An experimental feasibility study on fast pyrolysis of MSW-derived trommel fines for energy recovery and waste management

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Thesis summary

Trommel fines are solid wastes with particle sizes of <25 mm, which are obtained from the MSW recycling facilities. They represent a class of wastes with significantly high proportions of both inorganic and organic (biodegradable and non-biodegradable) materials, making their disposal problematic. In this research, the technical and economic feasibility of fast pyrolysis of trommel fines has been experimentally investigated for energy recovery, thereby eliminating the organic load and leaving an inert solid residue (glass, stones, ceramics etc.) for final disposal or other uses.

A batch of trommel fines, obtained from a UK Waste Management company, was fully characterized and prepared into suitable feedstocks for fast pyrolysis using an existing bubbling fluidised bed reactor system. A combination of physical processes including drying grinding, sieving and manual separation was used to obtain a dry pre-treated feedstock (PT) of suitable size range for fast pyrolysis. In addition, the PT feedstock was applied in an agitated wet treatment procedure to obtain two new feedstocks for fast pyrolysis by washing with water (AW) and with a 1.00 vol. % Decon Neutracon surfactant aqueous solution (AWS). Characterization results showed that different size fractions of the ‘as received’ trommel fines have differences in properties. Ash contents were high (>30 wt.%) and along with the volatile matter and higher heating values (HHV), varied in relation to particle sizes. By careful pre-treatment process design, the size fraction 0.5 mm – 2 mm, which was suitable for fast pyrolysis, had an experimental energy content of 13.8 MJ kg $^{-1}$. The energy contents of the AW and AWS feedstocks increased with a reduction in ash contents after the respective washing procedures.

A 300 g h^{-1} bubbling fluidised bed fast pyrolysis rig was used to investigate the effect of temperature and moisture content on product yields and process conversion efficiency of dry physically pre-treated trommel fines (PT) to determine their optimum processing conditions. Investigations were also undertaken to study the effect of feedstock pre-treatment method; dry (PT) and wet (AW and AWS) on both the pyrolysis products and process conversion efficiency. Using PT feedstock, the highest organic liquid yield and highest conversion efficiency was obtained between 500 °C and 550 ºC with <3 wt% feedstock moisture content. The organic liquid yield and the process conversion efficiencies increased with AW and AWS feedstocks, with AW feedstock giving the best results. The HHV of primary condensate from all feedstocks was greater than 30 MJ kg^{-1} and the washing procedure was found to reduce the nitrogen contents of the liquid products especially in the secondary condensate liquids.

The fast pyrolysis results were used to determine the economic feasibility of the fast pyrolysis technology at PT optimum processing conditions for energy recovery and management of trommel fines at different processing capacities. The PT fast pyrolysis was found to be economically feasible from 2000 kg h^{-1} processing capacity, with a capital investment payback period of 8.6 years at 20% interest rate. The net present value (NPV) increased with the AW and AWS feedstocks and further analysis showed that processing these feedstocks could still be economically feasible at capacities of approximately 1000 kg h^{-1}.

Overall, the results of this study suggest that the laboratory-scale fast pyrolysis rig used in this study and the developed economic model can form the basis for future research and process development for treatment of MSW.

Keywords: Trommel fines ash reduction, biodegradable municipal solid waste (MSW), dry and aqueous pretreatment, fluidised bed reactor, techno-economic analysis

Dedication

To Chief Sir & Lolo Lady Clement Enyinwa Eke

Acknowledgements

First and foremost, I would like to thank God Almighty for giving me the strength, knowledge, wisdom, ability and opportunity to undertake this research study and to persevere and complete it satisfactorily. Without his blessings, this achievement would not have been possible.

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Abbreviations

ACLF	Air-classified light fractions
AW	Agitated Washing
AWS	Agitated Washing with Surfactant (Decon Neutracon)
BA	Bottom ash
BMSW	Biodegradable municipal solid waste
CA	Civic amenity
CHP	Combined heat and power
Cum.PV	Cumulative present value
d.a.f.	Dry ash free
d.b.	Dry basis
DPC	Direct plant cost
DTG	Differential thermogravimetric
EBRI	European Bioenergy Research Institute
EC	Equipment cost
EfW	Energy from Waste
ESP	Electrostatic precipitator
FB	Free board
FC	Fix carbon
FA	Fly ash
GC	MS Gas chromatography – mass spectrometry
HDPE	High-density polyethylene
HHV	Higher heating value
IBA	Incineration bottom ash
KF	Karl-Fischer

LDPE	Low-density polyethylene
LFT	Landfill Tax
LHV	Lower heating value
LOI	Loss of ignition
MBT	Mechanical biological treatment
MCR	Moisture Content Run
MRF	Material recovery facility
MSW	Municipal solid waste
NPV	Net Present Value
PPE	Personal protective equipment
PT	Physical pre-treated Trommel Fines
PVC	Polyvinyl chloride
RES	Renewable Energy Sources
RDF	Refuse derived fuel
RO	Renewables Obligation
ROCs	Renewables Obligation Certificates
SC	Secondary condensate
SD	Standard deviation
TGA	Thermogravimetric analysis
TIR	Temperature Investigation Run
TPC	Total plant cost
TOE	Total of oil equivalent
VM	Volatile matter
WEEE	Waste electrical and electronic equipment
wt.%	Weight per cent

1 Introduction

1.1 Background

In the UK, as industrial areas developed, the idea of establishing norms for the cleaning of towns began to emerge by the mid-18th century. An early example is the Public Health Act of 1875, which was the first piece of legislation created to establish waste management norms. Further industrial development resulted in an increase in waste production, which resulted in the introduction of waste disposal methods, such as landfill and incineration, which are still in use today.

Municipal solid waste (MSW) is defined by the Landfill Directive 1999/31/EC (CEC, 1999) as waste from households, as well as other waste, which because of its nature or composition, is like waste from households. Also included in this category are wastes such as garden wastes and bulky items that local authorities may collect separately and which householders themselves take to civic amenity (CA) sites. Waste from households excludes local authority collected waste types that do not come directly from households, such as street bins, street sweepings, parks and grounds waste and compost like output.

In 2017, England produced a total of 26.3 million tonnes of MSW, an increase of 0.7% compared to the previous year and an increase of 1.2% compared to the beginning of this research in 2015. Around 43.6% of this waste (11.3 million tonnes) was recycled, re-used or composted. A wide variation in household waste recycling rates amongst individual local authorities, ranging from 14 to 65% was reported in 2016/17 (DEFRA, 2017). Around 39% of the total MSW generated was incinerated. MSW sent for incineration increased to 10.2 million tonnes, an increase of 0.9 million tonnes in 2016/17, with around 7.1 million tonnes being sent directly. (DEFRA, 2017). About 16% of the total MSW generated was sent to landfill. Waste sent to landfill decreased by 1.0 million tonnes to 4.1 million tonnes in 2016/17, with nearly 3.2 million tonnes being sent directly to landfill. Landfill tax continues to be the main driver for authorities to reduce waste to landfill (DEFRA, 2017). Figure 1.1 shows the municipal waste management methods in England over the past 10 years. From Figure 1.1 an increase in Energy from Waste (EfW) can be seen alongside an increase in recycling. Energy from waste (EfW) is the process of generating energy in the form of electricity and/or heat from the primary treatment of waste, or the processing of waste into a fuel source. Although the volume of waste sent to landfill is decreasing, further improvements in technologies and processes for both recycling and for EfW could reduce this even more. EfW has great potential to divert more waste from landfill whilst still leaving plenty of room to increase the volume of waste sent to recycling (DEFRA, 2017).

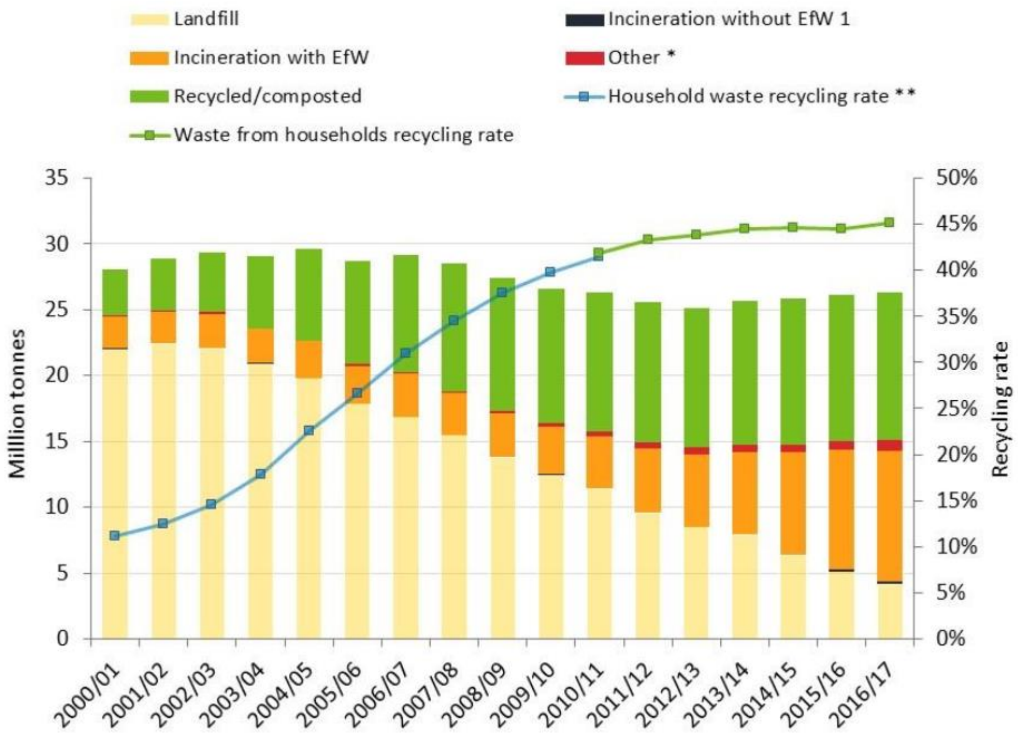

Figure 1.1: Local authority managed waste and recycling rates in England, 2000/01-2016/17 (Source: adopted from DEFRA, 2017)

Notes:

Incineration with energy recovery/without energy recovery includes incineration bottom ash (IBA) and metals from IBA.

* Other includes waste treated/disposed through other unspecified methods, process and moisture loss.

** The household waste recycling rate is based on a broader measure of waste (street bins, soil, household-related parks and grounds, and compost like output) and is not directly comparable to the ‘waste from households’ recycling rate.

The waste hierarchy (Figure 1.2) provides a classification of waste disposal methods by order of environmental impact. The three first stages of the waste hierarchy (prevention, re-use and recycling) aim at reducing the amount of waste produced and at giving a new use to materials instead of disposing of them. The waste hierarchy (Figure 1.2) set out that anaerobic digestion is preferable to composting since it provides the expectation of energy recovery. Furthermore, it establishes that recycling is preferable to energy from waste, which is preferable to landfill.

Although it is possible to re-use and recycle materials, residual waste subsists. As shown in the waste hierarchy (Figure 1.2) these materials should go through a process of energy recovery before final disposal. These energy recovery processes are (depending on the type of waste) anaerobic digestion and thermal treatment.

Figure 1.2: Waste Hierarchy (Recycle-more.co.uk, 2017)

Figure 1.3 summarises the present waste treatment situation. In Figure 1.3, thin arrows represent emerging technologies such as digestion fermentation, gasification and pyrolysis. Over the next sections the disposal methods including physical treatment, biological treatment, thermal treatment and landfill, will be analysed in greater detail.

Figure 1.3: Waste treatment: a complete overview (Michaël, 2007; Fitzgerald, 2013; Pitchell, 2014)

1.2 Waste Disposal Methods

As mentioned above, there are several disposal methods for waste including physical treatment or physical separation, biological methods, thermal treatment, and landfills. The main aim of this section will be to analyse in greater detail the main differences between these methods, particularly for MSW.

1.2.1 Physical treatment of MSW (size reduction, recycling and separation)

Recycling is defined as the process of transforming waste into new material so that it can be given a new use. Nowadays, recycling has become an increasingly important disposal method because of the implementation of relevant and binding national and international environmental legislation. Recycling targets imposed by EU legislation have been increasing over time (DEFRA, 2017). A material recovery facility (MRF), also known as materials recycling facility is a plant that receives, separates and prepares recyclable materials using a mixture of manual and automated methods, for marketing to end-user manufacturers to create new products.

Material recovery facilities struggle with a variety of unwanted materials (plastic bags, large objects, and trash) which increase the need for manual sorting, and which increases inefficiencies for MRF operators and ultimately for the communities they serve (Vangel Inc. 2017; Waste Advantage Solid Waste & Recycling Magazine, 2017). However, advances in technology make today's MRF facilities different and, in many respects, better than older versions. Today, MRF facilities are attracting renewed interest to address low participation rates for source-separated recycling collection systems and prepare fuel products and/or feedstocks for conversion technologies, giving communities the opportunity to recycle at much higher rates (The Balance, 2017; Plastics.americanchemistry.com, 2017). Separation technologies used in MRF facilities exploit varying properties of the different materials in the waste. These properties include the size and shape of different objects, their density, weight, magnetism, and electrical conductivity. A summary of the different options for waste separation is shown in Table 1.1.

Table 1.1: MSW separation techniques used in MRF facilities (Source: adopted from DEFRA 2013a)

Separation Technique	Separation Property	Materials targeted	Key Concerns
Trommels and screens	Size	Oversize – paper, plastic Small (Trommel fines) – organics, glass, fines	Air containment and cleaning
Manual separation	Visual examination	Plastics, contaminants (glass, stones etc.), oversize	Ethics of role, Health & Safety issues
Magnetic separation	Magnetic	Ferrous metals	Proven technique
Eddy current separation	Electrical conductivity	Non-ferrous metals	Proven technique
Air classification	Weight	Light – plastics, paper Heavy – stones, glass	Air cleaning
Ballistic separation	Density and elasticity	Light – plastics, paper Heavy – stones, glass	Rates of throughput
Optical separation	Diffraction	Specific plastic polymers	Rates of throughput

From Table 1.1 trommel screens are examples of separation techniques which are commonly used in municipal solid waste (MSW) treatment plants. They can be used for both raw MSW and the air-classified light fractions (ACLF) of wastes to separate solid materials into different sizes (Glaub, Jones and Savage, 1982; Kim, Matsuto and Tanaka, 2003; Zhang and Banks, 2013). MSW sorting process consists of three major units: shredding, air classification, and screening. Packer trucks deliver the sorted MSW to the MRF facility, which can process up to 30 tons/hr at maximum capacity per one line. The sorting process initializes in a bag-ripping unit, which aims to open plastic bags. The ferrous metal is then extracted from the MSW stream using magnets; and the recovered ferrous metal is conveyed to a ferrous storage bin from where it is recycled. MSW is then processed in a vertical hammermill shredder to reduce it to a normal size. Shredded MSW is taken to an air classifier, using a belt-type conveyor. Non-ferrous materials, such as aluminium cans and combustibles are crushed by the vertical hammermill shredder. A manual sorting unit is added prior to the vertical hammermill shredder for the recovery of aluminium cans for recycling. The air classifier, blowing from the vertical hammermill shredder, is intended to separate the inert materials, such as glass, ceramics, soil and so on, to reduce the content of heavy non-combustible material in the residual MSW streams. Light materials, passing through the air classifier, are sent into the trommel screen for advanced separation (Glaub, Jones and Savage, 1982; Kim, Matsuto and Tanaka, 2003; Zhang and Banks, 2013).

The dimensions of the openings on the surface of trommel screen can be varied to fine-tune the processing function and assure maximum combustibles recovery. Three waste streams can be trommeled and the particle size is controlled by the openings design on the surface of the trommel such that the material with the particle size less than 25 mm (trommel underflow) and the particle size between 25 mm and 100 mm (trommel middle flow) are separately arranged by two different sets of openings with a concentric shell configuration. The overflow, passing through this trommel screen, presents the lightest portion in the MSW with the size greater than 100 mm (trommel overflow), and can be identified as fluff refuse derived fuel (RDF). Refuse derived fuel (RDF) is a fuel produced from various waste such as MSW, industrial waste or commercial wastes, and consists largely of combustible components such as plastics, paper cardboard, and other corrugated materials (Fitzgerald, 2013; Pitchell, 2014). Both outputs with particle sizes between 25 mm and 100 mm and larger than 100 mm can be recycled or marketed as refuse derived fuel (RDF) for energy recovery (Fitzgerald, 2013; Pitchell, 2014). The trommel underflow (< 25 mm) passing through this trommel screen are by-products of mixed fractions, called trommel fines from the mechanical recycling of MSW and are usually sent to landfill. A schematic for MSW processing which generates trommel fines is shown in Figure 1.4.

Figure 1.4: Mechanical recycling of MSW (Source: adopted from Fitzgerald, 2013; Pitchell, 2014).

1.2.1.1. Trommel fines

Trommel fines (trommel underflow < 25 mm, in Figure 1.4) are a by-product produced during the mechanical recycling process (refer to section 1.2.1) of municipal solid waste (MSW). This by product consist of materials such as wood, aggregates, glass, ceramics and organics. In general, trommel fines are made up of various materials that are less than 25 mm (Figure 1.4) and contain both organic and inorganic components (Fitzgerald, 2013; Pitchell, 2014). The composition of trommel fines thus depends on the initial type and composition of MSW, on the severity of mechanical processing of the MSW and on the design of the trommel screen. The inorganic content of trommel fines includes inert materials such as stones, aggregates, glass and soil.

In general, the organic components of trommel fines include fibre, plastics, wood, food waste and textiles, and therefore can be used as an energy resource. Due to the organic contents in trommel fines, they are classified as biodegradable municipal solid waste (BMSW) and landfill sites have been their traditional home. However in the bid to further reduce the amount of BMSW waste being send to landfill (refer to section 1.2.4 and 1.3), trommel fines are now included in the UK’s Landfill Tax (Qualifying Fines) Order 2015, and this requires landfill operators to conduct loss of ignition (LOI) tests to determine the correct tax liability for trommel fines; £2.65 per tonne dry basis for 'less polluting' waste with <10% LOI, or £86.10 per tonne, (the current higher rate) for waste exceeding 10% LOI. For most operators this means landfill tax for this type of waste will increase. For example, an operator producing 40 tonnes per day of trommel fines (dry basis) could see their landfill tax bill increase from £100,000 to over £1,000,000 per year if it contains more than 10% LOI material (HMRC, 2014; Watts, 2016).

Therefore, the handling and disposal of trommel fines is now a major problem for the waste management industry, which requires further research. Some proposed methods to cope with this issue include further separation and classification of components of trommel fines, for example, to recover smaller fractions (< 2 mm) of plastics and paper for RDF. This may be an expensive option and the physical separation of inorganics and organics based on size and mass may no longer be feasible at smaller (< 2 mm) scales. Since the volatile matter content (plastics, paper cardboard, etc.) of trommel fines is one of the main concerns for their disposal via landfill (HMRC, 2014; Watts, 2016), technologies are required to make the composition of trommel fines suitable for processing for operators and regulators. The big question for waste processors to ask is what equipment will generate a high return of investment whilst eliminating landfill costs. The waste hierarchy, shown in Figure 1.2, sets the order of waste disposal methods to adopt. According to these regulations energy recovery before final disposal is a more favourable method than landfill because it provides energy from a renewable source.

1.2.2 Biological treatment of MSW (composting and anaerobic digestion)

A mechanical biological treatment (MBT) system is a type of waste processing facility that combines a MRF facility (refer to section 1.2.1) with a form of biological treatment such as anaerobic digestion and/or composting. MBT plants are designed to process mixed household waste as well as commercial and industrial wastes (DEFRA 2013a; Veolia UK, 2017). MBT process also generates trommel fines (Figure 1.4) as a by-product from the mechanical sorting of the waste streams, which is landfilled as their composition is not suitable for the biological process due to the high inorganic content.

Composting is the breakdown of the biodegradable organic component of waste by naturally occurring aerobic microorganisms. The microorganism breakdowns the waste organic fraction into carbon dioxide and compost. Compost is organic matter that has been decomposed and is recycled as a fertilizer and soil amendment. Compost is a key ingredient in organic farming but there is no green energy produced by systems employing only composting treatment for the biodegradable waste (Heartspring.net, 2017; Recyclenow.com, 2017).

Anaerobic digestion (AD) is the breakdown of biodegradable organic materials by micro-organisms in the absence of oxygen. Anaerobic digestion is a process which converts carbon-containing biodegradable matter such as food and garden waste, and farm slurry, into biogas - a methane-rich gas that can be used to generate electricity and heat. Alongside, a digestate fraction is obtained, which is seen a source of nutrients that can be used as a fertiliser. Increasingly AD is being used to make the most out of our waste by turning it into biogas-based renewable energy. AD benefits many different groups; including the local community, industry, farmers and energy entrepreneurs, government and the environment (Bioplex UK - The Future of Recycling, 2017; Biogen.co.uk, 2017).

Some MBT plants incorporate both anaerobic digestion and composting. This may either take the form of a full anaerobic digestion phase, followed by the composting of the digestate. Alternatively, a partial anaerobic digestion phase can be induced on water that is percolated through the raw waste, dissolving the readily available sugars, with the remaining material being sent to a windrow composting facility. By processing the biodegradable waste either by anaerobic digestion or by composting MBT technologies help to reduce the contribution of greenhouse gases to global warming (DEFRA 2013a).

1.2.3 Thermal treatment of MSW

Thermal treatment or energy-from-waste (EfW) is a waste treatment method that involves the application of high temperatures (> 200 °C) in the processing of waste feedstock. This method is particularly relevant as it sits on the penultimate stage of the waste hierarchy (Figure 1.2) where energy recovery takes place and thus it is a preferred option to landfill disposal. Another important aspect of thermal treatment is that it reduces the mass and volume of waste sent to the final stage of disposal. Thermal treatment processes can be divided into two major categories: incineration and advanced thermal treatment (Soderman, 2003).The difference between these two methods is the quantity of air involved in the process. Figure 1.5 shows the quantity of air associated to thermal treatment systems.

