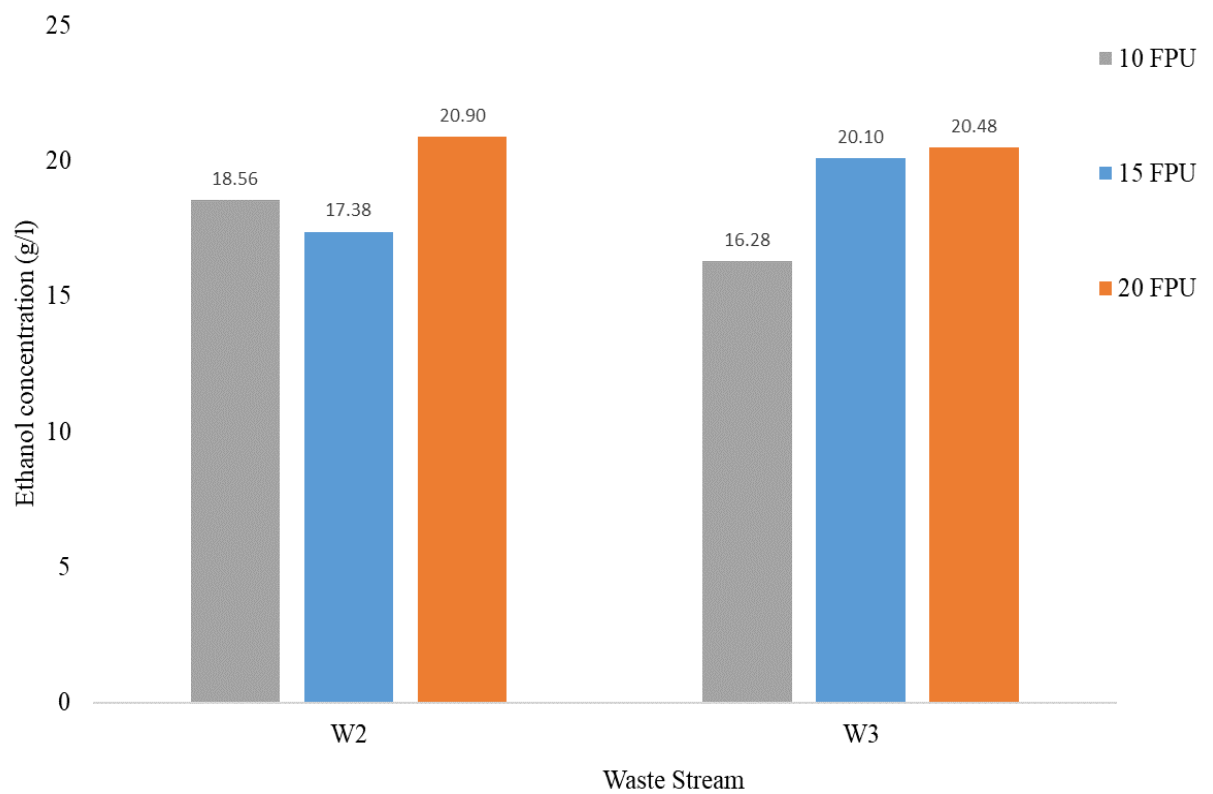


Figure B-2: Ethanol concentration of waste stream W2 and W3 at solids loading of 6wt.% and three different enzyme loadings of 10,15 and 20 FPU/gdS

## Appendix C: Detailed Experimental Method

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This section describes the step by step procedure for preparation of waste streams W1, W2 and W3 along with the experimental procedure for conduction, slow and fast pyrolysis experiments and bench scale fermentation experiments.

### C.1 Pre-treatment of Material

- The as received feedstock was dried for a period of 7 days in a tunnel green house with an approximate temperature of 40 °C.
- The dried material was subsequently milled to a particle size of 2mm using a Retsch SM 100 cutting mill.
- The milled sample was subsequently pelletized to increase the packing density inside both the slow and fast pyrolysis reactor setups. Pelletization occurred using an ABC Hansen pellet mill where the dried material was rehydrated with 30 wt.% water and passed through a 6 mm die.
- The pellet material was subsequently dried in an oven at 40 °C for a period of 7 days. The low drying temperature was to ensure that no degradation occurred to the biomass and plastic components of the waste stream.

### C.2 Slow Pyrolysis Experimental Setup

The schematic of the slow pyrolysis unit can be seen in Chapter 4 Figure 4-1. The setup consists of a nitrogen gas supply system, a tubular reactor, an electrically heated furnace and a stepwise condensation train. The detailed experimental procedure is described below.

#### C.2.1 Slow Pyrolysis Experimental Setup

- Weigh the quartz reactor tube and the sample boat. Then weigh off approximately 30grams of pelletized waste stream under investigation. Insert the quartz reactor

tube into the furnace and place the sample boat at the centre of the furnace. Connect the end caps and tighten each bolt alternatively to ensure the o ring seals correctly.