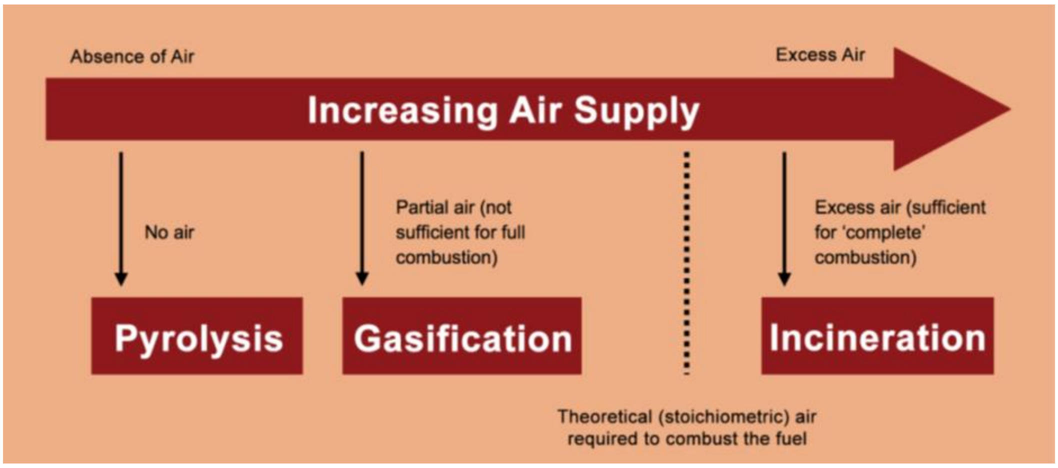

Figure 1.5: Relationship between level of oxygen and thermal treatment technology (Source: DEFRA, 2013)

From Figure 1.5, it is observed that incineration involves a reaction with excess air that will ensure a complete combustion. Pyrolysis takes place in the absence of air whilst gasification takes place in an air-lean atmosphere (Bridgwater 1999, 2000). This means that both use less than the stoichiometric amount of air required to combust the fuel, leading to chemical products (liquids, solids and gas) which can be further processed to obtain heat, electricity and chemicals. Pyrolysis and gasification are referred to as advanced thermal treatment because these processes are more versatile in terms of feedstock and process requirements than incineration whose only product is heat. A detailed description of the different types of pyrolysis processes can be found in section 2.4.1.

The differences in the amount of air required for incineration, pyrolysis and gasification can be visualized from the Figure 1.6 based on equivalence ratio of the actual fuel/air ratio to the stoichiometric fuel/air ratio defined by Eq. 1.1.

$$\mathrm{ER}\,(\phi) = \frac{\left(\frac{Air}{Fuel}\right)_{stoichiometric}}{\left(\frac{Air}{Fuel}\right)_{actual}} \qquad \textbf{(Eq. 1.1)}$$

Figure 1.6: Classification of thermal waste treatment technologies using Equivalence ratios (Kaupp and Goss, 1981)

P = pyrolytic gasification; G = gasification; C = combustion; FP = region of flaming pyrolytic gasification. Conventional pyrolysis is operated at temperatures around 500 °C.

1.2.4 Landfill

According to the EU official definition, landfill is a waste disposal site for the deposit of the waste onto or into land (i.e. underground). Landfill sites are divided into internal waste disposal sites and permanent sites. Internal waste disposal sites are landfill where a producer of waste is carrying out its own waste disposal at the place of production. On the other hand, permanent sites (i.e. lasting for more than one year) are used for temporary storage of waste (Official Journal, 1999).

Landfill generates diverse environmental issues for groundwater, air, and land. For example, the use of landfill produces a leachate which is associated to contamination of groundwater, thus potentially polluting water reservoirs; and air, through the emission of odours. Furthermore, the use of landfill reduces the available land for construction resulting in the need of using the green belt, designated area by the UK government for this type of activity. Moreover, from a waste management perspective landfill disposal prevents the recovery and re-use of materials. This has negative impact on recycling and ultimately will cause extra resources to be used. These damaging consequences led the European Union to adopt measures to restrict landfill use through the introduction of the Landfill Directive (Official Journal, 1999). In the UK, these measures were initially transposed into the implementation of the Landfill Tax (LFT) in 1996 to enable the UK to meet EU targets. The LFT applies to all waste disposed of via landfill at a licensed site, and it is charged by weight at two different rates (standard and inert) which can be seen in Figure 1.7 (Official Journal, 1999).

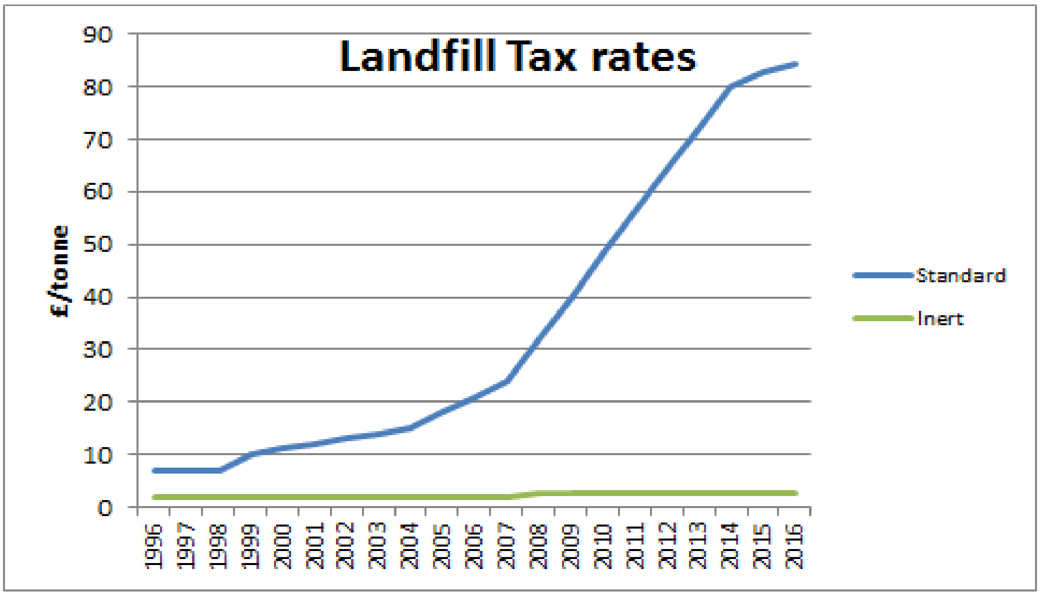

Figure 1.7: The evolution of landfill tax charge in the UK from 1996 to 2014 (HMRC,2014; Limited, 2017)

From Figure 1.7, the lower rate (green line) is applied to inerts (inorganic compounds) such as those defined in Landfill Tax (qualifying material). The standard rate (blue line) is applied to all other types of waste. Exemptions to the landfill tax include materials removed from the water, mining and quarrying waste, pet cemeteries, filing of quarries (under certain conditions) and waste from visiting forces (Limited, 2017).

The amount of waste sent to landfill have been dropping over the years (Figure 1.8), especially since the £8/tonne increase came in for the first time in 2008 (Figure 1.7). Figure 1.8 below shows the annual tonnage of MSW sent to landfill since 1998.

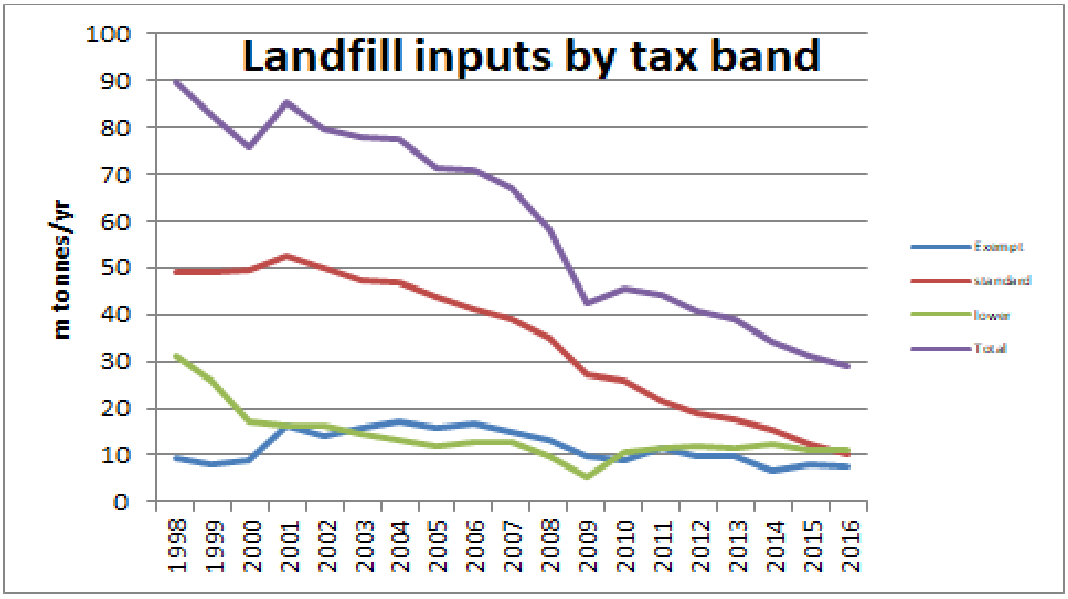

Figure 1.8: The evolution of landfill inputs by tax band charge from 1998 to 2016 (HMRC, 2014; Limited, 2017)

1.3 Strategies for Managing Waste in the UK

The year 1999–2000 saw the publication of waste strategies for England and Wales (Department of the Environment, Transport and the Regions, 2000), Scotland (SEPA, 1999) and Northern Ireland (Department of the Environment, 2000). All three strategies call for a reduction of the amount of MSW sent for landfill disposal and for increases in waste recycling and recovery. The main aspects of each strategy with respect to MSW are summarised in Table 1.2 and 1.3 (Burnley 2001).

These strategies are also intended to meet the requirements of the European Landfill Directive (Official Journal, 1999). Many of the Directive's requirements are already covered through existing UK legislation, but the principal article as far as these strategies are concerned is Article 5. This article calls for a phased reduction in the amount of biodegradable municipal solid waste (BMSW) disposed of to landfill:

- to 75% of the amount produced in 1995 by the year 2010;
- to 50% of the amount produced in 1995 by the year 2013;
- to 35% of the amount produced in 1995 by the year 2020.

These targets by date take account of a four-year delay for member states (such as the UK) that currently landfill over 80% of their MSW, and it is understood that the UK intends to make use of the delay. (Official Journal, 1999).

Table 1.2: United Kingdom waste strategies (Source: Burnley, 2001)

Table 1.3: Meeting the UK landfill directive and waste strategy targets by 2020 (Source: Burnley 2001)

According to DEFRA (2010a), in October 2010 after a nationwide consultation, the UK government committed to a better alignment of MSW-reporting as used in the UK, with the EU's definition of MSW. This also had implications for the reporting of BMSW diverted from landfill, which would begin to include biodegradable waste from the commercial sector. This would result in almost a doubling in waste reported as BMSW as reported by DEFRA (2010b). The reporting method was adjusted for the reporting year 2010 onwards – corresponding to a data year of 2007 onwards. Therefore, BMSW sent to landfill in the UK as reported in 2007 (23.3 million tonnes) was 63% higher than the figure reported for 2006 (14.3 million tonnes). This is a result of changing definitions for BMSW rather than increases in the amount of biodegradable waste being landfilled. Following the change in definition of BMW, the UK adjusted the Landfill Directive diversion targets. The old and new targets are shown in Table 1.4. (DEFRA, 2010a).

Table 1.4: Landfill Directive diversion targets according to old and revised definitions of BMSW (Source: DEFRA, 2010a)

	1995 quantity of BMSW	2010 Target (75% of 1995)	2013 Target (50% of 1995)	2020 Target (35% of 1995)
UK Target for landfill of BMSW under old definition (thousand tonnes)	18260	13695	9130	6391
UK Target for landfill of BMSW following 2010 revision (thousand tonnes)	35688	26766	17844	12491

Table 1.5 below shows that BMSW sent to landfill in the UK has fallen every year since the series began in 2010. By 2010, the 2013 target (50% of 1995, Table 1.4) had been exceeded and in 2015 represented 22 % of the 1995 baseline (Table 1.5). The new reporting methods, in line with EU definitions, present a more favourable picture of progress towards Landfill Diversion targets, presumably due to a more rapid diversion of commercial wastes from landfill.

Table 1.5: BMSW to Landfill as % of 1995 target baseline, UK and country split, 2010-15 (Source: DEFRA, 2016)

Year	UK	England	NI	Scotland	Wales
2010	36%	36%	46%	41%	33%
2011	33%	32%	28%	38%	29%
2012	29%	28%	32%	36%	28%
2013	26%	25%	24%	33%	27%
2014	24%	24%	26%	31%	23%
2015	22%	21%	25%	30%	17%
BMSW = Biodegradable Municipal Solid Waste Wales introduced new biodegradability factors in 2013 and have backdated 2010-12 Scotland revised figures for 2010-14 in 15/12/2016 update Source: Waste Data Interrogator, Defra Statistics					

1.3.1 Government aims

In 2011, DEFRA produced a review of the UK Government Waste Policy (DEFRA, 2011). This review stated government's support for efficient energy recovery from residual waste in order to provide environmental benefits, economic opportunities and a reduction in carbon emissions. The aim of the UK government is to get the most energy out of residual waste, as opposed to getting the most waste into energy recovery. Landfill should only be used as a last resort and only for waste where there is no better use. The government aims to overcome these barriers by ensuring EfW and its place in the waste hierarchy (Figure 1.2) is valued and understood by the public, businesses and households in the same way as re-use and recycling. It will also be important to ensure that any waste management legislations do not have negative consequences on the development of the EfW industry.

Further to this, in February 2014 DEFRA produced a revised guide to EfW (DEFRA, 2014) with the aim of increasing understanding of the process, the role it can play in the sustainable management of waste and how it can relate to other waste management options. The government's main aim is to prevent the production of waste in the first place and reduce the volume of residual waste. However, energy recovery will remain important as a means to divert non-reusable or recyclable waste from landfill as well as an important means of energy generation. There is currently a clear gap between the potential of EfW and the delivery. The government aims to improve this by facilitation change with further support and incentives for energy recovery to prevent valuable resources going to landfill.

There are various incentives, grants and schemes that the UK government uses to support both low carbon energy and to optimise the role of energy recovery in the waste hierarchy (Figure 1.2). Their aim is to ensure that there is the correct blend of incentives to support development as well as providing the necessary framework to address any market failures. Financial incentives are particularly available for the more novel technologies and for those whose energy outputs go beyond electricity (i.e. heat or transport fuels) (Ofgem.gov.uk, 2015).

The financing of energy recovery projects can be difficult as waste companies, local authorities and financial institutions all aim to minimise their risks, leading therefore to reliance on proven technologies and long term contracts. This makes it difficult for smaller companies and innovative technologies to break through. The Renewables Obligation (RO) is the government's main policy for the support of large scale renewable electricity in the UK. Electricity suppliers are legally obliged to purchase a proportion of their electricity from renewable sources or they incur a penalty. This is regulated by Ofgem through the use of Renewables Obligation Certificates (ROCs), with each type of renewable generation grouped into bands worth differing amounts of ROCs as seen in Table 1.6. These bands vary by technology and depend on a number of factors including cost, relative maturity, and future development potential. For EfW, only the renewable fraction of waste is rewarded with ROCs, and plants producing only electricity are not supported, as these plants are already well established and economically viable (Ofgem.gov.uk, 2015).

Table 1.6: Banding levels for the banding review period (2013-17) in England and Wales (Source: Gov.uk, 2018)

Band	Year 13/14 support (ROC/MWh)	Year 14/15 support (ROC/MWh)	Year 15/16 support (ROC/MWh)	Year 16/17 support (ROC/MWh)
Advanced gasification/pyrolysis	2	2	1.9	1.8
Anaerobic Digestion	2	2	1.9	1.8
Co-firing (low-range)	0.3	0.3	0.5	0.5
Co-firing (mid-range) *	0.6	0.6	0.6	0.6
Co-firing (high-range) *	0.7	0.9	0.9	0.9
Co-firing (low-range) with CHP*	0.8	0.8	1 **	1 **
Co-firing (mid-range) with CHP*	1.1	1.1	1.1 **	1.1 **
Co-firing (high-range) with CHP*	1.2	1.4	1.4 **	1.4 **
Co-firing of regular bioliquid	0.3	0.3	0.5	0.5
Co-firing of regular bioliquid with CHP	0.8	0.8	1 **	1 **
Co-firing of relevant energy crops (low range)	0.8	0.8	1	1
Co-firing of relevant energy crops with CHP (low range)	1.3	1.3	1.5	1.5
Conversion (station or unit)	1	1	1	1
Conversion (station or unit) with CHP	1.5	1.5	1.5	1.5
Dedicated biomass	1.5	1.5	1.5	1.4
Dedicated biomass with CHP	2	2	1.9	1.8
Dedicated energy crops	2	2	1.9	1.8
Energy from waste with CHP	1	1	1	1
Geothermal	2	2	1.9	1.8
Geopressure	1	1	1	1
Hydro	0.7	0.7	0.7	0.7
Landfill gas – closed sites	0.2	0.2	0.2	0.2
Landfill gas heat recovery	0.1	0.1	0.1	0.1
Microgeneration	2	2	1.9	1.8
Onshore wind	0.9	0.9	0.9	0.9
Offshore wind	2	2	1.9	1.8
Sewage gas	0.5	0.5	0.5	0.5
Building mounted solar PV	1.7	1.6	1.5	1.4
Ground mounted solar PV	1.6	1.4	1.3	1.2
Standard gasification/pyrolysis	2	2	1.9	1.8
Tidal barrage	2	2	1.9	1.8
Tidal lagoon	2	2	1.9	1.8
Tidal stream ***	5	5	5	5

Band	**Year 13/14 support (ROC/MWh)**	**Year 14/15 support (ROC/MWh)**	**Year 15/16 support (ROC/MWh)**	**Year 16/17 support (ROC/MWh)**
Waves ***	5	5	5	5
*Includes solid and gaseous biomass and energy crops **These support levels are only available in circumstances where support under the RHI is not available *** 5 ROCs subject to 30 MW cap at each generating station. 2 ROCs for any additional capacity added above 30 MW cap. CHP: Combined heat and power; PV: Photovoltaics are; RHI: Renewable heat incentive				

1.4 Energy recovery from waste

The UK has a legally binding target of achieving 15% of its total energy (electricity, heat and transport fuel) from renewables by 2020. EfW has a significant role in all of these energy sectors as seen in Figure 1.9 (REA 2011). Out of the total MSW produced in the UK in 2012 some 16.1% was processed in waste to energy plants. This accounted for some 5% of the country's total Renewable Energy Sources (RES) - an increase in the contribution of made by waste to energy plants of some 300% since 1996. A total of 1739 GWh electricity and heat combined. The total energy produced by bioenergy based technologies and waste treatment operation sites were 12,973 GWh. This represented an increase 620% in energy production these sources compared to 1996 levels. The energy produced from wastes in 2011 was 750 thousand tonnes of oil equivalent (toe). Of these 717,300 toes t was due to the production of electricity from waste – an increase of 928% since 1990. An additional 32,700 toe came from the generation of heat from wastes (DEFRA, 2015).

Over the past decade there has been a rapid increase in the number of EfW plants commissioned in the UK, and there is potential for many more. Waste and Resources Action Programme has compiled a list of all operational EfW plants in the UK, last updated in June 2015 (Wrap.org.uk, 2015). It gives details of 65 plants ranging in capacity from 450 – 2,000,000 tpa with output capacity ranging from 0.6 – 290 MWe. The output of these plants is either in the form of heat or electricity only or Combined Heat and Power (CHP). The feedstock varies and includes waste wood, MSW, tyres, biomass, poultry litter and other animal waste (Wrap.org.uk, 2015).

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Figure 1.9: The UK renewable energy policy framework (Source: REA 2011)

1.5 Aim and objectives of Thesis

It has been established, earlier in this chapter, that thermal treatment plays an essential role in the waste hierarchy and can be used to process trommel fines. It stands in the last position before final disposal enabling organic waste mass reduction with energy recovery (EfW). Among the thermal treatment options, fast pyrolysis offers an effective and sustainable technology to enable conversion of difficult-to-process solid wastes such as trommel fines (<25mm) due to their heterogenous composition thereby diverting such wastes from landfill. Among the different pyrolysis reactors, bubbling fluidised bed reactors can be operated to handle the fast pyrolysis of waste streams with high inorganic contents due to their reliability and ease to operate. Also, they are quite simple to scale-up from lab to commercial plant scale. However, the characteristics of the inert materials such as stones, aggregates and glass, particularly the particle size, brittleness and hardness, need to be considered to minimize the adverse effects on the pyrolysis process and products. The presence of stones, aggregates and glass can result in significant mechanical hardware problems, such as abrasive wear and tear of reactor interiors as well as blocking of moving parts. Hence the main aim and objectives of this research are:

Aim

- **The aim of this research is to investigate the technical and economic feasibility of using fast pyrolysis as a technology for the conversion of MSW trommel fines into renewable energy, thereby producing an inert solid for landfill disposal at**

low landfill tax rates. This research is arguably the first of its kind and aims to present a set of baseline data on the valorisation of trommel fines from MRF.

Objectives

1. To control and modify the characteristics of the trommel fines feedstock to fit with an existing lab scale bubbling fluidised bed fast pyrolysis reactor via appropriate feedstock preparation methods.
2. To investigate the effects of dry and wet physical pre-treatment of trommel fines on the characteristics of trommel fines.
3. To investigate the effect reaction temperature on yields and properties of fast pyrolysis products of dry physically pre-treated trommel fines to identify optimum temperature for highest organic yields.
4. To investigate the effect of feedstock moisture content on yields and properties of fast pyrolysis products of dry physically pre-treated trommel fines at optimum process temperature.
5. To investigate the effect of feedstock dry and wet pre-treatment methods on the yields and properties of fast pyrolysis products at optimum pyrolysis conditions.
6. To identify the feasibility parameters for techno-economic modelling of fast pyrolysis systems operation on the basis of feedstock pre-treatment method.

1.6 Structure of the Thesis

This thesis consists of eight chapters and the structure is described below.

- Chapter one provides an introduction and objectives of the research project. This chapter also outlines the structure of the thesis.
- Chapter two focuses on theory and literature review of previous work done on pyrolysis of municipal solid wastes (MSW) from which trommel fines are derived, sources of ash, ash control methods, fast pyrolysis processing and products, and effect of inorganics on fast pyrolysis.
- Chapter three describes methodology designed for the characterization of the feedstock used during this research, including the specific feedstock preparation procedures. The chapter also describes the fast pyrolysis of trommel fines using a 300 g h^{-1} fluidised bed reactor and accompanying liquid collection system. The problems encountered during the hot commissioning phase of the 300 g h^{-1} fluidised bed reactor to process trommel fines and the modification made to the process are presented and discussed. Details of mass balance calculations are also explained in this chapter, with methodologies for accounting for errors and losses. Product

analysis techniques for fast pyrolysis liquid, solid and gaseous products are also described.

- Chapter four presents and discusses results from the characterisation of the as received and pre-treated trommel fines feedstock.
- Chapter five presents and discusses results from the fast pyrolysis of pre-treated trommel fines, including mass balances. It gives a breakdown of the subsequent studies with varying temperature, moisture content and pre-treatment method.
- Chapter six presents the proposed alternative feeding system and fluidised bed reactor configuration for fast pyrolysis processing of trommel fines.
- Chapter seven presents and discusses the results of the feasibility parameters for dry and wet physically pre-treated trommel fines fast pyrolysis systems operation.
- Chapter eight provides an overall conclusion for the thesis and recommendations for future work relating to the entire research.

2 Literature review

2.1 Introduction

Due to the paucity of published literature on the thermal recovery of trommel fines, this chapter has focused on a review of previous work done on pyrolysis of municipal solid wastes (MSW) from which trommel fines are derived. Trommel fines are not compositionally too dissimilar to MSW, therefore by reviewing the thermochemical behaviour of MSW and its constituents, the link to trommel fines pyrolysis could be made. In particular, it has been important to focus on energy recovery and mass reduction as the important benefits of MSW pyrolysis. Hence a review of the yields and compositions of products of MSW pyrolysis has been undertaken. In addition, the effects of process parameters including pyrolysis temperature, moisture content and MSW component characteristics, particularly the ash content, on the distribution of fast pyrolysis products has been carried out. The technical requirements of the fast pyrolysis process for MSW as a technology for energy-from waste (EfW) are also reviewed. Using this approach, knowledge of the possible factors that are likely to affect the application of fast pyrolysis process on trommel fines may be established with a view to providing the basis for this present study.

2.2 Composition of MSW

Trommel fines are a by-product obtained during the mechanical recycling process of municipal solid waste (MSW) which are usually sent to landfill (refer to section 1.2.1.1). So, the composition of trommel fines thus depends on the initial composition of MSW. However, the composition of MSW varies greatly from place to place to country as well as varying significantly throughout the year. This can have a significant effect on EfW processes and products as well as other waste treatment options. In the UK, there can be a wide variation in MSW depending on how each council separates waste for collection. Most areas now have bins for collections of recycling, food waste, garden waste and residual (black bag) waste; however, there is still a variation in the types of waste accepted under each category (Fitzgerald, 2013; Pitchell, 2014). In this section, a detailed composition of MSW will be presented. This will be achieved by going stepwise into the nature of MSW (main materials) and its key properties. This is essential for improving MSW pre-treatment routes by identifying recycling opportunities, promoting waste abatement efforts or isolating specific fractions (Michaël, 2007; Fitzgerald, 2013; Pitchell, 2014).

Waste composition analysis can establish the type and quantity of materials present in waste, allowing collections and waste treatment technologies to be tailored to suit waste arisings

(Burnley et al., 2007; Dangi et al., 2011; Demirbas, 2011). The Figure 2.1 presents the composition of MSW in England from 2012-2016.

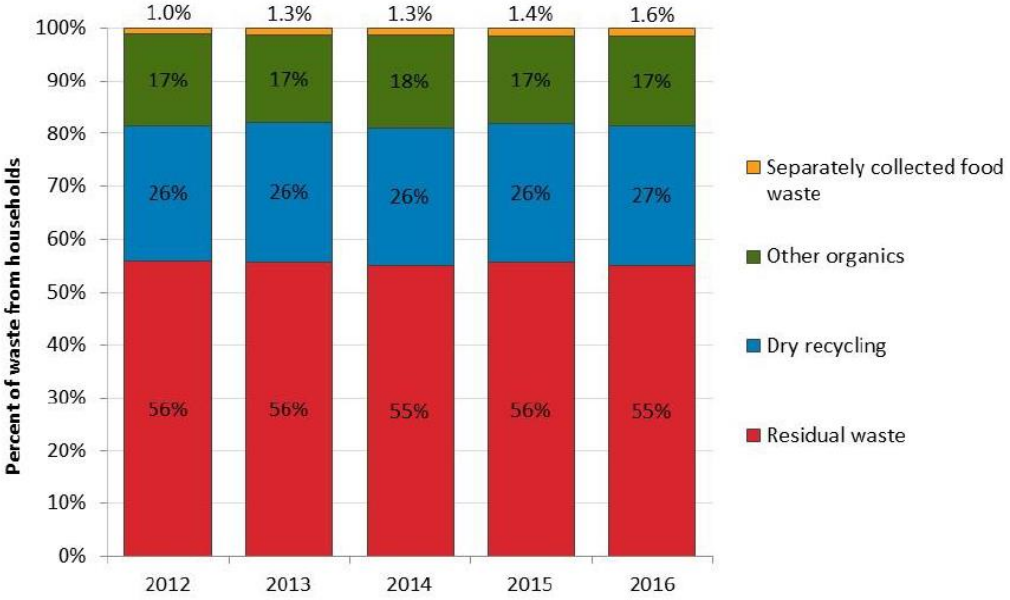


Figure 2.1: Waste composition: waste stream proportions as a percent of total "waste from households" 2012-2016, England (Source: DEFRA, 2017)

Notes

Residual waste includes residual waste from households' regular collections (black bags), bulky waste, and residual from civic amenity centres and rejects from recycling. It excludes waste diverted for recycling from residual waste.

Dry recycling includes paper and card, glass, plastic, waste electrical and electronic equipment (WEEE), scrap metals including those reclaimed from incinerator bottom ash as well as other materials.

Other organics includes green garden waste, mixed garden and food waste, wood for composting and other compostable waste.

According to DEFRA (2017), there is an EU target for the UK to recycle at least 50 per cent of waste generated by households by 2020. The England 'waste from households' figures seen here make a significant contribution to the UK estimates. With an England average national recycling rate of 43.6 % in 2016/17 (DEFRA 2017), Table 2.1 presents the composition of dry recycling portions of household waste and the composition of household waste after recycling sent to landfill in England tabulated from different literatures (Daskalopoulos et al., 1998; Muhle et al., 2010, DEFRA 2010; DEFRA 2015; DEFRA 2017). Despite the very exhaustive work carried out, several percentages of the total house hold waste after recycling sent to landfill remain poorly characterised.

Table 2.1: Composition of household waste dry recycling and after recycling sent to landfill (Source: Daskalopoulos et al., 1998; Muhle et al., 2010, DEFRA 2010; DEFRA 2015; DEFRA 2017)

	Household waste dry recycling (%)	**Household waste after recycling sent to landfill (%)**
Organic material	-	39.6
Paper and Paperboard	38.8	19.2
Plastics	7.9	10.4
Glass/ceramics	19.6	6.8
Metals	16.8	3.7
Textile & Others	17	20.3
Total	100	100

Notes:
Organic material includes green garden waste, mixed garden and food and kitchen waste, wood for composting and other compostable waste.
Metals includes waste electrical and electronic equipment (WEEE) & other scrap metals and incinerator bottom ash (IBA) metals.

According to DEFRA, (2017) the relative proportions of dry recycling over the 5 years from 2012 to 2016 are similar for many items. However, paper and card has seen a gradual decrease over that time. In 2016 these accounted for 5.4% points less of the total than in 2012, due to the gradual decrease in paper usage as a result of more and more organisations are becoming a paperless organisation (DEFRA, 2017), whilst the proportions of plastics and waste electrical and electronic equipment (WEEE) have each increased by 1.7 and 2.0 percentage points respectively in the last couple of years.

There are still opportunities to increase recycling and processing of household waste. In particular, there is need for increased treatment and disposal of non-recyclable household wastes sent to landfill, such as food, kitchen and garden waste, wood. In addition, recyclable material, such as paper, plastics, etc with high calorific values can be used as an energy resource in EfW technologies as they are affected by the UK's Landfill Allowance Trading Scheme. This means that the council must find other ways to dispose of this waste left over after recycling and composting instead of sending it to landfill (DEFRA, 2010). Among the inorganic waste fractions, metals can be recycled while inerts such as sand and glass require special treatment as they can affect the operation of many waste disposal methods including EfW technologies.

EfW technologies based on thermochemical processing methods such as pyrolysis, gasification and incineration rely on the presence of waste components with high calorific values (plastics, paper cardboard etc.). An increase in recycling could lead to lower percentages of these components such as paper, cardboard and plastics in the household waste after recycling sent to landfill, thereby changing the composition of wastes available for thermochemical EfW processes (DEFRA, 2017), which may be the only option capable of reducing their organic loads (measured as loss on ignition) prior to final disposal e.g. via landfills or land application. Therefore, established thermochemical EfW technologies would need to be adaptable to the changes in MSW compositions, extensive following recycling. Alternatively, entirely new technologies would be needed to deal with these new waste types.

Clearly, the household waste after recycling sent to landfill (Table 2.1) is a complex and heterogeneous mixture, made of materials with very different chemical structures and physical properties. However, a further obstacle is appearing: the category often referred to as “others” which includes tire/rubber, some construction/demolition, bulky items and appliances and household hazardous wastes (refer to section 2.2.1.8). This category is far from minute and may represent a significant share of the total biodegradable MSW amount and can therefore create difficulties for waste management handling. A better characterisation of this fraction may yield more optimised treatment.

2.2.1 Main Components of MSW

Each MSW category is made of several fractions which may exhibit significantly different composition and/or properties, the most important being amount and toxicity. Continuing our journey through the structure of MSW and looking further at the details, the next level refers to the different materials found in MSW which are further described in detail below.

2.2.1.1 Paper products

The enormous consumption of paper makes it the major component of the combustible fraction of solid waste, accounting for about 20% of the total household waste after recycling sent to landfill (DEFRA, 2015). It is an appropriate combustible material and has low contents of nitrogen and sulphur. It is a suitable feedstock for waste to-energy utilization (Khongkrapan et al., 2013). Paper is produced by pressing together moist fibres of cellulose pulp derived from wood, rags or grasses, and drying them into flexible sheets. It is a versatile material with many uses, including writing, printing, packaging, cleaning, and many industrial and construction processes. Cellulose is a straight polymer (polysaccharide) made of β-1,4-linked glucose units, i.e. bonds that join two monomers via an oxygen atom which favours hydrogen bonds between glucose units in the polymer but also with the adjacent polymers, building up a strong fibrous structure as seen in Figure 2.2 (Michaël, 2007).

Additional ingredients are sometimes used to change the appearance and properties of the paper products. To mention a few, calcium carbonate is added to paper to produce glossy paper used for magazines, while Kraft paper (brown paper used for packaging) is treated with sodium sulphate. During use, the appearance of paper is changed with the application of ink and dyes to derive the final products such as newspapers magazines, etc., which represent waste paper objects (Michaël, 2007). The chemical composition of ink used for printing magazines, newspapers, etc., vary significantly. The chemical bases of ink are water/petrochemical solvents/oil, further complicating the final composition of used or waste paper. The colourant is either dye or pigmentation (examples: calcium carbonate, titanium oxide, barium sulphate, aluminium hydrate). Various additives (resin, humectant, etc.) to change the ink properties complete the complex chemical makeup of most waste papers found in MSW (Michaël, 2007).

Figure 2.2: Cellulose unit found in paper products (Source: Michaël, 2007)

Evans et al. (1987a, b) reported that pyrolysis (refer to section 2.4.1) of cellulose starts at temperatures as low as 150 °C and at temperatures below 300 °C results in the formation of carbonyl, carboxyl and hydroperoxide groups, elimination of water, production of carbon monoxide and carbon dioxide with a char residue left over. Low temperatures (< 300 °C) will produce low yields of fast pyrolysis organic liquid products. However, at temperatures above 300 °C pyrolysis of cellulose results in yields of liquid products above 80 wt.%. Cellulose decomposes initially to form activated cellulose (Bradbury et al., 1979). Literature studies have shown that, from the formation of activated cellulose two parallel reaction pathways with different main products occur, depolymerisation and fragmentation (ring scission). Depolymerisation produces monomeric anhydrosugars, furans, cyclopentanones and pyrans and other related products while ring scission produces hydroxyacetaldehyde, linear carbonyls, linear alcohols, esters, and other related products (Bradbury et al., 1979; Lin et al., 2009; Zhu et al., 2010).

Zhou et al. (2013) investigated the pyrolysis of printing paper and cardboard during pyrolysis between 400 °C and 600 °C in a fixed bed reactor to simulate real fixed bed gasifier conditions. For both type of waste char and oil yields decreased with increasing temperature from 400 °C to 600 °C, while syngas yields increased. Cardboard pyrolysis produced a higher tar yield and a lower char yield than printing paper and the maximum tar yield from printing paper was around 400 °C. The gas produced consisted of CO_2, CO, H_2, CH_4 and other light hydrocarbons (C_2-C_4) and their concentration was dependent on the process temperature. The major oil components were phenolics, benzenes, naphthalenes, benzofurans and cyclopentens. Aliphatic compounds occupied a quite small fraction of the oil. Similar results were reported by various other literature for pyrolysis of different type of waste paper (Li et al., 2005; Yang et al., 2007; Korkmaz et al., 2009; Biswal et al., 2013; Haydary et al., 2013; Sarkar and Chowdhury, 2014; Zhang et al., 2014; Chattopadhyay et al., 2016; Zheng et al.,2017). This extensive study could be very useful in predicting the behaviour of paper waste during pyrolysis.

2.2.1.2 Yard trimmings and wood (biomass residues)

Yard trimmings are made up of biomass residues (organic matter used as a fuel) of various sorts which include grass, leaves and woody materials (stem, branch, etc.) as well as wastes like pallets or demolition wood make up about 22% of the total organic fraction found in household waste after recycling sent to landfill (DEFRA, 2015). There is limited literature on pyrolysis of yard trimmings or garden waste, because there are mainly converted into compost, which is a reasonable solution to the problem of disposal. However, this process needs both a long time period and controlled conditions to result in a good quality fertilizer. Due to increase in garden waste and limited available area for composting, there is a need to propose a faster method to treat this type of garbage. (DEFRA, 2015). In this case pyrolysis could be considered. Hedman et al. (2005) warn against the uncontrolled burning of garden waste, due to alarmingly high emissions of dibenzodioxins, dibenzofurans and polychlorinated biphenyls. Some literature studies investigated the pyrolysis of leaves (Biswal et al. 2013; Jutakridsada et al. 2016), branches (Lievens et al., 2015; Lui et al., 2015), bark (Garcìa-Pérez et al., 2007) and grass (Kelkar et al., 2014; Mehmood et al., 2017), but usually only certain species. Despite this it can be assumed that garden waste will behave like other types of biomass (wood, paper etc.) during pyrolysis.

The main components of general biomass are cellulose, hemicellulose and lignin (Table 2.2). As presented in section 2.2.1.1 about paper, cellulose is a linear polymer of glucose units; hemicellulose is also a polymer of sugar units (mannose, galactose, 4-O-methyl-D glucuronic acid, xylose or arabinose) however, it is shorter than cellulose (only 50-200 units) and branched. Hemicellulose is therefore more of a family of compounds and an example, arabinoxylan, is presented in Figure 2.3. Literature studies have shown that the primary hemicellulose components are glucomannans and xylan which when pyrolysed form varying yields of char and depolymerisation products. Glucomannans produce similar pyrolytic products to cellulose, as the glycosidic bonds are cleaved and able to form a stable monomeric anhydrosugars. Xylan however, follows an alternative pyrolytic dehydration pathway which results in an increased char formation (Shen and Bridgwater, 2010; Shen et al., 2010; Zhu et al., 2010).

The third main component, of biomass, lignin, is a complex aromatic polymer and the most common monomers with a high degree of cross-linking as presented in Figure 2.4. This leads to a very strong three-dimensional structure apparently random and unorganised and explains why lignin is not as degradable as cellulose and hemicellulose and why its valorisation is currently an active field of research. Garcia-Perez et al. (2008) reported that lignin when pyrolysed produces high char yields and low liquid yields compared to both cellulose and hemicellulose. The liquid product has three specific groups, large molecular oligomers which account for most of the liquid product and the other two groups are monomeric phenolic compounds and light compounds such as acetic acid (Oasmaa et al., 2003; Garcia-Perez et al., 2008).

Finally, extractives and ash make up about 1 - 5 wt.% dry basis of the biomass/wood matter. Extractives are natural products extraneous to a lignocellulose cell wall. Extractives are of two main sources (FPL 1979): compounds directly involved in the metabolism of the plant, and secondary products, which have undergone further chemical modification by non-metabolic processes or from external sources. This fraction is extremely diverse and includes (not exhaustive): aromatic compounds, simple sugars, free amino acids, proteins, free fatty acids, resin (carboxylic) acids, chlorophyll, alkaloids etc. (Stenseng, 2001). Certain extractives are common to many different plants, while others are characteristic of a family, or even a species. Extracts may positively influence the properties of the wood. For example, extractives can protect wood from degradation (anti-microbial and anti-fungal activity), add colour and odour to wood, and improve strength properties. However, extractives can cause problems in papermaking (resin acids); contribute to corrosion of metals in contact with wood; present health hazards and affect colour stability of wood to light (Stenseng, 2001).

Table 2.2: Typical composition of biomass/wood (% dry matter) (Source: Gronli, 1996; Stenseng, 2001)

	Spruce (Gronli 1996) (wt%)	**Pine (Gronli 1996) (wt%)**	**Wood (Stenseng 2001) (wt%)**
Cellulose	43.1	40.9	40-45
Hemicellulose	26.5	25.7	20-30
Lignin	28.4	28.6	20-30
Extractives	2.0	4.8	1-5 (up to 30) [a]
[a] - for some tropical species.			

Figure 2.3: A hemicellulose example – arabinoxylan (Source: Michaël, 2007)

Figure 2.4: Most common monomers of lignin ("monolignols") - (a): p-coumaryl alcohol; (b): coniferyl alcohol (predominant lignin monomer in softwoods); (c): sinapyl alcohol (Source: Michaël, 2007).

2.2.1.3 Food waste

Any substance consumed to provide nutritional support for an organism is regarded as food. Food waste make up about 60% of the total organic fraction found in household waste after recycling sent to landfill (DEFRA, 2015). Food waste tend to reduce the heating value of the liquid product from pyrolysis process and increases the moisture in the liquid products (Zhao et al. 2011). They are usually of plant or animal origin, and contain essential nutrients, such as proteins which are polymers of amino acids, fat (fatty acids, i.e. carboxylic acids), carbohydrates (biological macromolecules used in the storage and transport of energy, they include mono-, di-, oligo- and polysaccharides) water, fibre (polysaccharides like cellulose or lignin), vitamins and minerals/inorganic matter (Ca, P, Fe, Na, K, Cu, Zn, Mg, Mn).

The various proportions of the components are depending greatly on the food item and a complete overview of the values is impossible (Michaël, 2007; Lin et al., 2013). However, food waste can be divided into several groups as follows: organic crop residues, catering waste and derivatives (including used cooking oils), animal by-products and mixed domestic food waste (Lin et al., 2013). Three representative examples are briefly presented here:

- ***Bone composition***: Made up of 65 to 70% of inorganic substances. Most of this inorganic substance is a sole compound called hydroxyapatite, i.e. $Ca_{10}(PO_4)_6(OH)_2$. About 30 to 35% of bone is composed of organic material (on a dry weight basis). Of this amount nearly 95 % is a substance called collagen. Collagen is a fibrous protein found in connective tissue in animals made up of amino acid with rather unusual high levels of glycine, praline, hydroxyproline and hydroxylysine. The remaining organic fraction includes substances such as are chondroitin sulphate, keratin sulphate, and phospholipids (Samuel 1985).
- ***Meat composition (muscle)***: Mostly made of muscle with components such as: water (about 75%), protein (about 20%), fat (about 5%), and ash/minerals (about 1%) such as Ca, P, Na, K, S (main elements) and Fe, Cu, Zn, Mn, Al, Si and Mg (Samuel 1985).
- ***Legume composition (potato)***: A raw potato is made of about 80% water. The rest is mostly carbohydrates (about 20%, including so-called “fibre”), followed by proteins, lipids, minerals (Fe, Ca, Mg, P, K, Na) and vitamins (Samuel 1985).

2.2.1.4 Plastics

Plastic make up about 10% of the total household waste after recycling sent to landfill (Table 2.1) (DEFRA, 2015) and as most plastics are not biodegradable, and their deposition in landfills is not a desirable solution from an environmental standpoint. Plastics are materials consisting of any of a wide range of synthetic or semi-synthetic organic compounds obtained by polymerization reactions and can be moulded into solid objects. Depending on their properties, plastics can be used for various applications from films for food packaging to bulletproof vests (Kevlar). In biodegradable MSW the largest fractions are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate(PET) and polyvinylchloride (PVC) (López et al., 2011).

The contents of plastic waste vary with the region and the season (Wu et al., 2014) and there is also a lot of controversy about the pyrolysis of these wastes, due to the release of toxic and greenhouse gases (Paradela et al., 2009; Wu et al., 2014). Paradela et al. (2009) reported that only very high temperatures (> 700 °C) can prevent the release of dioxins and furans from plastics, but this requires huge quantities of energy. However, Sharuddin et al. (2016) concluded that pyrolysis has great potential to convert plastic waste to valuable, energy-bearing liquid oil, gas and char. Therefore, it is one of the best solutions for plastic waste conversion and it is also economical in terms of operation. The flexibility that it provides in terms of desired products can be achieved by changing operating parameters accordingly. Figures 2.5 – 2.9 present the structures of some plastics commonly found in MSW: (Michaël, 2007).

Figure 2.5: Polyethylene (PE) (Source Michaël, 2007)

Figure 2.6: Polystyrene (PS) (Source Michaël, 2007)

Figure 2.7: Polyvinyl chloride (PVC) (Source Michaël, 2007)

Figure 2.8: Polyamides (PA, general reaction) (Source Michaël, 2007)

Figure 2.9: Polyester (Source Michaël, 2007)

2.2.1.5 Glass

Glass make up about 7% of household waste after recycling sent to landfill (Table 2.1) (DEFRA, 2015). Glass is a non-crystalline amorphous solid that is often transparent and has widespread practical, technological, and decorative usage in, for example, glass containers which make up most of the glass fraction contained in the biodegradable MSW. Other examples include window panes, tableware, and optoelectronics. Soda-lime glass represents 90% of the produced glass and contains 60-75% of silica (SiO_2), and the additional components are sodium (or potassium carbonate) Na_2CO_3 (12-18%) and calcium oxide CaO (5-12%). Other ingredients are often added to change glass properties. The most common are lead oxide at least 20%, which are also called crystal or boric oxide. Coloured glass is obtained by adding metals or metal oxides in concentrations usually lower than 2-3% (Douglas et al., 1972; Pfaender, 1996).