- Weigh condensers 1 to 3 and ensure that they are arranged in a stepwise manner (one slightly below the other)
- Place silica beads in condensers 4 and 5. This is done to trap any small molecules that are still entrained in the gas phase. Subsequently weigh the condensers. As with condensers 1 to 3, ensure that condensers 4 and 5 are placed in a stepwise manner.
- Weigh the rubber connectors and connect the condensers to each other.
- Before starting to purge the reactor system a leak test must be done. This is done by attaching vacuum pump to the end of the condensation system and checking that the vacuum pressure remains constant for 5 minutes.
- Start the flow meter and allow it to warm up. Once the reading on the flow meter reaches  $0 \pm 0.1$  lpm, open the nitrogen gas bottle and set the flow rate to 0.5 lpm and allow the system to purge for 30 minutes.
- While the system is purging, collect the cooling medium (dry ice) and place it around condensers 2 to 5.
- Once the reactor is finished purging, start the heating program. The heating program for slow pyrolysis was as follows:
  - The sample was heated to the desired temperature at  $25\text{ }^{\circ}\text{C}/\text{min}$ .
  - Once the desired temperature was reached, the sample was held there for an additional 60 minutes.
- Once the heating program has finished switch off the furnace and allow the reactor to cool down to  $80\text{ }^{\circ}\text{C}$ .

- Once the reactor has reactor 80 °C start dismantling and weighing the condensation and all connection pipes, starting with condenser 5.
- Once the condensation system has been dismantled and weighed, the reactor is on average at a temperature of < 40°C. Before dismantling the reactor system, turn off the nitrogen flow by set the control valve position of the flow meter to closed. Proceed to weigh both the quartz reactor tube and the sample boat. Once this is done and all samples have been collected, commence with the cleaning of the experimental setup.

### **C.3 Fast Pyrolysis Experimental Setup**

Due to the laminations associated with the heating rate that the slow pyrolysis system could provide, a new induction heating pyrolysis system was developed for fast pyrolysis experiments and is depicted in chapter 5 Figure 5-1.

#### **C.3.1 Calibration of Infrared Thermocouple**

Induction heating can be defined as the process by which a metal object is heated by high frequency alternating current. The main difference between induction heat and conventional resistance heating is that heat is generated inside the object (the metal reactor) compared to an external heat source which transfers heat to the object by conduction. As a result of an induction system using an alternating electrical current, the use of a standard K type thermocouple to measure the temperature at the surface of the reactor was not possible, as the induction current interferes with the thermocouple distorting its reading. In order to measure the temperature at the surface of the reactor an infrared (IR) thermocouple was used. IR thermocouple works by measuring the emissivity of a material and relates this back to a temperature. The emissivity of the IR thermocouple used in this study was set by a trial and error approach. The reactor was heated to the desired temperature. Once the desired temperature was reached, the induction field was turned off and a K type thermocouple

connected to a hand held temperature reader was placed inside the reactor to measure the temperature. Depending on the temperature difference, the emissivity was either increased or decreased until the IR thermocouple and the K type thermocouple read the same temperature to within 1 °C.

### **C.3.2 Experimental Procedure of Fast Pyrolysis**

- First weigh the stainless steel reactor, graphite gasket and sample boat. Once this is done, weigh 30grams of pelletized waste sample. Place the sample boat in the middle of the reactor and assemble it by tightening the bolts alternatively to ensure the reactor seals correctly. Once done, place the reactor inside the induction coil.
- Weigh the components that make up the condensation train (metal condensation pot, shell and tube condensers and electrostatic precipitator (ESP)). Assemble the condensation system and connect it to the reactor, making sure that the sample boat inside the reactor is not disturbed from its position.
- Check for leaks using the vacuum pump and that the vacuum pressure remains constant for 5 minutes.
- Once the leak test is done, start to purge the system with nitrogen for 30 minutes.
- Connect the cooling water flow pipes to the two condensers and start the chiller. Make sure the chiller's temperature is set at 5 °C.
- Collect dry ice to place round the collection pot.
- Once the system has purged, first set the flow rate to 2.5lpm and connect the ESP power source and ensure it is set at 12 KV.
- Once this is done, start the heating program. The heating program for fast pyrolysis was as follows:
  - The sample was heated to the desired temperature at 250 °C/min.

- Once the desired temperature was reached, the sample was held there for an additional 30 minutes.
- Once the heating program has finished, switch off the furnace and allow the reactor to cool down to 80 °C.
- Once the reactor has reached 80 °C, start dismantling and weighing the condensation and all connection pipes starting with the ESP.
- Once the condensation system has been dismantled and weighed, the reactor was on average at a temperature of < 40°C. Before dismantling the reactor system, turn off the nitrogen flow by setting the control valve position of the flow meter to closed. Proceed to weigh both the stainless steel reactor and gasket and the sample boat. Once this is done and all samples have been collected, commence with the cleaning of the experimental setup.

#### **C.4 Experimental Procedure for 20L Fermentation**

This section describes the experimental procedure for 20l fermentation experiments.

##### **C.4.1 Sterilization and Preparation of Feedstock and Fermentation Medium.**

- A total of 7.3L fermentation medium consisting of 3g/L of corn steep liquor and 0.62 g/l of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  was added to the 20L reactor. Along with the initial amount of substrate to bring the solids loading to 6wt.%
- The reactor was sterilized by making use of steam at 121 °C and a pressure of 200 kPa for a period of 15 minutes. Once this was done, the reactor was allowed to cool down to the fermentation temperature of 37 °C.
- The inoculum consisting of yeast MH1000 and enzyme (viscamyl flow) was added in the following amounts:
  - MH 1000 5% v/v
  - Enzyme 15 FPU/gdS



- The fermentation was allowed to proceed for 12 hours before a sample was taken to be analysed for ethanol. Sampling was done before any subsequent substrate feeds occurred.
- Additional substrate was fed at 3wt.% until final solids loading of 27wt.% was achieved. All additional substrate was first sterilized in an autoclave at 121°C for 15 minutes before being fed to the reactor.
- Additional ethanol samples were taken up until the final solids loading was reached. To ensure that the conversion of the substrate was completed, ethanol sample was taken for an additional 24 hours after the last substrate feed.