During pyrolysis the glass particle could end up in the reactor bed and or char pot. They can contribute to secondary cracking in the pyrolysis vapours which results in increased reaction water yields and decreased organic yields in bio-oil (Philpot, 1970; Sekiguchi, and Shafizadeh, 1984; Czernik, Johnson, and Black, 1994; Agblevor, and Besler, 1996; Diebold, and Czernik, 1997; Miskolczi, Ateş, and Borsodi, 2013) (refer to section 2.6.4).

2.2.1.6 Metals

Metals make up about 4% of household waste after recycling sent to landfill (Table 2.1) (DEFRA, 2015). According to Tchobanoglous et al. (2002) and DEFRA (2015); ferrous metals represent more than 50% of the total metal products found in MSW. The other important metal is aluminium (cans, foils, etc.). Another class of metals that is particularly interesting as it is (considered) highly toxic are the so-called heavy metals. Heavy metals, as defined by the EU Directive 67/548/EEC, are antimony (Sb), arsenic (As), cadmium (Cd), chrome (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), tellurium (Te), thallium (Tl), tin (Sn) and their compounds (oxides, chlorides, etc). Also included are manganese (Mn) and zinc (Zn).

Heavy metals are often trace compounds but pose serious issues as their biological, ecological and human toxicity are very serious. The relative concentrations of heavy metals vary very much as they reflect the very different MSW compositions and definitions, thus very little consistency is found. Heavy metals can be found in all MSW fractions at various concentrations and are therefore difficult to sort out before MSW treatment. Identification of major sources are important such as the MSW fractions (or individual items) containing the highest concentrations of heavy metals and the MSW fractions contributing the most to the total amount of heavy metals. However, there is little agreement in the literature, due to the inconsistency of the MSW data quality (Sørum 2000; Jung 2006).

Based on literature findings some types of plastic packaging contain high levels of heavy metals (Sb, Cr) and according to most sources, are heavy contributors to the total output of several heavy metals (Sørum 2000; Liou 2003; Jung 2006). Glass may contain significant amounts of metals or metal oxides as colour additives (refer to section 2.2.1.5). Paper products do not contribute vastly to the total amount of heavy metals, even though pigments or coatings may contain (heavy) metal compounds (Sørum 2000); virgin biomass and food scraps do not contain high levels of heavy metals, but demolition wood is often contaminated by heavy metals found in treatment additives. Textiles and rubber (refer to section 2.2.1.7 and 2.2.1.8 respectively) are not major contributors. However, the “others” contains some items with high concentrations of heavy metals such as electronic appliances, paint pigments and batteries for example (refer to section 2.2.1.8).

2.2.1.7 Textile

Textile waste is considered as one of the fastest growing sectors in terms of household waste (Mather, 2014), and they make up about 18% of the total ‘Textile & Others’ fraction found in household waste after recycling sent to landfill (DEFRA, 2015). Textiles are flexible materials consisting of a network of natural or artificial fibres (yarn or thread). They are used in clothing, carpets, towels, tents, flags, industrial filters, etc. Textiles can be of animal origin such as wool, silk or cashmere, and of vegetal origin such as cotton, hemp, flax or linen, or of synthetic origin like acrylic, Nylon, polyester or Lycra (Reed and Williams, 2004; Michaël, 2007; Yang et al., 2007).

Wool is a natural protein fibre and it is composed of keratin-type protein. Cotton is a polysaccharide, a polymer of sugars like wood. Cotton is almost exclusively made of pure cellulose (refer to section 2.2.1.1), while acrylic fibres (or polyacrylonitrile) are a synthetic polymer of acrylonitrile used as a cheap alternative to natural fibres (Reed and Williams, 2004; Yang et al., 2007). There is lack of comprehensive analysis and limited literature on pyrolysis of textile waste and reported studies have mainly focused on char production (Reed and Williams, 2004; Yang et al., 2007; Nahil and Williams; 2010; Chowdhury and Sarkar, 2012; Barısçı and Öncel, 2014; Mather, 2014; Balcik-Canbolat et al., 2017).

Reed and Williams, (2004) investigated the pyrolysis of five samples of natural fibres: hemp, flax, jute, coir and abaca, in a fixed bed reactor for their potential to produce activated carbon from pyrolytic char by physical activation. The five samples of natural fibres consist mainly of cellulose (about 60%) and hemicellulose (about 12 wt% to 20 wt%) and smaller amounts of lignin, except coir, which contains more lignin (41–45 wt%) and less cellulose (36–43 wt%). The highest product yield obtained was the liquid, which was composed of a hydrocarbon liquid with high water content. The char yield varied between 24.6 wt% from jute and 34.4 wt% from coir. The gas yield did not exceed 30 wt%, and its composition was dominated by CO, CO_2, H_2, CH_4 and C_2H_6 with minor concentrations of other hydrocarbon gases up to C_4. Similar results were reported by Yang et al. (2007) (pyrolysis of textiles), Nahil and Williams (2010) (pyrolysis of acrylic textile fabric) and Chowdhury and Sarkar, (2012) (pyrolysis of Indian textile waste composed mainly of cotton). This composition is typical for pyrogas obtained from biomass.

2.2.1.8 Others

2.2.1.8.1 Tyres/rubber

Tyres are made of synthetic rubber and the increasing number of motor vehicles complicates the handling of used tyres. Rubber represent about 4% of the total ‘Textile & Others’ fraction found in household waste after recycling sent to landfill and they, consist of polymers of the organic compound isoprene, with minor impurities of other organic compounds, plus water. They are variety of monomers (or mixture of monomers), often with additives depending on the applications. Common monomers are presented in Figure 2.10.

Figure 2.10: A - Isoprene; B – butadiene; C – methylpropene. (Source: Loadman, 2012)

2.2.1.8.2 Construction/demolition

Sometimes mixed with MSW depending on the collecting system. They make up about 17% of the total ‘Textile & Others’ fraction found in household waste after recycling sent to landfill and are mostly made of bricks, stones (minerals), metals, wood wastes, plastics, fibreboard, textiles, concrete (mineral aggregates, generally gravel and sand, and water), asphalt (produced from petroleum products), soil, cardboard, steel and hazardous wastes among others. Heavy metals may also be present (paint, treated wood) (Tchobanoglous 2002).

2.2.1.8.3 Bulky items and appliances

Bulky item and appliances make up about 15% of the total ‘Textile & Other’ fraction found in household waste after recycling sent to landfill (DEFRA, 2015) and they are mostly made up of durable goods such as computers, washing machines, furniture, etc. They are very complex manufactured items which contains almost all the fractions of MSW previously discussed in the sections above. Thus, their thermal degradation pathway depends on the type and composition of each item which can be made up of a combination of different fractions of MSW.

2.2.1.8.4 Household Hazardous Wastes (HHW)

HHW are a highly toxic family of compounds and they make up about 1% of the total ‘Textile & Other’ fraction found in household waste after recycling sent to landfill and are mainly composed of paint (latex and oil), pesticides, cleaners, solvents, HHW containers (50% of total HHW), household and car batteries and automobile oil (DEFRA, 2015).

Paint is composed of a binder (the film itself), a diluent (to adjust the viscosity) and additives. Typical binders include (synthetic or natural) resins such as acrylics, polyurethanes, polyesters, oils, or latex. Typical diluents include organic solvents such as alcohols, ketones, esters, glycol ethers or water. Typical additives include pigments, dyes, catalysts, thickeners and stabilisers. Chemical pesticides (herbicides, fungicides, insecticides, etc) are chemical compounds used to fight any type of pest attacking human food or propagating diseases (Michaël, 2007).

2.2.2 Characterization of MSW and its components (glass and metal not included)

The average proximate, elemental analyses and calorific value of MSW and their components are of interest because fast pyrolysis process (refer to section 2.4.1) is affected by the characteristics of the feedstock (Miskolczi et al. 2013). For example, the moisture content of the feedstock is a major parameter that influences the product water (refer to section 2.7.4) and composition of the liquid product (Miskolczi et al. 2013). Also, the volatile matter content of the feedstock will influence the product yields of any pyrolysis process (Zhou et al. 2013) and the ash content may impact side reactions and act as a catalyst for unwanted reactions that impact negatively on oil product quality and yields (Bernardo et al., 2010; Yuan et al., 2014; Gao et al., 2016a; Gao et al., 2016b).

To present a complete picture of the different fractions of MSW, a literature survey covering a very large number of products from all the MSW fractions was conducted. The data collected from this literature search is presented in the subsequent sections regarding proximate, elemental analyses and calorific value of MSW.

2.2.2.1 Proximate analysis

Table 2.3 shows the tabulated results of the proximate analysis of MSW and its components. This literature search highlights the heterogeneous nature of all the MSW fractions. However, even though the data are quite spread, this literature search show that the organic fraction of MSW (biomass residues and food scraps) have relatively high moisture content (10-40 wt.% in biomass, 4-80 wt.% in food waste). Volatile mater (dry basis) is high at about 60-80 wt.%, while the ash fraction rarely exceeds 10 wt.% except for some cases (bone, biomass husks). The level of fixed carbon is (by difference) about 10-20 wt.%. Paper has a volatile mater above 70 wt.% and low ash content (less than 5 wt.%), except glossy, recycled and coated paper which exhibit high ash content (25-30 wt.%). Plastics have above 90 wt.% volatile matter and no ash or moisture. The ‘Other’ fraction (tyres etc.) have a volatile mater at about 30-70 wt.%, ash content about 3-13 wt.% and level of fixed carbon about 11-30 wt.%. The MSW samples have a relatively high moisture content (3-60 wt.%), and the volatile matter varies between 30-80 wt.%. The ash content also varies between 9-40 wt.%, while the level of fixed carbon is about 4-14 wt.% (Werther et al. 2000; Sørum et al. 2001; Patumsawad et al. 2002; Michaël, 2007).

Table 2.3: Proximate analysis of MSW and its components

Sample	VM $^{a,\ c}$	FC $^{b,\ c}$	Ash ^{c}	Moisture ^{c}	Reference
PAPER (wt.%)					
Newspaper	88.5	10.5	1	ND	Sørum et al. 2001
Cardboard	84.7	6.9	8.4	ND	Sørum et al. 2001
Recycled paper	73.6	6.2	20.2	ND	Sørum et al. 2001
Glossy paper	67.3	4.7	28	ND	Sørum et al. 2001
Paper and card	76-81	8-12	2-5	5-10	Michaël, 2007
Cartons	90.9	4.5	1.2	3.4	Michaël, 2007
Newspaper	85.9	10.7	3.5	ND	Michaël, 2007
Glossy paper	70.6	4.5	24.8	ND	Michaël, 2007
BIOMASS (wt.%)					
Palm fibre	46.3	12	5.3	36.4	Saenger et al. 2001
Wood chips	82	ND	0.5	40.8	Lyngfel et al. 1999
Wood chips	81.13	8.52	3.86	6.49	Michaël, 2007
Manure	40.4	10.5	42.3	6.8	Annamalai et al. 2003
Manure dry	50.2	ND	40.4	ND	Annamalai et al. 2003
Wheat straw	66.3	21.4	13.7	ND	Demirbas, 2004
Beech wood	82.5	17	0.5	ND	Demirbas, 2004
Oak wood	77.6	21.9	0.5	ND	Demirbas, 2004
Cotton refuse	81	12.4	6.6	ND	Demirbas, 2004
Sunflower husk	69.1	19.9	1.9	9.1	Werther et al. 2000
Palm fibre	46.3	12	5.3	36.4	Werther et al. 2000
Coconut shell	70.5	22	3.1	4.4	Werther et al. 2000
Malt waste	67.4	15.5	6	11.1	Winter et al. 1999
Straw	65.4	19.7	6.8	8.1	Winter et al. 1999
Wood	67.9	11.3	0.8	20	Michaël, 2007
FOOD (wt.%)					
Rape seed	81.7	7.9	5.5	4.9	Onay et al. 2001
Food waste	17.1	3.5	1.1	78.3	Michaël, 2007
Fried fats	97.6	2.4	0	0	Michaël, 2007
Bone meal A	58.2	11.4	25.9	4.5	Michaël, 2007
Soy proteins	84.3	11.7	4	ND	Michaël, 2007
PLASTICS (wt.%)					
Polyethylene	100	0	0	1.1	Ndaji et al. 1999
Polystyrene	99	1	0	ND	Courtemanche et al. 1998
Polypropylene	100	0	0	ND	Courtemanche et al. 1998
PMMA	100	0	0	ND	Courtemanche et al. 1998
PVC	91	9	1	ND	Courtemanche et al. 1998
HDPE	100	0	0	ND	Sørum et al. 2001
LDPE	100	0	0	ND	Sørum et al. 2001
PVC	94.8	4.8	0.4	ND	Sørum et al. 2001
OTHER (wt.%)					

Sample	**VM** [a, c]	**FC** [b, c]	**Ash** [c]	**Moisture** [c]	**Reference**
Waste tyre	67.3	28.5	3.7	0.5	Kim et al. 1994
Scrape tyre	61.9	29.5	8	0.7	González et al. 2001
Tyre	52.3	21.7	13.7	ND	Courtemanche et al. 1998
Leather	75.3	11.8	12.9	ND	Michaël, 2007
MSW (wt.%)					
RDF	73.4	8.9	17.7	3.2	Zevenhoven et al. 1999
MSW UK (db)	63	4	32.2	32.43	Patumsawad et al. 2002
MSW K-L	31.36	4.37	9.26	55.01	Patumsawad et al. 2002
RDF-A	76.2	13.6	10.2	3.7	Guilin et al. 2000
RDF-B	72.5	3.9	12.5	11.1	Guilin et al. 2000
[a] VM – Volatile matter; [b] FC – Fixed carbon; [c] dry basis; ND – Not detected					

2.2.2.2 Elemental analysis and calorific values

Table 2.4 shows the tabulated results of the elemental analysis and calorific from all the MSW and its components. This literature search show that the organic fraction of MSW (biomass residues and food scraps) have an elemental composition (dry ash free basis) of 20-50 wt.% C; 20-45 wt.% O; 3-11 wt.% H; 0.2-5 wt.% N; 0.1- 0.9 wt.% S/Cl with calorific value of 9-20 MJ kg^{-1}. Paper has an element composition (dry ash free basis) of 30-50 wt.% C; 40-65 wt.% O; 4-6 wt.% H; 0.08-0.2 wt.% N; 0.02- 0.2 wt.% S/Cl with calorific value of 9-20 MJ kg^{-1}. The elemental composition (dry ash free basis) of plastics was proposed to be 30-86 wt.% C; 0.1-35 wt.% O; 4-14 wt.% H; 0.05-12 wt.% N; 0.02- 0.3 wt.% S/Cl with calorific value of 20-47 MJ kg^{-1} (Werther et al. 2000; Sørum et al. 2001; Patumsawad et al. 2002; Michaël, 2007).

The ‘Other’ fraction (tyres etc.) have an elemental composition (dry ash free basis) of 50-87 wt.% C; 1-28 wt.% O; 4-8 wt.% H; 0.4-10 wt.% N; 1- 2 wt.% S/Cl with calorific value of 8-37 MJ kg^{-1}. The elemental MSW composition was proposed to be (dry ash free basis): 25-60 wt.% C; 12-40 wt.% O; 2-12 wt.% H; 0.2-2 wt.% N; 0.1- 0.2 wt.% S; 0.1-0.2 wt.% Cl with 0.1-0.4 wt.% S/Cl with calorific value of 7-22 MJ kg^{-1}. The differences observed can be attributed, not only to statistical differences but also consumption habits and the different “definitions” of MSW (household waste or inclusion of industrial and commercial wastes) (Sørum et al. 2001; Patumsawad et al. 2002; Michaël, 2007).

Table 2.4: Elemental analysis and calorific values of MSW fractions

Sample	**C** [a, g]	**H** [b, g]	**O** [c, g]	**N** [d, g]	**S/CL** [e, f, g]	**HHV (MJ kg^{-1})** [g]	**Reference**
PAPER (wt.%)							
Newspaper	52.1	5.9	41.86	0.11	0.03	19.3	Sørum et al. 2001
Cardboard	48.6	6.2	44.96	0.11	0.13	16.9	Sørum et al. 2001
Glossy paper	45.6	4.8	49.41	0.14	0.05	10.4	Sørum et al. 2001
Newspaper	44.7	5.8	49.4	0.1	<0.02	ND	Michaël, 2007
Glossy paper	31.5	4	64.4	0.08	<0.02	ND	Michaël, 2007
BIOMASS (wt.%)							
Palm fibre	51.5	6.6	40.1	1.5	0.3	ND	Saenger et al. 2001
Wood chips	50.6	6.3	43	0.14	ND	ND	Lyngfel et al. 1999
Wood chips	48.9	10.61	40.13	0.21	0.15	ND	Michaël, 2007
Manure	29.9	3.57	20.3	2.3	0.9	9.65	Annamalai et al. 2003
Manure dry	29.6	3.35	23.3	2.55	0.81	13.4	Annamalai et al. 2003
Wheat straw	41.8	5.5	35.5	0.7	ND / 1.5	ND	Demirbas, 2004
Beech wood	49.5	6.2	41.2	0.4	ND	ND	Demirbas, 2004
Sunflower husk	51.4	5	43	0.6	0	ND	Werther et al. 2000
Palm fibre	51.5	6.6	40.1	1.5	0.3	ND	Werther et al. 2000
Coconut shell	51.2	5.6	43.1	0	0.1	ND	Werther et al. 2000
Malt waste	47.98	6.64	40.01	4.99	0.38	ND	Winter et al. 1999
Straw	49.04	5.65	44.82	0.43	0.06	ND	Winter et al. 1999
Wood	47.6	6.4	45.3	0.2	0.2	19.6	Michaël, 2007
FOOD (wt.%)							
Rape seed	62.1	9.1	24.9	3.9	ND	ND	Onay et al. 2001
Bone meal A	52.68	6.78	27.03	11.08	0.34/0.5	ND	Michaël, 2007
Soy proteins	52.24	7.43	25.04	14.73	0.56	ND	Michaël, 2007
Fat	76.23	12.12	11.55	0	0.019	39.56	Michaël, 2007
PLASTICS (wt.%)							
Polyethylene	85.7	13.9	0	0	0	ND	Ndaji et al. 1999
Polystyrene	92	8	0	0	0.04	44.5	Courtemanche et al. 1998
Polypropylene	86	14	0	0	0	43.4	Courtemanche et al. 1998

Sample	**C [a, g]**	**H [b, g]**	**O [c, g]**	**N [d, g]**	**S/CL [e, f, g]**	**HHV (MJ kg^{-1}) [g]**	**Reference**
PMMA	60	8	32	0	0	25.8	Courtemanche et al. 1998
PVC	38	5	0	0	0/57	19.2	Courtemanche et al. 1998
HDPE	86.1	13	0.9	ND	ND	46.4	Sørum et al. 2001
LDPE	85.7	14.2	0.05	0.05	0	46.6	Sørum et al. 2001
PVC	41.4	5.3	5.83	0.04	0.03/47.7	22.8	Sørum et al. 2001
PET	62	4.2	33.2	0.1	0.3	ND	Michaël, 2007
Polyamide	62.4	9.8	15.7	12	0.1	ND	Michaël, 2007
OTHER (wt.%)							
Waste tyre	83.8	7.6	3.1	0.4	1.4	8.5	Kim et al. 1994
Scrape tyre	86.7	8.1	1.3	0.4	1.4	36.2	González et al. 2001
Tyre	71.9	4.7	7	1.36	1.6	29.1	Courtemanche et al. 1998
Leather	53.01	7.74	27.75	9.94	1.56	ND	Michaël, 2007
MSW (wt.%)							
RDF	48.4	7	25.2	0.84	0.12	19.1	Zevenhoven et al. 1999
MSW UK (db)	35.81	4.82	24.43	0.78	0.41	ND	Patumsawad et al. 2002
MSW K-L	46.11	6.86	28.12	0.23	ND	17.1	Patumsawad et al. 2002
RDF-A	46.6	6.8	34.51	1.28	0.13	20.64	Guilin et al. 2000
RDF-B	41.7	5	36.3	0.75	ND	18.39	Guilin et al. 2000
MSW	58	8	38	0.5	0.3	ND	Rogaume et al. 2002
Typical MSW	25	3	20	0.5	ND	ND	Ruth et al. 1998
MSW	15-30	2-5	12-24	0.2-1	ND	7-14	Michaël, 2007
MSW	42.4	6.1	35.1	2.2	ND	17.2	Michaël, 2007
MSW	35	11.7	30.2	ND	ND	ND	Tchobanoglous 2002

[a] C – Carbon; [b] H – Hydrogen; [c] O – Oxygen; [d] N – Nitrogen; [e] S – Sulphur; [f] CL – Chlorine; [g] dry basis; ND – Not detected

2.2.2.3 Composition of MSW ash

Solids are inevitably discharged from thermal process and these solids include metals together with carbon. Larger particles of solids in the thermal treatment reactor (pyrolysis) are usually discharged as bottom ash and slag. Lighter solids are usually collected when the gas is separated with the use of cyclones and filters. In addition, volatile metals such as lead, tin, cadmium and mercury will be carried in the gas until such point that the gas is cooled for them to be sufficiently condensed (DEFRA 2007; 2013).

The composition of MSW varies over time and from country to country, due to the differences in lifestyle and waste recycling processes of a country thus, the ash content will vary too. Generally, the chemical and physical characterization of ash will depend on the compositions of the raw MSW, the operational conditions, the type of pyrolysis process and air pollution control system design (He et al., 2004). The ash composition is important as they impact side reactions and act as a catalyst for unwanted reactions that impact negatively on oil product quality and yields (Bernardo et al., 2010; Yuan et al., 2013; Gao et al., 2016a; Gao et al., 2016b).

The chemical composition of ash shows that the inorganic fraction of MSW (bottom ash and fly ash) is mainly made of oxides of silica (Si), calcium (Ca), iron (Fe), sodium (Na), aluminium (Al), magnesium (Mg) and potassium (K). The average composition of ash may vary greatly (see Tables 2-5 – 2-11 for tabulated composition) with the changing nature of MSW and the process conditions. For unsorted (or partly sorted) MSW, the concentrations of Fe and Al species may be significantly increased. Furthermore, trace metals (heavy metals) are present and represent about 1% of the total ash material. Despite the very exhaustive work carried out, several fractions of the MSW ash composition remain poorly characterised (Bernardo et al., 2010; Yuan et al., 2013; Gao et al., 2016a; Gao et al., 2016b).

Table 2.5: Oxide compositions in MSW fly ash (FA)

Type	FA (a) (wt. %)	FA (b) (wt. %)	FA (c) (wt. %)	FA (d) (wt. %)	FA (e) (wt. %)	FA (f) (wt. %)	FA (g) (wt. %)	FA (h) (wt. %)
SiO_2	18.8	11.47	19.4	13.6	18.5	20.5	6.35	27.52
Al_2O_3	12.7	5.75	10.1	0.92	7.37	5.8	3.5	11
CaO	24.3	29.34	19.7	45.42	37.5	35.8	43.05	16.6
Fe_2O_3	1.6	1.29	1.8	3.83	2.26	3.2	0.63	5.04
MgO	2.6	3.02	2.8	3.16	2.74	2.1	1.38	3.14
K_2O	4.3	7.02	8.1	3.85	2.03	4	4.59	8.24
Na_2O	5.8	8.7	8.9	4.16	2.93	3.7	5.8	
SO_3	6.4	N/A	N/A	5.18	14.4	N/A	4.64	8.34
P_2O_5	2.7	1.69	N/A	N/A	1.56	N/A	N/A	N/A
TiO_2	1.5	0.85	1.9	3.12	1.56	N/A	N/A	1.88

Note: (a) Alba et al., 1997; (b) Romero et al., 2001; (c) Cheng et al., 2004; (d) Pan et al., 2008; (e) Andreola et al., 2008; (f) Haiying et al., 2007; (g) Gines et al., 2009; (h) Yang et al., 2009

Table 2.6: Oxide compositions MSW bottom ash (BA) and MSW incineration ash (MSWI)

Type	BA (150-200 mesh) (a) (wt. %)	MSWI ash (b) (wt. %)	MSWI ash (c) (wt. %)	MSWI ash (d) (wt. %)	BA (e) (wt. %)	BA (f) (wt. %)	BA (g) (wt. %)
SiO_2	27.8	29.4	12.01	5.44	13.44	46.7	49.38
Al_2O_3	9.9	18	8.1	3.1	1.26	6.86	6.58
CaO	25.9	27.2	13.86	42.55	50.39	26.3	14.68
Fe_2O_3	4	13.3	1.21	1.69	8.84	4.69	8.38
MgO	3.3	1.6	2.65	1.83	2.26	2.22	2.32
K_2O	1.8	0.9	7.41	4.31	1.78	0.888	1.41
Na_2O	3.3	3.6	17.19	4.82	12.66	4.62	7.78
SO_3	N/A	N/A	N/A	12.73	0.5	2.18	0.57
P_2O_5	6.9	N/A	N/A	1.62	N/A	0.855	N/A
TiO_2	2	N/A	N/A	0.92	2.36	0.77	N/A

Note: (a) Gupta et al., 2005; (b) Shih et al., 2003; (c) Michaël, 2007; (d) Qian et al., 2006; (e) Pan et al., 2008; (f) Andreola et al., 2008; (g) Gines et al., 2009

Table 2.7: Heavy metals found MSW fly ash (FA)

Type	FA (a) (mg kg^{-1})	FA (b) (mg kg^{-1})	FA (c) (mg kg^{-1})	FA (d) (mg kg^{-1})	FA (e) (mg kg^{-1})
Ag	31-95	ND-700	N/A	N/A	N/A
As	31-95	15-751	N/A	93	N/A
Ba	920-1800	88-9001	N/A	4300	539
Cd	250-450	4-2211	25.5	470	95
Co	29-69	2.3-1671	N/A	N/A	14
Cr	140-530	21-1901	118	863	72
Cu	860-1400	187-2381	313	1300	570
Hg	0.8-7	0.9-73	52	N/A	N/A
Mn	0.8-1.7	171-8500	N/A	1600	309
Ni	95-240	Oct-70	60.8	124	22
Pb	7400-19000	200-2600	1496	10900	2000
Se	6.1-31	0.48-16	N/A	41	N/A
Zn	19000-41000	2800-152000	4386	25800	6288
Sn	1400-19000	N/A	N/A	N/A	N/A
Sr	80-250	N/A	N/A	433	151
V	32-150	N/A	N/A	37	N/A
Note: (a) Hjelmar, 1996; (b) WRMUTI, 2000; (c) Youcai et al., 2002; (d) Chang et al., 2008; (e) Wu et al. 2006					

Table 2.8: Heavy metals found in MSW bottom ash (BA)

Type	BA (a) (mg kg^{-1})	BA (b) (mg kg^{-1})	BA (c) (mg kg^{-1})	BA (c) (mg kg^{-1})	BA (d) (mg kg^{-1})
Ag	4.1-14	0-38	8.5-10.7	N/A	N/A
As	19-80	1.3-45	209-227	160	13
Ba	900-2700	47-2000	1104-1166	N/A	N/A
Cd	1.4-40	0.3-61	6.8-7.8	110	3
Co	<10-40	22-706	49.6-53.1	N/A	N/A
Cr	230-600	13-1400	323-439	260	900
Cu	900-4800	80-10700	4139-4474	N/A	500
Hg	<0.01-3	0.003-2	N/A	N/A	2.6
Mn	<0.7-1.7	50-3100	869-894	N/A	280
Ni	60-190	9-430	216-242	N/A	180
Pb	1300-5400	98-6500	2474-2807	N/A	2700
Se	0.6-8	ND-3.4	230-265	130	N/A
Zn	1800-6200	200-12400	4261-4535	N/A	600
Sn	<100-1300	N/A	N/A	840	960
Sr	170-350	N/A	N/A	N/A	N/A
V	36-90	N/A	N/A	N/A	N/A
Note: (a) Hjelmar, 1996; (b) WRMUTI, 2000; (c) Michaël, 2007; (d) Forteza et al., 2004					

Table 2.9: Chloride Content of MSW fly ash (FA)

Type	Chloride content (mg kg^{-1})	Reference
Fly ash	5749	Pan et al., 2008
Fly ash	8670	Andreola et al., 2008
Fly ash	45000-100000	Hjelmar, 1996
Fly ash	19000-210000	Michaël, 2007
Fly ash	120000-200000	Qian et al., 2006
Fly ash	131000	Ferreira et al., 2003
Fly ash	83800	Gines et al., 2009
Fly ash	103200	Yang et al., 2009
Fly ash	215000	Wu et al. 2006

Table 2.10: Chloride Content of MSW bottom ash (BA).

Type	Chloride content (mg kg^{-1})	Reference
Bottom ash	2876	Pan et al., 2008
Bottom ash	149500	Michaël, 2007
Bottom ash	201100	Qian et al., 2006
Bottom ash	2300	Forteza et al., 2004
Bottom ash	1760	Andreola et al., 2008

Table 2.11: Loss on Ignition of MSW incinerator fly ash (FA) and bottom ash (BA)

Type	Loss on ignition (wt. %)	Reference
Fly ash	4.3	Hjelmar, 1996
Fly ash	9.73	Pan et al., 2008
Fly ash	13.36	Yang et al., 2009
Bottom ash	3.24	Pan et al., 2008
Bottom ash	4.59	Michaël, 2007

2.3 Ash control

There are a number of methods that can be used to control the ash content in MSW. Ash control can be used to limit MSW ash content during pre-treatment (sample preparation) or can be used to reduce the total MSW ash content after processing such as leaching. Each method for controlling ash content has its own advantages and disadvantages.

2.3.1 Physical

Literature has shown that grinding of feedstock can be used as a pre-treatment to open up the structure and overcome natural resistance to chemical, biological or thermal degradation (Mani et al., 2004) and thus can be applied to trommel fines to prepare it for fast pyrolysis process. However, it is very important that the sample is not ground any more than required as there is a minimum particle size that can be processed in certain fast pyrolysis rigs (refer to chapter 3) due to blockages. Literature studies have also shown that grinding of feedstock to a suitable size fraction for fast pyrolysis results reduces the ash content (Zwart et al., 2006; Bridgeman et al., 2007) therefore, to achieve a lower ash content feedstock particle smaller than 0.25 mm should be removed. In this study particles below 0.25 mm have shown to have higher ash content compared to larger particle fractions (refer to chapter 4). Another physical pre-treatment is separation of inorganics such as glass, stones, metals etc., as they contribute to the ash content.

2.3.2 Washing

Different approaches have been used to pre-treat feedstock including with water (Jenkins et al., 1996; Davidsson et al., 2002; Harmsen et al., 2005 Tan et al., 2009; Mayer et al., 2012). This process is aimed at reducing the chlorine, salts, alkali and heavy metal and thus can be applied to trommel fines to prepare them for fast pyrolysis process. To improve the efficiency of washing pre-treatments a suitable feedstock size fraction is required (refer to Section 2.3.1); due to an increased surface area is required for efficient washing techniques.

Water washings remove most of soluble alkali metals and are more efficient when the wash is agitated. Water washes have been shown to be efficient in potassium, sodium and chlorine removal (Jenkins et al., 1996), also around 90% of alkali metals in biomass is present in water soluble form (Baxter et al., 1998). Curie et al., 2003 reported that up to 72.8% of Ca, Na, K and Cl were removed at 10:1 liquid/solid ratio and about 12.3% removal was achieved for Cr. Alkali metal cations have been reduced in a higher quantity using this method than compared to alkali earth metals; this is expected due to the difference in solubility (Fahmi et al., 2007). Some of the ash content in MSW is due to soil contamination a small proportion of phosphorus can be expected to be removed even though it tends to be insoluble (Fahmi et al., 2007). This is beneficial to the pyrolysis process as phosphate compounds are known to promote char formation and are used for this purpose in fire retardant materials (Stevens et al., 2006; Gaan et al., 2007). Water washing are more suited to high ash content biomass, as biomass with lower ash contents (woody biomass) have a higher concentration of alkali metals bound to the organic structure which limits the effect of water washing. Water washing could be a feasible alternative. However, one drawback is that a large amount of heavy metal will be released with the soluble salts (Raven et al., 1983). For the recovery of heavy metal, the most significant factor is the control of pH followed by the liquid-to-solid ratio (Delhaize et al., 1995).

Davidsson et al., 2002 studied release of alkali compounds from untreated and washed biomass samples in a nitrogen atmosphere at two temperature ranges, one being 200 – 500 °C which can be associated to a pyrolysis process. They showed that water washing, and acid washes have a limited effect on alkali metal removal from biomass. By using a water wash alkali emission was reduced by 5 - 30%, acid washing reduced the alkali emission by 70% (Davidsson et al., 2002). Harmsen et al., 2005 reported that strong acid washes (e.g. hydrochloric acid) decrease the amount of hemicellulose and cellulose in biomass due to hydrolysis (the chemical breakdown of a compound due to reaction with water), therefore increasing the ratio of lignin. This leads to lower yields of bio-oil and increased char and gas yields, while weaker acid washes (e.g. acetic acid) can either partially or fully hydrolyse hemicellulose. Weaker acid washes have little or no effect on cellulose content but do not decrease metal ion content as much as a strong acid wash. Strong acid washes completely hydrolyse hemicellulose and cellulose increasing porosity of the biomass due to their removal and weak acids only partially hydrolyse hemicellulose therefore the porosity is not increased as much. Similar findings have reported by other literature (Park et al., 2005; Tan et al., 2009; Shen et al., 2010; Mayer et al., 2012). Complete alkali removal by water or acid washing was not possible. Although acid washing has high efficiency, it is neither economical nor environmentally friendly.

Chemical additives such as surfactants can be added to the washing solution to aid in ash reduction. Surfactants are widely used in numerous commercial and industrial products, including detergents, emulsifiers, wetting agents and dispersants (Ying et al., 2002). They are compounds that lower surface tension between two liquids or between a liquid and a solid. Coulson et al. (2009) studied the addition of a surfactant (wetting agent) to water to try and improve ash removal. They found that the surfactant sped up the wetting of biomass by swelling the capillaries by twice their original size permitting the water to pass quicker through the smaller diameter capillaries, allowing water to wash the entirety of the biomass reducing the ash content considerably. These smaller capillaries may not have been washed without a surfactant present in the solution. As the capillaries were swelled it reduced the water retention, resulting in less water being held by the biomass (Coulson et al., 2009).

The main reason for adding a surfactant to the washing solution is to aid in inorganic material removal from biomass, therefore anything else removed from the biomass is detrimental to the washing procedure. Jamur et al. (2010) reported that a disadvantage of using surfactants is that they are non-selective and may allow for extraction of lipids as well as proteins Jamur et al. (2010). However, surfactant added to a water wash is still a very useful technique as it helps to increase the efficiency of ash removal and should be considered when examining the economic merit due to less water being retained by biomass; therefore, reducing drying requirements.

There are two main problems with washing, the first being that the biomass has to be dried so that the moisture content is below 10% due to fast pyrolysis requirements (refer to Section 2.4). Secondly if the biomass is acid washed the acid must be separated and recovered or disposed, which increases the operation costs of pre-treatment. Acid washed biomass must be rewashed with deionised water to remove certain ions remaining from the acid, such as chlorine ions from a hydrochloric acid wash. If chlorine ions were to remain in pre-treated biomass it can lead to negative effects on bio-oil yields and quality, due to catalytic cracking of the pyrolysis vapours. This increases the water supply demand which can increase operation costs dramatically.

2.3.3 Feedstock blending

Adapting the idea of blending biomass with coal for power stations, different varieties of waste could be blended together to achieve desirable ash contents. For example, if a 30% ash content waste is blended with a 10% ash content waste, the overall mixture of waste will have an ash content that falls within these percentages. This could result in reduced washing requirements (refer to Section 2.3.2) as only a certain proportion of waste would have to be washed and when dried could be blended with unwashed waste to decrease the overall ash content. There are a number of biomass varieties that can be blended (Vassilev et al., 2010) such as woody biomass, herbaceous and agricultural biomass, animal and human waste and contaminated biomass (Table 2.12).

Table 2.12: Waste varieties and examples

Waste groups	**Examples**
Woody waste	Soft or hard, branches, foliage, bark, chips, pellets, sawdust, other
Herbaceous and agricultural waste	Grasses, straws, residues (fruits, shells, grains, seeds, bagasse, fodder), others
Animal and human waste	Meat-bone meal, chicken litter, manures, others
Contaminated waste	Sewage sludge, paper pulp, waste paper, chip board, ply wood, others
Biomass mixtures	Blend from above varieties

2.3.4 Thermal

Torrefaction is a thermal process to convert waste such as MSW into a coal-like material (refer to section 2.4), which has better fuel characteristics than the original waste. Literature studies has shown that torrefaction can be used to control the ash content in a feedstock (Uslu et al., 2008; Van der Stelt et al., 2011; Basu, 2013; Nordin et al., 2013; Bilgic et al., 2015). Torrefied feedstock is more brittle, making grinding easier and less energy intensive. Therefore, the feedstock is easier to pelletize resulting in less ash content, easier storage and transportation. The process is generally conducted at temperatures ranging between 200 °C and 350 °C (Nordin et al., 2013) and operated at ambient pressure with an inert atmosphere to avoid oxidation and combustion of the feedstock (Van der Stelt et al., 2011). The torrefaction process is initiated by moisture evaporation, followed by partial devolatilization. The residence time can vary from a few minutes to several hours. The char, which is the major product, has a substantially higher energy density than the feedstock. Depending on the processing temperature, torrefaction can be classified as light (below 240 °C) and severe (above 270 °C) torrefaction (Bilgic et al., 2015). The advantages of torrefaction are the increase in energy density, improved grindability, reduced moisture content, and decreased susceptibility to microbial degradation. The resulting char can be utilized as high-quality fuel in various applications including cofiring in power plants, entrained flow gasification, and small-scale combustion facilities (Uslu et al., 2008). The char can also be used as a water purification adsorbent and for in situ soil remediation purposes (Basu, 2013).

Literature studies on torrefaction of MSW are few when compared with literature on pyrolysis. Research have mainly been conducted to investigate the physical and chemical properties of torrefied MSW (Poudel et al., 2015; Yuan et al., 2015; Yu et al., 2016). The types of materials used as feedstock include food waste (FW), PVC plastic, discarded tyres, and wood residues. Anta et al. (2003); Yu et al. (2016) and Gao et al. (2016) studied the behaviour of organic and inorganic pollutants in the torrefaction process when waste materials are used as feedstock. Generally, heavy metals with high boiling points (e.g., Pb and Zn) tended to be retained in the chars, whereas those with low boiling points such as Hg tended to enter the gas phase. Gao et al. (2016) reported that volatilization of heavy metals in torrefaction was suppressed at slow heating rates. However, organic pollutants such as dioxins and dioxin-like compounds were mainly retained in the chars, with minor amounts found in the volatile fractions.

2.3.5 Leaching process

This process is used to extract the heavy metals from ashes and to further recover them from the leachant solutions. To recover the heavy metals, their concentration must be high to ensure recovery and the leaching of heavy metals depends on the type of extraction solvent, the pH, as well as the liquid-to-solid ratio (Goldberg, 1988; Mizutani, 1996; Ferreir et al., 2002).

Youcai et al. (2002) reported that an increase in pH in the leaching solution will lower the leachability of heavy metals as insoluble hydroxides will form at higher pH, and further suggested that using Ethylenediaminetetraacetic acid (EDTA) could be an effective agent for extracting heavy metals (Youcai et al., 2002). Different leaching agents were evaluated for municipal solid waste incineration (MSWI) fly ash leaching, in which it was concluded that using strong mineral acid results in high leaching of many elements; organic acids were not effective as leaching agents for metals; EDTA showed good removal of some metals like Cu and Pb; NH_4NO_3 was effective for Cu removal. Water washing pre-treatment followed by bioleaching for heavy metal extraction from MSWI fly ash was demonstrated by Wang et al. (2009), and this green technology may be regarded as an alternative to conventional physicochemical methods for heavy metals removal in fly ash (Wang et al., 2009). Leaching is a good practice for promoting the use of MSWI fly ash as well as recovering the metals for re-use (Karlfeldt et al., 2010).

Zhang et al. (2006) investigated the temperature effect on metal extraction using a hydrothermal process. The MSW ash was pre-treated by water washing and this effectively extracted 67% of Na, 76% of K and 48% of Ca. Then the ash was treated by acid under hydrothermal conditions. Hydrothermal treatment accelerated the dissolution of the ash and promoted the reaction of acid with toxic metals such as Cr, Cd, and Pb. Zhang et al. (2006) reported that the behaviour of metals in ash followed hydrothermal leaching and hydrothermal precipitation under hydrothermal conditions. The optimum conditions suggested used hydrochloric acid with 10:1 liquid/solid ratio under 150 °C for five hours. Under hydrothermal conditions, the acid reacted with all metals in the ash while preferentially reacting with Ca at ambient conditions (Zhang et al., 2006).

2.4 Energy from waste (EfW) technologies for MSW

EfW technologies are thermochemical conversion process that use heat to treat waste materials such as MSW mainly include combustion, gasification, pyrolysis, and torrefaction and thus can be applicable to trommel fines. These processes are generally characterized by high temperatures (>300 °C) and fast conversion rates. Figure 2.11 shows the major differences between combustion, gasification, pyrolysis, and torrefaction in terms of operating conditions and conversion products. According to the literature, combustion is performed with excess oxygen, with heat and/or power as the main output (Yin, 2012; Basu, 2013). While gasification, pyrolysis, and torrefaction are all performed in the absence of oxygen or with significantly less oxygen than what is required for complete combustion (Yin, 2012; Basu, 2013). The operating conditions (e.g., temperature, heating rate, and oxygen supply) and the yield of products (gas, oil/condensable, and char) varies between these three processes. The fast heating rates and moderate temperatures of pyrolysis favour the generation of liquid products. The low temperatures and long residence times of torrefaction primarily yield chars, and the high temperatures and heating rates of gasification mainly generate gas products (condensable and non-condensable gases). However, gasification, pyrolysis, and torrefaction cannot be defined as completely separated processes because, for instance, pyrolysis can be considered as an incomplete gasification process and torrefaction as an initial stage of gasification and pyrolysis (Yin, 2012; Basu, 2013).

Figure 2.11: Comparison of combustion, gasification, pyrolysis, and torrefaction, with major products illustrated (Source: Yin, 2012)

The advantages of gasification, pyrolysis, and torrefaction of MSW over traditional MSW combustion are mainly related to the increased energy efficiency, generation of value-added products, and improved pollution control (Klinghoffer, 2013). The intermediate products from gasification, pyrolysis, and torrefaction may be suitable for a wide range of applications, from high-quality fuels to fine chemicals. The low operating temperatures compared to those in MSW combustion can also potentially reduce the risk of alkali volatilization, fouling, slagging, and bed agglomeration (Arena, 2012). Furthermore, thermochemical conversion systems for gasification and pyrolysis are commonly equipped with product cooling and collection units, which may enable improved control of emissions of organic and inorganic pollutants (Young, 2010).

Despite the advantages in energy and material recovery, gasification and pyrolysis of MSW remains a subject of debate because of the potential negative environmental impact. Similar to combustion based processes, trace amounts of inorganic and organic pollutants (e.g., heavy metals and dioxins) could be formed and emitted into the air, soil, and water bodies. The characteristics and distribution of these pollutants are highly dependent on the operating conditions and technologies used, which will not be discussed in this section. Only pyrolysis will be reviewed in this section as it is the primary process used in this research with more focus on fast pyrolysis (Young, 2010; Arena, 2012; Yin, 2012; Basu, 2013; Klinghoffer, 2013).

2.4.1 Pyrolysis

As described above pyrolysis is the thermochemical degradation of organic material at high temperature, in the absence of oxygen or in an atmosphere of inert gases. Compared to incineration, pyrolysis has a lower process temperature (~500 °C), lower emissions of air pollutants and the scale of pyrolysis plants is more flexible than incineration plants (Wyrzykowska-Ceradini et al., 2011; Chen et al., 2014). Pyrolysis provides an opportunity of transforming materials of low-energy density into bio-fuels of high-energy density, at the same time recovering high value chemicals (Chowdhury et al., 2012; Biswal et al., 2013). The benefits of this process are that different type of organic matter can be used such as wood, organic waste (soft and hard biomass) residues from agriculture, forestry, pulping industry. Some examples are forest residues (Oasmaa et al., 2003; Azeez et al., 2010; Faccini et al., 2013; Michailof et al., 2014), food (Mahmood et al., 2013; Moraes et al., 2012) and agricultural waste (Duman et al., 2011; Moraes et al., 2012). The fractions of MSW subjected to pyrolysis mainly consist of paper, cloth, plastics, food waste and yard waste. Nowadays, pyrolysis is getting attention for its flexibility to generate a combination of solid, liquid and gaseous products in different proportions just by the variation of operating parameters such as temperature or heating rate. The successful application of pyrolysis is the appropriate choice of input materials and the setting of optimal process conditions. For these reasons, the suitability or unsuitability of selected types of waste and their mixtures for the pyrolysis process has been verified many times by laboratory experiments with subsequent assessment of the quantity and quality of the individual products of pyrolysis (Grycová et al., 2016).

Depending on the operating conditions, pyrolysis can be conducted in the fast (i.e., in seconds) (the primary focus of this study), intermediate (i.e., in minutes) or slow mode (i.e., at moderate temperatures for hours). They differ in process temperature, heating rate, solid residence time, feedstock particle size, etc. However, relative distribution of products is dependent on pyrolysis type and pyrolysis operating parameters as shown in Table 2.13 (Balat et al. 2009).

Table 2.13: Comparison between the different processes of pyrolysis and product yields (Source: Balat et al. 2009)

By comparing the product yield distribution, fast pyrolysis is the preferred technique for obtaining high yields of liquid products (bio-oil). Depending on the feedstock used it produces 60%–75% of oily products (oil and other liquids) with 15%–25% of solids (mainly biochar) and 10%–20% of gaseous phase which can be used within the process to provide the process heat requirements so there are no waste streams other than flue gas and ash. The bio-oil is viscous, acidic, and thermally unstable and contains a high amount of oxygenated compounds (Bridgwater 1999, 2000). Advances in current pyrolysis techniques are aimed at producing bio-oil of high quality so that it can replace or supplement the current fossil fuel usage. The fast pyrolysis process of feed to liquid may be defined as a two-stage process defined by significant changes in temperatures. The first stage involves heating the feed to pyrolysis temperature and the second stage involves rapid quenching of the formed vapours (Bridgwater 1999, 2000). The following features have been reported by literature studies to be essential for fast pyrolysis. They are discussed in detail below as they are considered during this research.

2.4.1.1 High heating rates

Literature studies agreed on high heating rates (>100 °C per second) as a requirement of the fast pyrolysis process mainly to minimise char formation (Samolada et al., 1994 and Lédé et al., 2007). High heating rates are essential to the fast pyrolysis process. The heat transfer to the biomass particle is mainly through conduction and convection depending on reactor configuration. Convection happens mostly between any hot fluidising gas and the biomass particle while conduction occurs between the heat transfer medium and the biomass particle.

The high heating rate during the fast pyrolysis process in fluidised beds (like the one used during this study) is made more efficient via the 3 methods discussed below.

Preheated fluidising gas

The fluidising gas used for the fast pyrolysis process is sometimes pre-heated to reduce the temperature gradient that would be caused by a cold stream of gas entering a reactor operating at pyrolysis temperatures of 400 ºC and above.

Fluidising medium

In fluidised bed systems, the process is not started until the fluidising medium is at pyrolysis temperature and this is mainly to ensure that the high heating rate required by the process is achievable.

Small biomass particles

The liquid yield of the process is due to the release of volatiles caused by thermal degradation. The thermal conductivity of biomass particles is relatively low and to ensure complete devolatisation of the particles in minimal time, the particle sizes are kept to a minimum as bigger particle would reduce the heating rates and increase residence times.

2.4.1.2 Optimum reaction temperature

Literature studies have reported that the optimum fast pyrolysis process temperature for maximum oil yield to be in the region of 500-600 ºC for several types of biomass (Samolada et al., 1994; Piskorz et al., 1998; Bridgwater, 1999; Bridgwater & Peacocke, 2000; Uzun et al., 2006; Buah et al. 2007; Pattiya et al., 2008; Zheng et al., 2008; Azeez et al., 2010; Heo et al.,2010; Velghe et al. 2011; Zhou et al. 2013; Chen et al. 2014; Ding et al. 2016). This temperature is important for achieving high oil yields. Temperatures significantly higher than this range results in the extended cracking of pyrolysis vapours. Samolada et al., 1994 concluded that process temperature is the parameter that significantly affects the yields of pyrolysis products. It is essential that during any design and operation considerations, the ability of the system to reach and maintain this temperature range is achieved.

2.4.1.3 Short vapour residence time

The composition and quality of the liquid product is impacted by the time taken between the formation and quenching of the fast pyrolysis vapours. High temperatures promote vapour cracking and the longer the vapours are exposed to high temperature, the greater the extent to which cracking will occur. Vapour residence times <2 seconds are known to be the optimum for high liquid yields from fast pyrolysis. Longer residence times are known to impact negatively on organic liquid yields due to cracking reactions (Peacocke, 1994; Hague et al., 1998; Bridgwater & Peacocke, 2000).

2.4.1.4 Char and ash removal

Char is a by-product of the pyrolysis process and it contributes to secondary cracking in the vapours from the degrading biomass particles (Di Blasi, 2008). This is because it contains metals from the original biomass feedstock that catalyse cracking reactions. Char is also known to promote instability in the cooled liquid as it accelerates polymerisation which increases the viscosity of the oil product (Jones, 2006). Almost all the ash produced in the process is retained in the char. The removal of char from the process is therefore important to maintain a high product quality. In many fluidised bed systems as is the case in the primary unit used in this research, char is removed by a cyclone although the use of hot vapour filtration is also gaining popularity (Agblevor and Besler 1996; Bridgwater & Peacocke, 2000).

2.4.1.5 Rapid vapour quenching

Liquid product collection is the second key stage of the fast pyrolysis process. Quenching to the liquid product is usually achieved through vapour contact with a liquid which is immiscible with the bio-oil. Bridgewater reports that though the method is effective, careful considerations need to be given to design parameters and temperature control to avoid differential condensation of heavy ends. Light ends collection is also important to reduce oil viscosity. (Bridgwater 1999; Bridgwater et al., 1999; Bridgwater & Peacocke, 2000).

2.5 Fast pyrolysis reactors for bio-oil production

The reactor is the central component when considering an entire fast pyrolysis system. Since it is the key component, many reactors have been developed to improve upon old methods and create proprietary technology. The reactor type being used for the fast pyrolysis of waste for bio-oil production must be given great importance because of the large amount of heat to be transferred across the reactor wall to ensure material degradation. There are a number of fast pyrolysis reactors that are used or have been developed which include bubbling fluidised bed reactors, circulating fluidised bed reactors ablative reactor, and rotating cone, (Bridgwater et al. 2000; Scott et al. 1999; Bridgwater 2003; Mohan et al. 2006; Bridgwater, 2011).

There are also other fast pyrolysis reactor concepts that have been researched and these include using vacuum pressure to quickly remove pyrolysis vapours, entraining biomass in a flow of hot gas, screw and augur kiln move biomass through a hot reactor rather than using fluids, fixed bed pyrolysis reactors, microwave pyrolysis reactors and drop tube reactors.

These reactors typically either have low liquid yields or are complicated, but they have had some commercialization efforts and are reviewed by Bridgwater et al., 2002; Bridgwater, 2011; Hulet et al.,2005; Mohan et al. 2006; Bridgwater, 2007, and among others.

However, these reactors will not be reviewed here. Only the bubbling fluidised bed reactors will be reviewed in this section as it is the primary reactor used in this research. Refer to recent pyrolysis reviews by Mohan et al. (2006), Bridgwater, (2007), Bridgwater, (2011) and Czajczynska et al., (2017) for comparisons of reactor technologies, and Bridgwater & Peacocke, (2000) and Czajczynska et al., (2017) for a particularly in-depth review of many fast pyrolysis reactor technologies and configurations.

2.5.1 Bubbling fluidised bed reactors

The oldest and well-understood is the bubbling fluidised bed reactor (BFB) or more simply fluidised bed as shown in Figure 2.12 (Bridgwater, 2007). Biomass fast pyrolysis originated at the University of Waterloo in the 1980s. A shallow fluidised bed concept for thermal processing was used for the systems. Bridgewater, 2000 reports that the University of Waterloo can be credited with laying the foundation of modern fast pyrolysis. Research from the University of Waterloo is regarded as the most extensively published and publicised (Robinson, 2000). The success of the Waterloo fast pyrolysis system led to the development of other fluidised bed units that operate on the same principle. Similar units have been built at universities and research centres across the world including NREL, University of Stuttgart, Technical Research Centre, Finland and Aston University (Piskorz et al., 1998). The systems vary in sizes and capacity from 0.1-7 kg/h units. Four of the fast pyrolysis units including the 150 g/h, the 300 g/h (used for the primary objective of this research), the 1 kg/h and the 7 kg/h units at the European Bioenergy Research Institute (EBRI) in Aston University operate on the principle of the Waterloo system.

Fluidised bed reactors are currently used in commercial production of bio-oil and extensively used in academic research. They are the most popular choice of reactor due to their reliability, good reaction zone temperature control, high heat transfer from bed material, short hot vapour residence time (below 2 seconds) and ease to operate. They are quite simple to scale up from lab to commercial plant scale. Fluidised-bed reactors are characterized by a high heating rate and good blending of the feedstock. Therefore, such reactors are widely used in laboratory studies in order to describe the influence of temperature and residence time on pyrolysis behaviour and products. (Williams and Williams, 1999a; Dai et al., 2001a, b; Mastral et al., 2002, 2003). This type of reactor seems to be a good solution for waste pyrolysis.

The heat transfer material inside a bubbling fluidised bed reactor is often silica sand supported by a perforated distributor plate within a cylinder which provides a constant temperature distribution within the bed. Silica sand is a very efficient heat transfer material due to its high solid density. An inert fluidizing gas is forced through the plate causing the bed media to fluidize. The high gas flow rate also shortens the vapor residence time and allows for efficient char/vapor separation by means of a cyclone. The bubbling fluidised bed has high heat transfer rates and is simple to construct and operate (Bridgwater, 1999; Mohan et al., 2006). Bio-oil yields between 70 –75 wt.% are often achieved with woody biomass. Scaling up the fluidised bed is well understood. Heat transfer limitations due to low bed height-to-diameter ratios cause temperature gradients and prevent scale-up past a point. Low thermal efficiencies in the fluidised bed reactor are due to the cooling and reheating of the re-circulated gas stream (Scott et al., 1999).

Figure 2.12: Bubbling fluidised bed reactor schematics (Source: Scott et al., 1999)

Feedstocks used in a bubbling fluidised bed reactor must be prepared to a certain specification. The particle size of the feedstock must be between 0.25 - 3.00 mm and have been dried to below 10% moisture content (Bridgwater & Peacock 2000). Although fluidised-bed reactors have been extensively adopted in laboratory studies, their industrial application is not common for MSW pyrolysis talk less of trommel fines. The reason is that the separation of bed material from coke, along with its external heating and recirculation, is complicated. However, Dong et al. (2016) proved, that it is possible to obtain high quality pyrolytic oil from MSW in a fluidised bed reactor. As for its application to trommel fines pyrolysis, in addition to the problems of bed material separation, trommel fines pre-treatment (the primary objective of this research) needs to be dealt with thoroughly, as they are expensive steps.

2.6 Fast pyrolysis system

There are several parts to a complete fast pyrolysis system (refer to Figure 2.12), starting with receiving and storage of the feedstock. Next is feedstock preparation for fast pyrolysis processing. Fast pyrolysis processing includes reactor configuration, char separation and liquid collection. Fast pyrolysis vapours can then be upgraded. This section describes briefly each stage of a fast pyrolysis system except for the reactor configuration which has been previously described in section 2.5.1.

2.6.1 Reception and storage

This usually consist of simply a concrete slab low capacity system (3 t h^{-1}), which is covered to ensure that the feedstock does not become wetter due to rain therefore increasing drying requirements. Higher capacity systems will use a number of systems for reception and storage such as weighbridge, tipping units, conveyors, bunker storage and reclamation (Bridgwater and Peacocke, 2000).

2.6.2 Feed drying

Drying is usually essential as all feed water ends up in the liquid products (Bridgwater 1999; Bridgwater and Peacocke, 2000). The use of low grade process heat can be used to dry feed biomass, such as char combustion or flue gases from combustion of product gas.

2.6.3 Feed particle size reduction

Different feed particle sizes can be used depending on the pyrolysis reactor type (refer to Section 2.5). The feedstock particle size must be small enough so that rapid heating and heat transfer can occur to achieve optimal liquid yields.

- less than 3 mm for a fluidised bed reactor (refer to chapter refer to section 2.5.1)

Literature studies have shown that to achieve the high heating rates and low residence times required for complete thermal degradation in fast pyrolysis, smaller feedstock particles are essential to the fast pyrolysis process because reduced particle size in general resulted in increasing heating rate and consequently higher yield of the liquid product. (Bilbao et al., 1994; Diebold and Bridgwater, 1994; Di Blasi, 1996; Kumar and Kolar, 2006; Luo et al., 2010). This study has also shown that grinding of the feedstock to a suitable size fraction for fast pyrolysis can result in reduced ash content (refer to Section 4.1.1).

2.6.4 Char and ash separation

Most of the ash in the feedstock is retained in char, therefore efficient char removal results in successful ash removal. Char as a by-product of the fast pyrolysis process contributes to secondary cracking in the vapours from the degrading feedstock particles (Philpot, 1970; Sekiguchi, and Shafizadeh, 1984; Czernik, Johnson, and Black, 1994; Agblevor, and Besler, 1996; Diebold, and Czernik, 1997; Miskolczi, Ateş, and Borsodi, 2013), which results in increased reaction water yields and decreased organic yields in bio-oil. Due to these secondary cracking reactions rapid and complete char separation is desired and can be achieved by using a single cyclone unit or a number of cyclones in series.

2.6.5 Liquid collection

The gaseous products from fast pyrolysis consist of aerosols, true vapours and non-condensable gases (ref). These require rapid cooling to minimise secondary reactions and condense the true vapours, while the aerosols require additional coalescence or agglomeration. (Peacocke and Bridgwater, 2004; Bridgwater, 2011). The collection of liquids from a fast pyrolysis unit typically uses a quench column and an electrostatic precipitator (ESP), which is the preferred method at both laboratory and commercial scale units. The vapour product has a low partial pressure of condensable products due to the large volumes of fluidising gas, and this is an important design consideration in liquid collection. An electrostatic precipitator is very effective in recovering the aerosols from the gaseous stream (Bridgwater, 2011).

2.6.6 Improving pyrolysis technology

As pyrolysis technologies improve and the quest for suitable alternative and renewable energy sources continues fast pyrolysis will play a big role in waste management and the handling of trommel fines. Generally, there are two methods that can be used to improve the final quality of the bio-oil produced from fast pyrolysis. The first is to improve the quality of the feedstock prior to the fast pyrolysis processing. This can be achieved by adequate pre-treatment of the feedstock prior to pyrolysis (the primary aim of this research, refer to Chapter 3 and 4). The second option is to upgrade the final product, which can be achieved in different ways – physically, chemically and by introducing a catalyst to fast pyrolysis process to crack the vapour. These methods have been extensively reviewed by Bridgwater 1994; Czernik and Bridgwater, 2004; Zang et al., 2006; and Bridgwater, 2011.

2.7 Factors influencing MSW pyrolysis product yield and quality

In the UK, the waste is often not segregated, and waste materials are often not collected separately according to their criteria. MSW consists mainly of paper, cloth material, yard waste (including fallen leaves and branches, etc.), food wastes, plastics and a small amount of leather and rubber, metals, glass, ceramic, earthen materials and miscellaneous other materials. Due to the complexity of MSW, most research has studied the pyrolysis of single components such as paper, plastics, fabric, lignocellulosic materials and putrescible (Di Blasi, 1996; Wu et al., 2002, 2003; Wu et al., 2005; Zheng et al., 2008, 2009; Luo et al., 2010; Ates et al., 2013; Miskolczi et al., 2013), refuse-derived fuel (RDF) pellets (Cozzani et al., 1995; Garcia et al., 1995a,b; Lin et al., 1999; Buah et al., 2007; Dou et al., 2007; Grammelis et al., 2009; Bosmans et al., 2013) in laboratory scale experiments and the sample pyrolyzed is usually specially prepared (dried and ground into very small particles) and then thoroughly mixed to unify the composition. It is relatively easy to see what happens during the pyrolysis of a small homogeneous sample of material under laboratory conditions. However, the components do not act independently during fast pyrolysis. The interactions between the different individual fractions of MSW and the pyrolysis products have also been explored by Williams and Williams, (1997); Williams and Williams, (1999b); Sørum et al., (2001); Grieco and Baldi, (2012); Ding et al., (2016), but not as extensively.

The composition and quality of products from the fast pyrolysis of MSW using real samples or co pyrolysis of mixed waste samples is one of the best ways of providing information for possible factors that might influence the fast pyrolysis of trommel fines process due to their similarities in composition, thus it is very important to review literature of MSW samples and co-pyrolysis of mixtures of waste, whose composition resembles trommel fines composition. This approach leads to a knowledge of the possible factors that are likely to affect the composition and yields of products from trommel fines fast pyrolysis process. The following factors have been shown over the course of several research studies to have a direct impact on product yield, quantity and quality. They are discussed in detail as they are considered during this research.

2.7.1 Feedstock composition

The composition of the waste used in the process determines to a large extent the composition of the liquid product. The distribution of the components of the waste i.e. cellulose, hemicellulose, lignin, and ash content are mainly responsible for this. Different anatomical parts of the waste may also favour char, oil and gaseous products in different compositions (Franz, 1968). Occasionally different types of waste streams are combined with the aim of improving the liquid products (Onal et al., 2012).

The influence of inorganics present in the feedstock during pyrolysis has previously been studied (Raveendran et al.1995; Nik-Azar et al.1997; Muller-Hagedorn et al. 2003; Lee et al. 2005) and found that the inorganic species catalyse feedstock decomposition and char reforming reactions, resulting in the reduction of liquid yields and the formation of char and non-condensable gases. It is also known that the alkali metals influence the thermal decomposition mechanism during fast pyrolysis by enhancing the fragmentation (ring scission) of the monomers making up the macro polymer chains (Scott et al. 2001; Fahmi et al. 2007). These suggest that the content and composition of ash are important parameters which affect the yield and chemical composition of the pyrolysis products.

Ghetti et al., (1996) studied the effect of feedstock lignin content on burning characteristics of bio-oil products using thermogravimetric analysis (TGA) technique and concluded that feedstock of low lignin content produces a lighter pyrolysis oil in terms of density and viscosity. So therefore, it could be said that the content of lignin in waste can affect the bio-oil quality in terms of viscosity, molecular weight, stability and combustion behaviour.

Zhao et al. (2011) investigated the impact of impurities such as food wastes, paper, textile and especially soil on the pyrolysis of waste plastics. Emissions, gas and liquid products from pyrolysis of waste plastics and impurities were studied. In addition, the transfer of elemental N, Cl, and S from the substrates to the pyrolysis products was also investigated. It was found that the presence of food waste reduced the heat value of the pyrolysis oil and increased the moisture in the liquid products. Therefore, the food residue should be removed, but the soil enhanced the waste plastic pyrolysis by improving the quality of gas and oil products. The presence of food residue, textile and paper led to higher gas emissions.

Miskolczi et al. (2013) compared pyrolysis oil from MSW and MPW at 500 °C with a commercial oil (a so-called standard product) and found that pyrolysis oil from MPW with or without catalysts meets most of the requirements in commercial oil, whereas pyrolysis oil from MSW has a much higher water content and cannot meet the requirements in terms of the cetane index and corrosion test, in addition to the issue of its unqualified distillation data. Water in liquid products mainly comes from biomass pyrolysis, so if oil production is desired, it is suggested that MPW instead of whole MSW be pyrolysed.

Xue et al. (2015) investigated the co-pyrolysis of red oak wood and high-density polyethylene in a continuous fluidised bed reactor in a temperature range from 525 to 675 °C. Also, Grieco and Baldi, (2012) studied the interaction of polyethylene mixed with biomass (paper and beech wood sawdust) during co-pyrolysis. They noted that the amount of char and gas increased by increasing the biomass materials and the amount of oil decreased. The same conclusion was made by Paradela et al. (2009). In general, the presence of a lignocellulosic material resulted in a strong decrease of ethylene and C_3 hydrocarbons (originating from plastic), and a significant increase of CO and CO_2 (derived from biomass). In turn, hydrogen, methane and ethane are less affected by sample composition.

Zhou et al. (2015) decided to observe the interactions between orange peel, tissue paper and PVC during pyrolysis, because food residue, plastics and paper compose the major part of MSW. They checked the composition of gases obtained during co-pyrolysis. They found, that the interaction of orange peel and tissue paper was small. The interaction of orange peel and PVC was noticeable and stopped the production of alkyls and alkenes and weakened the peaks of HCl and C_6H_6. The interaction of tissue paper and PVC was significant; these interactions promoted pyrolysis at low temperature (below 300 °C). The residue of tissue paper and PVC increased due to interactions and the generation of CO_2, alkyls, alkenes, and carboxyls was strongly influenced. They reported that the char of a mixture of cellulose and PVC had fewer hydroxyl groups and more C = O and C = C bonds compared with the char of pure paper. However, an artificial mixture of waste, no matter how accurate, cannot be as valuable as a real portion of MSW. Data obtained can be carefully used as an indication for designing real processes of MSW treatment using pyrolysis.

Chattopadhyay et al. (2016) investigated the co-pyrolysis of plastics and paper in different proportions at 800 °C. Pure paper biomass was converted into gas, liquid and char, which were approximately 53%, 15% and 32%, respectively. On the other hand, pyrolysis of a mixture of plastics made it possible to obtain about 51.5% of gas, 21% of liquid and 27.5% of char. A clear interaction between paper and plastics during co-pyrolysis is observed, resulting in the increase in liquid products with more plastic content in the feedstock, while gaseous and solid products have followed the inverse trend. Usually there is several times more biomass than plastics in MSW. The most representative would be a sample containing three times more biomass than plastic. The pyrolysis of such a mixture gave about 55% of gaseous products, 17% of liquids and 30% of solid residue.

Research by Fang et al. (2016) used MSW as an addition in the pyrolysis of industrial waste. They investigated the co-pyrolysis of paper sludge and municipal solid waste. MSW was considered as a mixture of food waste, fruit waste, wood, paper, PVC and textiles. The samples were heated from room temperature to 1000 °C, at heating rates of 30, 40, and 50 °C/min, with a nitrogen flow rate of 80 ml/min. The initial decomposition temperature of MSW was 267 °C while paper sludge was 306 °C, almost 40 °C higher. The pyrolysis residue masses of MSW and paper sludge were 17.45% and 53.88%, respectively. The terminated temperature for MSW (927 °C) was about 60 °C higher than that for paper sludge. All the above indicates that paper sludge might contain more substances unsuitable for pyrolysis, such as the inorganic minerals in residual coatings, and other ash.

2.7.2 Feedstock particle size

Heat transfer in feedstock particles is mainly achieved through conduction and convection. Most feedstock particles are irregularly shaped and tend to have lengths several times their thickness (Diebold and Bridgwater, 1994; Kumar and Kolar, 2006). During fluidised bed fast pyrolysis, more than 90% of the heat requirement for a biomass particle is achieved via conduction through contact with the fluidising medium (Bridgwater et al., 1994). To achieve the high heating rates and low residence times required for complete thermal degradation, smaller biomass particles are essential to the process (Bilbao et al., 1994). In most pilot and lab scale units, particle sizes are usually limited to between 2-3mm to mitigate the effect of incomplete devolatisation and meet requirements for short vapour residence times and minimal cracking of formed vapours (Diebold and Bridgwater, 1994; Bridgwater et al., 1994).

Luo et al. (2010) investigated the effect of particle size on the composition and yields of products from pyrolysis of three MSW components. The three MSW components selected were plastics, kitchen garbage and wood. The MSW components were crushed and sieved into three different size fractions (<5, 5–10 and 10–20 mm). For all the samples tested, the gas yield was observed to decrease with increase in particle size. Smaller particle size was reported to improve the heat and mass transfer and hence produced higher amount of light gases. Plastics, among the samples, had the highest gas yield due to ease in breaking of the molecular structure and high volatile content. The gas yield from kitchen garbage was found to be highly sensitive towards the particle size; decrease in particle size increased the gas yield by 82.8%. Fewer yields were reported (27.5%) in gas yield from wood in same size variation but, no effect was seen in from plastic due to its 100% volatility. The main components identified in gas were H_2, CO, and CO_2 with small amounts of C1 and C2 hydrocarbons. The weight percentages of char and tar were directly proportional to particle size for all the three samples. A minor variation in tar yield was observed with plastic particle size with no char produced. The tar and char yields from wood and kitchen garbage had was reported to have a significant decrease with decrease in particle size and the tendency was more pronounced for kitchen garbage than for wood. The ash content in char from kitchen garbage and wood increased with decreasing particle size (Luo et al., 2010). The same conclusion was made by Di Blasi, (1996) who reported on the influence of particle size on MSW pyrolysis and concluded that reduced particle size in general resulted in increasing heating rate and consequently higher yield of the liquid product.

2.7.3 Process temperature

The influence of pyrolysis temperature on the yields and composition of pyrolysis products have been discussed in the literature. Buah et al., (2007) investigated the effects of various pyrolysis parameters on the pyrolysis products of MSW in form of refuse-derived fuel (RDF). Temperature was reported to have a significant influence on the yield and composition of the pyrolysis products. As the temperature was raised from 400 °C to 700 °C, the char yield fell from 49.8 to 32.3% while the oil and gas yields improved from 30 to 50% and 18.6 to 20.1%, respectively. The particle size characteristics of chars at 500 – 700 °C were similar, whilst the char obtained at 400 °C contained more coarse particles. This indicated that the low pyrolysis temperature favour formation of harder chars. The surface area of char was reported to improve with temperature. The percentage of fixed carbon and ash content in char increased with temperature and a reverse was seen in the case of volatiles. Evolution of CO and CO_2 was reported at low temperatures and H_2 at high temperatures. The evolution of gases during heating to 700 °C occurred mainly within two temperature ranges. Evolution of CO and CO_2 occurred mainly at lower temperatures, between 200 °C and 480 °C, and H_2 with lower concentrations of CO and CO_2 at higher temperatures between 580 °C and 700 °C. The Fourier-transform infrared spectroscopy (FTIR) spectra of oil samples indicated the presence of alkenes, carboxylic acids and their derivatives, polycyclic and substituted aromatics.

Velghe et al. (2011) studied the fast pyrolysis of MSW samples from a treatment plant. The average calorific value of the MSW sample waste was 27 MJ/kg and the samples were dried before pyrolysis. The fast pyrolysis process was characterized by a short residence time (<2 sec) at a constant temperature of 450, 480, 510 and 550 °C. The best temperature for fast pyrolysis was 510 °C and at this temperature the oil yield was the highest, 67.0 ± 0.4 wt.%. This liquid fraction contained the highest yield of waxy material and oil. The oil has the lowest water content and a satisfactory heat heating value, which makes it promising as a fuel. The oil fraction was rich in aliphatic hydrocarbons (63.5% with 44.1% alkenes) besides 23.5% of aromatic compound $_{d}$C8 – C28 aliphatic hydrocarbons can be useful as chemical feedstock in several industries. Apart from having a low water content the oil has a heating value comparable to that of Diesel, which makes it a good candidate for use as a fuel. Furthermore, the gas phase obtained also had excellent properties. It contained mainly hydrocarbons and had a heating value of around 20 MJ Nm^{-3}. Ethane, ethene, propene, 2-methyl-1-propene, pentane, 2-methyl-1-pentene, and acetaldehyde were present in significant proportions and the gas can be valuable as feedstock for the chemical Industry.

Zhou et al. (2013) investigated the pyrolysis behaviour of pelletized MSW including, char properties and swelling/shrinkage properties in a fixed bed reactor over a temperature range from 450 °C to 900 °C. A significant effect of temperature on the conversion of pelletized waste was observed. A total of 83% of the RDF sample was converted in the first 100 s at 800 °C, whereas the respective residues for 700°C and 600 °C were 26% and 72% of the initial sample. When the temperature was reduced to 500 °C or lower, it was impossible to reach the conversion levels obtained at 700 °C or higher, even when the operation times were much longer. The sample initially experienced a slight swelling and subsequently a significant contraction was observed. The swelling ratio was observed to increase ominously when the temperature reached 180 °C, a temperature at which plastics start to melt and enter the thermoplastic transition. Also, evaporation of moisture and volatiles, the pyrolysis of cellulosic groups burst through the particle resulting in the formation of an unstable liquid contributing to the swelling ratio. The SEM image of char produced at 550 °C from pyrolysis of RDF illustrates the surface to be covered by a thin layer of smooth material generated due the plastic melting during pyrolysis process. With increase in temperature the fluffy structure of the char was predominant, and the fluffy filamentous fibres increase the integrity of the solid waste particle (Zhou et al., 2013).

Chen et al. (2014) reviewed the pyrolysis of MSW components, focusing on the effect of temperature on product composition, distribution and heating values of the products produced. A mixture of kitchen waste, paper, cloth, bamboo, plastics and glass was pyrolyzed at temperatures ranging from 500 to 900 °C using a laboratory scale fixed bed reactor. Increasing the temperature caused an increase in gas production and a decrease in char and oil. Additionally, the heating value of char increased with increasing temperature from 18.3 MJ/kg at 500 °C to 30.4 MJ/kg at 900 °C.

Dong et al. (2016) also studied the pyrolysis of MSW, using a fluidised bed. They considered the influence of temperature on the MSW conversion. A simulated waste sample was composed of food waste (29 wt.% rice and 29 wt.% cabbage), cardboard (13 wt.%), plastic (17 wt.% polyethylene and 3 wt.% polyvinyl chloride), textile (2 wt.%), timber (5 wt.%), and rubber (2 wt.%). The temperature played an important role in MSW pyrolysis and researchers found that the syngas yield rose from 60.1 wt. % or 1.0 Nm^{-3} kg_{MSW} at 550 °C to 68.8 wt. % or 1.2 Nm^{-3} kg_{MSW} at 850 °C. At the same time oil and char yields decreased. The major components of the syngas obtained at 650 °C were CO, H2, CO2, C2H2, CH4, C2H6 and C2H2 with the concentration about 9 mol.%, 5.5 mol.%, 5 mol.%, 4 mol.%, 3 mol.%, 0.5 mol.% and 0.1 mol.%, respectively. The lower heating value was approximately 6 MJ/ Nm3. Because the next step after pyrolysis was gasification the researchers did not consider the char or liquid composition. However, the syngas properties made it good gaseous fuel.

2.7.4 Moisture Content

The moisture content of the feedstock can vary considerably depending on the type of feedstock, its origin and treatment before it is used for pyrolysis. This can have a detrimental effect on EfW process and the quality of the fuel. The moisture in the feedstock eventually ends up in the products of the process mainly the liquid product. As water is an unwanted compound in most liquid product, due to its lowering effect on the heating values. Marsh et al., (2008) investigated the relationship between the calorific value and moisture content of typical waste and biomass components and found that an increase in the moisture content of a fuel leads to a decrease in the calorific value. Chen et al. (2014) also investigated the effect of moisture content in MSW components, focusing on its effect on product composition and the lower heating value (LHV) of the syngas produced (Chen et al., 2014). Polyethylene (PE), paper pulp and bamboo were pyrolysed using a laboratory scale fixed bed reactor. For paper and bamboo components, an increase in moisture content led to a decrease in the production of H_2 but an increase in tar yields. This also led to a decrease in the LHV of the produced gas with the highest LHV achieved for a moisture content of 0%. This confirms findings by Marsh et al that an increase in moisture content reduces the calorific value of the fuel. This was not true, however for the pyrolysis of PE which produced the highest LHV of the syngas with a moisture content of 66.7 % (Chen et al., 2014).

Kelbon and Bousman, (1988) studied the pyrolysis of biomass with 10%, 60% and 110 wt.% moisture content. They reported that the onset of pyrolysis can be delayed by up to 150 seconds depending on the moisture content of the feed. This is because the moisture in the feed must be evaporated before the thermal degradation of the particle will begin. The presence of water has also been shown to cause secondary reactions in some cases. Further research has also backed up the claim that moisture in the feedstock usually ends up in the oil product as discovered by Maniatis (1988) during pyrolysis of bone dry samples and particles with 10% moisture. A moderate amount of moisture is known to impact positively on the viscosity of the oil product. Bridgewater and Peacocke, (2000) recommends that the moisture content for biomass for fast pyrolysis processes be around 10%.

2.8 Degradation process of different wastes during pyrolysis

The product yields from pyrolysis processes are of significant interest for EfW technologies. The desirable products vary greatly between technologies dependant on whether the gas, liquid or solid products are to be utilised for energy production. However, the reduction of solid waste is also an important factor due to the role of EfW as a waste management option. Literature studies have been conducted to establish the thermal degradation behaviour of

MSW components. As previously described in section 2.7.3 the pyrolysis process temperature is also an important factor as it has a varied effect on different components of MSW. Cepeliogullar et al. (2014) reported that the thermal degradation of plastics occurred in a temperature range of 200-550 °C and for biomass a range of 120-800 °C. Skreiberg et al. (2011) and Chen et al. (2014) reported that biomass behaves similarly to paper, newspaper, cardboard and some food wastes during pyrolysis. Pyrolysis processes typical operate at a temperature between 400 and 800 °C (Lupa et al., 2013).

The majority of research has been undertaken using TGA as well as using laboratory scale equipment. The ease of use, short experimental time and high accuracy of results has made TGA a popular option for studying the pyrolysis behaviours and especially the thermal degradation of MSW. This can be especially beneficial for analysis of individual components of MSW. Heikkinen et al. (2004) used TGA to study the pyrolysis of 41 individual components of waste. If the pyrolysis of these individual components were investigated in a laboratory scale rig, this number of investigations would take a long time. TGA is therefore an important option for the analysis of MSW. For TGA investigations, a very small sample size is used, usually around 10mg, which although allows for quicker reactions than the larger samples used for laboratory scale investigations. Although beneficial for individual components, this could cause problems for investigations on MSW mixtures due to the highly heterogeneous nature of waste and difficulties in getting an accurate representation of this in a sample of approximately 10 mg. As well as this, problems could develop when scaling results up to represent commercial scale pyrolysis.

2.8.1 Pyrolysis of paper, newspaper and cardboard wastes

Wu et al. (2003) investigate the pyrolysis products from newspaper waste using TGA. Two stages of mass loss were reported; the first stage between temperatures of approximately 226 and 366 °C and the second stage between approximately 366 and 676 °C. The first stage was attributed to the production of low and intermediate molecular mass volatiles such as H_2, H_2O and hydrocarbons and the second stage of mass loss was attributed to the conversion of C to CO and CO_2. Wu et al. (2003) also reported the final residual mass to be 9.45% of the initial sample.

Ahmed and Gupta, (2009) investigated the syngas yield produced from the pyrolysis of paper using a laboratory scale reactor. Samples of 35 g were pyrolysed at temperatures of 600 to 1000 °C. Ahmed and Gupta, (2009) reported a rapid increase in flow rate of the produced gas was found at the beginning of the process at all temperatures followed by a rapid decrease until the flow rate reached zero. Increase in pyrolysis temperature increased the peak flow rate of the produced syngas significantly from approximately 2.4 g/min at 600 °C to nearly 12 g/min at 1000 °C (Ahmed and Gupta, 2009). This was attributed to the higher temperature allowing for the breakdown of long chains of hydrocarbons, therefore leading to an increase in the yield of syngas.

Skreiberg et al. (2011) investigated the thermal behaviour of glossy paper using TGA and a macro-TGA. A sample of 200 g was pyrolysed in a N_2 atmosphere at a heating rate of 5 K/min up to a temperature of 900 °C. Skreiberg et al. (2011) reported a solid residue of 28 % and it was found that glossy paper started to release volatiles at a temperature of approximately 250 °C. A second stage of mass loss was observed which was attributed to the conversion of calcium carbonate ($CaCO_3$) to calcium oxide (CaO) and CO_2 (Skreiberg et al., 2011). $CaCO_3$ is a common additive to make paper glossy. This further highlights the challenges of the heterogeneous nature of MSW components.

Chen et al. (2014) also investigated the pyrolysis of paper using a TGA system. The paper studied by Chen at al. (2014) had a lower ash content, higher fixed carbon and slightly higher volatile content of 10%, 10% and 80% respectively compared to 25%, 4.5% and 70% respectively for the glossy paper studied by Skreiberg et al (Skreiberg et al., 2011 and Chen et al., 2014). Chen et al. (2014) reported that the main mass loss of paper occurred between 300 and 400 °C which was the same as that found by Singh et al. (2013) in a TGA study of the pyrolysis of paper cup waste.

2.8.2 Pyrolysis of plastic wastes

The pyrolysis of plastics is a complex process and varies significantly with the different plastic fractions of MSW which further highlights the challenges of the heterogeneous nature of MSW components. Mastral et al. (2003) investigated the pyrolysis products of HDPE using a laboratory scale fluidised bed reactor (Mastral et al., 2003). The gas yield was found to be 33.5% and the wax and oil yield was 68.5% with respect to the mass of the sample at the lowest temperature investigated of 640 °C. An increase in pyrolysis temperature up to 780 °C led to a significant increase in the production of gas to the detriment of wax and oil yields. A temperature increase from 780 °C to 850 °C led to a decrease in gas yields from 102.2% to 89.1% respectively and an increase in wax and oil yields from 9.6% to 16.2% respectively (Mastral et al., 2003).

Kumar and Singh, (2013) also investigated the pyrolysis of high-density polyethylene (HDPE) with the aim of producing petroleum products. The pyrolysis of HDPE is usually conducted between 500 °C and 800 °C to produce oil, gas, wax and solid residue. It was found that the thermal degradation of HDPE begun at approximately 380 °C and was complete at a temperature of 510 °C (Kumar and Singh, 2013). The composition and quantity of each of the products from pyrolysis of plastic wastes is dependent on the type of the plastic waste and the process conditions. Kumar and Singh, (2013) found that at temperatures below 400 °C, the condensable products were low viscous liquids and above 450 °C, these became high viscous wax products. Kumar and Singh, 2013 also reported that at pyrolysis temperature of 550 °C, the pyrolysis products were found to be 8.83% oil, 0.68% solid residue, 52.02% wax and 38.47% gas/volatiles with respect to weight (Kumar and Singh, 2013). As the temperature increased, the pyrolysis reaction rate also increases leading to a decrease in reaction time. Faravelli et al. (2003) studied the thermal degradation of polyethylene (PE) and polystyrene (PS) and reported similar findings to Kumar and Singh, (2013). They found that PS degradation began at a temperature of approximately 360 °C (Faravelli et al., 2003), and for PE, the degradation temperature was found to be much higher at 410 °C. Total thermal decomposition was achieved at a temperature of 450 °C for PS and 550 °C for PE (Faravelli et al., 2003).

Heikkinen et al., (2004) studied the pyrolysis behaviour of Polyvinyl Chloride (PVC) along with 40 other individual waste components using TGA. It was found that all plastics, except PVC, reached a maximum rate of decomposition between 410 °C and 515 °C. PVC, as reported by Chen et al. (2014), degraded in two stages. Heikkinen et al. (2004) reported that the first stage at 305 °C was attributed to the release of hydrogen chloride (HCl) due to dehydrochlorination. The second stage was observed at 468 °C and was attributed to the degradation of the remaining hydrocarbon residue. Heikkinen et al. (2004) suggested that these plastics, except for PVC, could be classed as one class due to the similarities in the pyrolysis behaviours tested. They also suggested that PVC is separated from waste streams due to the release of hydrochloride. The temperature at which thermal degradation for PVC began, as found by Cepeliogullar et al. (2014) was 220 °C. This is slightly lower than the initial degradation temperature of 305 °C found by Heikkinen et al. (2004). Cepeliogullar et al. (2014) also studied the gas yields produced from the pyrolysis of PET and PVC at 500 °C and reported them to be 76.9% and 87.7% respectively.

Singh et al. (2012) studied the pyrolysis of waste plastics (various mixes) derived from post-consumer MSW mostly made up of HDPE and Polyethylene Terephthalate (PET), although the exact composition is not stated. Thermal degradation was reported to begin at approximately 410 °C and was completed by approximately 480 °C, similar to the initial thermal degradation temperature for PE as reported by Faravelli et al., 2003 although complete degradation of PE required a higher temperature. However, Cepeliogullar et al., 2014 found that the thermal degradation of PET begun at 350 °C, this is slightly lower than the temperature of 410 °C for PE reported by Kumar and Singh, (2013).

Chen et al. (2014) investigated the pyrolysis behaviour of polyester fabrics along with PVC and PE using TGA. Polyester fabrics could also be classed under the plastic fractions of MSW. The pyrolysis behaviour of polyester was found to be like that of PE with thermal degradation of polyester beginning at approximately 390 °C and 410 °C for PE. The thermal decomposition process was complete for polyester at approximately 410 °C and approximately 490 °C for PE. However, the pyrolysis behaviour of PVC was reported to be very different with mass loss occurring in two stages; the first between 250 °C and 380 °C and the second between 400 °C and 550 °C (Chen et al., 2014).

2.8.3 Pyrolysis of food waste

The pyrolysis of food waste is also a complex process and varies significantly with the different food waste fractions of MSW which further highlights the challenges of the heterogeneous nature of MSW components. The pyrolysis of selected food wastes, such as fruit peels (Aguiar et al., 2008; Mopoung et al., 2008; Miranda et al., 2009), potatoes peels (Liang et al., 2015), nuts shells (Haykiri-Acma et al., 2006; Apaydin-Varol et al., 2007; González et al., 2009), orange peel (Chen et al., 2014) or bones and meat (Purevsuren et al., 2004; Ayllón et al., 2006) has been investigated and reported in literature. However, many of the literature focused on their effect on bio-chars. Girotto et al. (2015) highlighted the problem of food waste utilization to produce useful products such as bio-oils and, pyrolysis was mentioned as a method with the potential to treat food waste, but the effectiveness of the process is strongly dependent of waste composition. Pyrolysis of mixture of food waste have been considered in limited applications so far, because of the high composition variability of this waste (Girotto et al., 2015).

Chen et al. (2014) also investigated the thermal degradation of dried orange peel and dried Chinese cabbage along with paper, polyester, PVC and PE. They reported for both type of food waste, most of the mass loss occurred at temperatures between 200 and 400 °C with minimal further mass loss after this point, like the findings reported by Heikkinen et al. (2004) who studied the thermal degradation of bread, banana and starch using TGA. It was found that most of the mass loss of these samples occurred between temperatures of 209 °C and 346 °C.

Liu et al. (2014) investigated the temperature profiles of food waste collected from a residential area in China by pyrolysis with microwave heating, however, the composition of the products obtained was not considered. Fruits, plastic and shells were removed from the raw food waste; thus, the remaining three main components were white rice, vegetable leaves, and meat/ bones, with proportions of 32.69%, 44.23% and 23.08%, respectively. When the microwave power was increased from 300 to 600 W, the yield of solid residue decreased sequentially, the gas yield increased continuously, and the bio-oil yield first increased, and then decreased. The optimal level of power for pyrolysis was 400 W.

Zhang at al. (2015) conducted a similar investigation to Liu at el. (2014). Zhang at al. (2015) reported that for the fast pyrolysis of food waste at 600 °C, there were various oxygenates in the pyrolysis vapour product (e.g., acetic acid; furfural; 2-cyclopenten-1-one, 2-hydroxy-; 2-cyclopenten-1-one, 2-hydroxy-3-methyl-; cyclopropyl carbinol; 1,4:3,6-dianhydro-pd-glucopyranose; benzofuran, 2,3- dihydro-), and there were almost no hydrocarbons and aromatics. Moreover, the oxygen content in the pyrolysis vapour product was very high at about 32.26%.

Apart from the main components of pyrolysis products it is worth considering the presence of other potentially unsafe compounds. The transformation of food materials during pyrolysis can produce many pollutants, such as sulphurous compounds, heavy metals, nitrogen compounds, etc., and the concentration of these components is also heavily dependent on the composition of the raw material in the process. Debono et al. (2015) studied the reaction pathway of nitrogen compounds during the pyrolysis of various organic wastes. They investigated food waste and sewage sludge from cruise ships and also common softwood from gymnosperm trees (each alone and as a mixture) using a homogenous portion of 5 g of waste placed in the reactor, which was heated at 20 °C min^{-1} to 500 °C, while purged by argon as a carrier gas. When heated, wastes were transformed into char, tars and gas. Debono et al. (2015) reported that the nitrogen distribution in condensable products (char and tars) was high so that the nitrogen in the wastes is presumably stable and they observed the presence of 18 nitrogen compounds in the pyrolysis gas. NH_3, HCN (hydrogen cyanide) and three types of compounds were identified: nitriles, heterocyclic compounds and amides. In the tar fraction they identified 72 nitrogen compounds, which can be divided into six families: nitriles, heterocyclic compounds with one nitrogen atom, heterocyclic compounds with two nitrogen atoms, amides, amines and oximes (Debono et al., 2015). However, they concluded that in organic wastes, like waste food, the main sources of nitrogen are the proteins hence, they can be considered as the main sources of nitrogen products. Therefore, the pathway proposed in this study was based on the degradation of proteins (Debono et al., 2015).

Grycová et al. (2016) investigated the pyrolysis of samples of waste cereal and peanut crisps at a final temperature of 800 °C. They obtained 62% and 46% of oils with a heating value 12 MJ kg^{-1} and 25 MJ kg^{-1} from peanut crisps and cereal, respectively. However, they recommended its further use for energy recovery after the separation of water, because of the noticeable water content. The gas yield was about 15–25 wt.% and the gaseous components were analysed. The reported that the variation of the gas compositions as a function of temperature was clear: there was an increase in temperature accelerated hydrogen evolution. On the other hand, the concentrations of measured hydrocarbons and carbon monoxide decreased with the increasing temperature as described by Kalinci et al. (2009). The sorption capacity of chars was investigated, too. The surface area of tested pyrolysis chars was very small (below 10 m^2 g^{-1}) (Grycová et al., 2016). Thus, they recommended that in order to use them further, their surface area could be increased by activation and/or some chemical treatments.

2.8.4 Pyrolysis of mixed MSW

Due to the heterogeneous nature of MSW, the behaviour of MSW during pyrolysis is complex and varied and is dependent on the composition and characteristics of the waste. The pyrolysis products are strongly influenced by the type of reactor, temperature and heating rate, pressure ranges and the presence of catalysts. Several researchers have investigated these pyrolysis characteristics using TGA (Sorum et al., 2000; Wu et al., 2002; Heikkinen et al., 2004; Zheng et al., 2009; Skreiberg et al., 2011; Velghe et al., 2011; Singh et al., 2012; Chen et al., 2014; Zhou et al., 2015).

Velghe et al. (2011) studied the pyrolysis of mixed MSW containing carpet, residues of plastic, metal, drinks cartons, paper and different fractions of synthetic materials and an organic fraction using a fixed semi-batch reactor. The main gases produced at the start of pyrolysis were found to be CO_2 with smaller amounts of CO and minor amounts of light hydrocarbons. The volumes of CO_2 and CO were found to decrease as the pyrolysis time increased.

As well as investigating the behaviour of MSW mixtures, research has also been undertaken to establish the interactions of individual MSW components during pyrolysis. Zheng et al. (2009) reported that interactions between similar components of MSW, such as paper, biomass and food waste, during pyrolysis was small, whereas interactions between PE and biomass was significant especially at higher heating rates. Skreiberg et al., (2011) also investigated the interactions of mixtures of paper, biomass and food waste using TGA confirmed Zheng et al. (2009). It was found that the gas composition from MSW mixtures showed relatively quantitative and qualitative summative behaviour based on that found for single components of MSW.

Faravelli et al., (2003) investigated the thermal degradation of a mixture of PE and PS using TGA. It was found that if the mixing of the PE and PS was poor then the thermal decomposition of each polymer behaved independently. However, if the mixing of the polymers reached a molecular scale, partial interactions and co-pyrolysis was observed. Increased mixing of the components led to an increase in the volatilisation of the PE during the depolymerisation of the PS.

2.9 Fast pyrolysis products and their possible applications

Fast pyrolysis of MSW is usually aimed at energy recovery, because the products (liquids, solids, gas) often have good properties as fuels. Energy, especially electricity is always a desirable product, which is easy to sell and, parts of the products can be combusted to meet the fast pyrolysis energy demand. Fast pyrolysis also makes it possible to convert waste into an energy source for the home (Jouhara et al., 2017), and on a larger scale pyrolysis plants may use the fast pyrolysis products for other purposes, which increases the profitability of the process. The composition of the bio-oil and some properties of solid products from fast pyrolysis of MSW could make them favourable as a raw material for some industry sectors. The relative proportions of products from fast pyrolysis processes are subject to a combination of factors including reactor configuration, vapour residence time and temperatures.

2.9.1 Fast pyrolysis liquid products

The bio-oil produced from fast pyrolysis of MSW are usually composed of a mixture of organic compounds with an appreciable proportion of water (from both the original moisture of the feedstock and reaction water produced during fast pyrolysis), and also char. The ratios of the components are dependent on the configuration of the fast pyrolysis process, reaction conditions, extent of char removal, condensation method and the composition of the initial feedstock. Liquids produced from fast pyrolysis of MSW have a low viscosity and typically is a dark brown, free-flowing liquid and with an irritable smell (Bridgwater, 1996; Bridgwater, 2011). Depending on the initial feedstock and the mode of fast pyrolysis, the colour can be almost black through dark red-brown to dark green, being influenced by the presence of micro-carbon in the liquid and chemical composition. High nitrogen content in the feedstock can impart a dark green tinge to the liquid (Bridgwater, 2011).

Fast pyrolysis liquid products often contain a high moisture fraction (15-30 wt. %) (Bridgwater, 1996, Bridgwater, 2011), which makes them difficult to apply. The presence of water has positive and negative effects on liquid product characteristics; water lowers the heating value but reduces the viscosity. The liquid product can separate into two phases due to increasing water contents (Oasmaa, and Czernik, 1999). A tar-like product with a high viscosity forms a bottom layer, with a low viscosity aqueous phase forming on top. The aqueous phase, comprises mainly of lighter organic compounds from the decomposition of cellulose and hemicellulose, while the tar-like product (water insoluble phase) is composed of larger and heavy compounds commonly referred to as pyrolytic lignin (Bridgwater, 1999; Oasmaa, and Czernik, 1999). The liquid product usually has an oxygen content of 35-40%, and over 300 compounds make up the liquid product. (Bridgwater, 1996; Bridgwater, 2011)

Diebold, (2002) reported that the major organic components of the liquid products are continuously reacting in order to attain chemical equilibrium. The continuous organic reactions taking place even after the formation of the liquids are responsible for the aging witnessed in the liquid product during storage and these can alter the physical and chemical characteristics of the product (Diebold and Bridgwater 1994). The components of the liquids make its properties very likely to change over time dependent on storage conditions. Although the liquid product has been successfully stored for several years in normal storage conditions in steel and plastic drums without any deterioration that would prevent its use in any of the applications tested to date, polymerisation reactions within bio-oils are known to continue until heavy lignin rich fractions separate from other components into sludge like liquids (Fratini et al., 2006). An increase in liquid product molecular weight will be observed as the product ages due to the reaction of carbohydrate based constituents, which leads to an increase in viscosity. These constituents such as aldehydes and ketones can jointly account for up to 25 % of its composition (Diebold, and Czernik, 1997; Oasmaa, and Kuoppala, 2003)

Velghe et al. (2011), research based on an MSW with an average calorific value of 27 MJ kg^{-1}, found that to produce oil, the optimal fast pyrolysis conditions is at approximately 510°C with a proper feeding rate. Under such conditions, the associated liquid product contains the highest yield of waxy material and oil and the lowest water content, the lowest oxygen to carbon ratio and a high heat value, which makes it a promising fuel. In regard to the composition, the oil fraction is rich in C8–C28 aliphatic carbons (63.5% with 44.1% alkenes) in addition to 23.5% aromatic compounds. Physical properties such as viscosity, the research octane number and the motor octane number, pour point, flash point or Diesel index could be a good indication of pyrolytic oil quality as a fuel (Khan et al., 2016)

Fast pyrolysis liquids offer more opportunities for use than gas, but, depending on the composition of the feedstock and the process parameters, the composition of the liquid product from pyrolysis may differ radically. Pyrolytic oils originating from MSW consist largely of the following compounds: acids, sugars, alcohols, ketones, aldehydes, phenols and their derivatives, furans and other mixed oxygenates. Phenolic compounds are often present in high concentrations (up to 50 wt %), consisting of relatively small amounts of phenol, eugenol, cresols, xylenols, and much larger quantities of alkylated (poly-) phenols (Mohan et al., 2006). They can be used for the production of heat, electricity, synthetic gas or chemicals (Figure

2.13). Temperatures between 500 and 600°C provide the highest yields of oil, when biomass is processed with heating values of around 15–20 MJ/kg. Fast pyrolysis liquids can substitute for fuel oil or diesel in many static applications including boilers, furnaces, engines and turbines for electricity generation which has been thoroughly reviewed by Bridgwater, (2011) and many aspects have not changed very much.

Figure 2.13: Applications for fast pyrolysis products (Source: Bridgwater, 2011)

2.9.2 Fast pyrolysis solid products

Fast pyrolysis processes leave a residue of high carbon content char with almost all the ash contained in it and relatively low amounts of oxygen and hydrogen. The fast pyrolysis char can be either separated from the other products, as with in this research (refer to Section 4.1), where it can be used for other applications or it can be burned to provide process heat (circulating fluidised bed reactor) (refer to Section 2.4.2) as chars from fast pyrolysis can have heating values of up to 23 MJ/kg (Wang et al., 2005b; Jiang, 2006; Yi, 2007). Fast pyrolysis solid residue can be added to soil to improve upon its characteristics as a soil amendment (BIOCHAR) (Lehmann et al., 2006).

The research conducted by Wang et al. (2005b); Jiang, (2006) and Yi, (2007) show that solid product from MSW pyrolysis could be a valuable fuel due to its relatively high LHV. However, in most cases, solid product is gasified in a later step or combusted and melted because solid fuel is not as attractive as gas and oil. In addition, before outputting solid product as a fuel product, a pre-treatment step, such as sorting out metals and pebbles, is needed; this increases the cost and weakens its competition with rational fuel. Zhang et al. (2012) explored the potential of adopting char from MSW pyrolysis as biochar and found that the properties of the solid product from MSW pyrolysis are like those of normal biochar from biomass: the solid product from MSW pyrolysis was rich in hydroxy-OH, fatty C-H, carboxyl group-COOH, aromatic rings C-H and C=C bonds on its surface, and the application of the char to the soil could increase the cation exchange capacity and pH of the soil and improve soil fertility. However, the accumulation of inorganics (heavy metals, glass, etc.) in the solid product and their mobility to the soil may hinder this application. This highlight the need for adequate pre-treatment method to reduce the inorganic content of the feedstock (e.g. trommel fines) prior to fast pyrolysis process (refer to Chapter 4).

2.9.3 Fast pyrolysis gas products

The final product of pyrolysis processes are the non-condensable gases formed because of the thermal degradation of the feedstock. The amount of non-condensable gases produced from any fast pyrolysis process is dependent on numerous factors including process temperature and reactor configuration (Bridgwater 1999). The efficiency of the vapour quenching process will also impact the amount of non-condensable gases produced with very efficient quenching producing less gases. Fast pyrolysis gases mainly consist of carbon monoxide, carbon dioxide, methane, hydrogen, ethane and propane. The gases can be utilised for energy purposes, but their use is dependent on process scale because of relatively low energy content (Goyal et al., 2008).

In some fast pyrolysis systems flue-gas or an inert gas can be used for fluidisation (Bridgwater 1999), this results in the fast pyrolysis product gas becoming diluted with the fluidising gas. The pyrolysis system that is used in this research uses nitrogen to fluidise the reactor bed material (refer to Chapter 3), resulting in the fast pyrolysis product gas being heavily diluted. The fast pyrolysis product gas was only used for analysis of gas composition and mass balance purposes (refer to Chapter 3). In general, a higher temperature and catalyst addition will increase the gas yield and reduce the char yield. The gas yield is usually lower than 1 Nm kg^{-1}, and its averaged LHV is approximately 15 MJ N m^{-1} when the pyrolysis temperature is not lower than 600°C. (Hwang et al., 2014).

Literature studies have shown the dominant gases from pyrolysis of waste to be CO, CO_2, H_2, H_2O and light hydrocarbons (C_1-C_4), varying significantly with pyrolysis temperature and fuel characteristics (Williams et al., 1997; Mastral et al., 2003; Wu et al., 2003; Conesa et al., 2009; Skreiberg et al., 2011; Singh et al., 2012; Zhou et al., 2014). The key advantage of pyrolysis, is the ability to produce a CO and H_2 rich gas. Lupa et al., 2013 reported that, the most important gases for the consideration of energy generation from EfW processes are CO, CO_2, H_2O and H_2 with CO and H_2 being the gases of most importance as they have a high calorific value (CV) of 10 and 13 MJ/kg respectively. Lupa et al. (2013) also reported a heating value of 11-17 MJ Nm^{-3} from plasma-arc pyrolysis of waste, which is comparable to other studies where values of 13-20 MJ Nm^{-3} from the pyrolysis of waste (Raveendran et al., 1996), 5- 16 MJ Nm^{-3} from the pyrolysis of biomass (Velghe et al., 2011) and 13-15 MJ Nm^{-3} also from the pyrolysis of biomass (Chen et al., 2003).

2.9.4 Standardized product

Currently, there is no "standardized product" from the MSW pyrolysis process that is ready for the market, except for the electricity or heat produced by burning syngas, oil or char in the facilities, which presently do not meet any standards for conventional fuels and materials. However, the existing commercial pyrolysis processes coupled with gasification or combustion facilities (Bracker et al., 1998; Martin et al., 1998; Hauk et al., 2004; Malkow, 2004; Marculescu et al., 2007) are too complicated and expensive, limiting the application of pyrolysis to the places where it is highly demanded due to the desire to prevent long-distance transport and the increased difficulty in finding new sites for incinerators and landfills. As an effective waste-to-energy convertor, MSW pyrolysis is receiving increased attention because gas, oil and even char are needed in small cities and towns where scarcity of commercial fuels is common.

According to Ohmukai et al. (2008) and Zhao et al. (2011), MSW pyrolysis process should be formulated to provide high-quality gas and avoid oil output. In this case, the multi-sectional reactor has the advantage of providing a chance for product reforming, and hot char can be used in one of the reactor section to modify oil and promote gas yield (Wang et al., 2014). Defining standardized products from MSW pyrolysis will help to normalize the pyrolysis technology and enhance its application. Syngas, with a moderate LHV and huge market, is a potential standardized product, especially in the places where fuel gas is needed for utility boilers and domestic gas. A definition of syngas standard for its market is necessary and at the same time quality normalization for the char is also necessary if the pyrolysis alone is adopted.

2.10 Effect of inorganics on MSW fast pyrolysis

In pyrolysis process, all the products are collected or recycled, the use of the MSW pyrolysis process makes it easier to reduce or avoid corrosion and emissions by retaining alkali and heavy metals, sulphur and chlorine within the process residues, and reduce thermal NOx formation due to the lower temperatures and reducing conditions used in the process when compared to combustion and gasification. Advantageously, the smaller fuel gas volume associated with pyrolysis requires lower-dimensioned gas clean-up devices, which reduces investment and operation costs. However, Cl and S species such as HCl and SO_2 (or H_2S) may still occur in the fuel gas yielded, and other contaminants may exist in the liquid and solid products. This section describes the effect MSW inorganic content can have on fast pyrolysis product produced.

The environmental impact of the formation of inorganic (i.e., HCl and heavy metals) and organic (i.e., polychlorinated dioxins and furans) contaminants in the pyrolysis of solid waste has been previously investigated (Bernardo et al., 2010; Yuan et al., 2014; Gao et al., 2016a; Gao et al., 2016b). The general conclusion is that organic pollutants and heavy metals tended to remain in the liquid and char fractions, respectively. Miskolczi et al. (2013) investigated contaminants in pyrolysis products from MSW and found that pyrolysis liquids had contaminants such as, K, S, P Cl, Ca, Zn, Fe, Cr, Br and Sb; in the gas phase, S, Cl and Br occurred. K, S, P Cl, Ca, Zn, Fe, Cr, Br, Sb and Pb were also found in water scrubbing the gas. PVC is an inevitably harmful component in MSW, which emits HCl during pyrolysis, would cause corrosion to the facility and contaminate the gas and liquid products. Yuan et al. (2014) found that HCl emission begins as soon as the melting of PVC occurs. However, HCl emission behaviour would be significantly changed by other components in the MSW, depending on whether these components enhanced or hindered heat transfer to PVC. Chen et al. (2008) found that, during the pyrolysis process of RDF, HCl emission is completed at the low temperature stage (230–400 °C), while the release of NH3 begins at 260 °C and goes through a much wider temperature range. In the temperature range of 300 to 600 °C, a large amount of SO_2 was detected. Therefore, not only gas but also liquid products can be contaminated with NH_3 and SO_2. A diversity of HCl emission behaviours has been reported during MSW pyrolysis (Slapak et al., 2000; Kim, 2001; Ma et al., 2002; Zhu et al., 2008; Ren et al., 2009). However, studies also showed that the formation of some undesired inorganic by-products containing Cl, Br, and S could be reduced with the use of catalysts or adequate feedstock pre-treatment methods (Miskolczi et al. 2013).

The solid product from MSW pyrolysis is accepted as a low-grade fuel instead of a waste stream. However, the solid product from certain waste pyrolysis processes can be toxic. Bernardo et al. (2010) reported that solid residue produced in the co-pyrolysis of different wastes (plastics, pine biomass and used tyres) contained inorganic contaminants (Cd, Pb, Zn, Cu, Hg and As) and organic contaminants (volatile aromatic hydrocarbons, alkyl phenols, etc.) and were classified as hazardous and ecotoxic wastes. Therefore, proposed that industrial waste streams should not be mixed with MSW in pyrolysis facilities where char is output.

Yu et al. (2016) compared the behaviour of heavy metals in MSW pyrolysis with that in incineration and reported that the release of heavy metals in rapid-heating incineration generally exceeded that observed in pyrolysis. The volatilities of some heavy metals, e.g., Zn and Pb, were reduced in pyrolysis compared to those in incineration. It was concluded from that study that pyrolysis is a better choice for MSW treatment in terms of controlling heavy metal contamination. Chen et al. (2014) reported that, due to contaminants appearing in the pyrolysis products, a single pyrolysis process should be equipped with products improving facilities, hence, why for commercial pyrolysis plants, combined pyrolysis and gasification or/and combustion technologies were adopted and in addition emission control devices were installed for syngas or flue gas scrubbing.

Different measures have been reported to ease the environmental effects associated with pyrolysis of MSW, including the use of catalysts to upgrade the quality of the products, the removal of inorganics in the feedstock via appropriate feedstock pre-treatment and the interception of HCl, SO_2, and NH_3 from the gaseous phase. Industrial pyrolysis apparatuses using gas engines are always installed with gas improving & scrubbing devices because gas engine has more rigid requirements for syngas cleaning than boiler combustion (Arena, 2012).

Miskolczi et al. (2013) reported that the liquid products could be improved by using catalysts which decreases the concentrations of K, S, P, Cl and Br in the oil products. Bhaskar et al. (2002) investigated the effect of catalysts on HCl removal from PVC pyrolysis and found that the use of catalysts had a very strong absorbing effect on HCl, reaching 63% of the theoretical value. Brebu et al. (2005) investigated the effect of catalysts on the pyrolysis of a plastics mixture containing PE, PP, PS, an acrylonitrile–butadiene–styrene copolymer with a brominated flame retardant and antimony oxide synergist (ABS–Br) and PVC and reported that the use of catalyst had a strong effect for the removal of bromine from the decomposition oil, and exhibited high efficiency for chlorine removal; however, were found to have a low effect in nitrogen removal. In addition, the separation of inorganics and certain key components from MSW would upgrade the pyrolysis quality. Zhao et al. (2011) studied the transfer of Cl, S and N from food waste, paper and fibre to the liquid products in a pyrolysis process and found that the presence of food waste would result in higher contents of Cl and S in the oil and reduce the heat value of the pyrolysis oil at the same time; therefore, the separation of food wastes was suggested.

To improve the solid products quality, Wang et al. (2012) and Rajarao et al. (2014) reported that higher pyrolysis temperature will help to reduce its volatile organic matter, increase its specific surface area and LHV but suggested that streams with high heavy metal contents should be avoided feeding to the pyrolyser. Although many measures are reported, only syngas scrubbing before combustion and the preparation of the solid products for gasifier are available in practice. To improve the environmental profit by applying MSW pyrolysis technologies to waste disposal, appropriate feedstock pre-treatment is required to reduce the inorganic content of the feedstock and the solid and liquid products need further characterization regarding their environmental aspects

2.10.1 Pyrolysis oil stability

Polymerisation reactions within bio-oils are known to continue until heavy lignin rich fractions separate from other components into sludge like liquids (Fratini et al., 2006). An increase in bio-oil molecular weight will be observed as the product ages due to the reaction of carbohydrate based constituents. These constituents such as aldehydes and ketones can jointly account for up to 25% of its composition (Diebold and Czernik, 1997; Oasmaa et al., 2003). The instability of bio-oil can be observed by an increase in viscosity and water content over time, this is known as aging. Aging can be catalysed by bio-oil inorganic content (Diebold and Czernik, 1997; Oasmaa et al., 1999; Oasmaa et al., 2003; Diebold, 2000). The change in viscosity is greater than in water content.

During bio-oil storage the chemical composition changes towards thermodynamic equilibrium this result in changes to the viscosity, molecular weight and co-solubility Diebold and Czernik, 1997; Oasmaa et al., 2003). Ideally a bio-oil should be single phase, but during storage the bio-oil can separate into two phases (refer to Section 2.9.1), which can be classified into water soluble and water insoluble categories. The water-soluble phase of most bio-oils is composed of lighter organic compounds while the water insoluble phase is composed of larger and heavy compound commonly referred to as pyrolytic lignin (Sipila et al., 1998).

Diebold, (2000) reported that chemical reactions taking place during bio-oil aging change the polarity of the bio-oil components because certain reactions taking place produce water and compounds which are relatively nonpolar, therefore the overall water content is increased, and the overall polarity of the organic content is decreased. This leads to an increased potential of phase separation occurring with the aged bio-oil (Diebold, 2000). Aging of bio-oil leads to formation of larger molecules (increase in molecular weight), this also increases the potential of phase separation as the compounds decrease in solubility (Yu et al., 2007). Literature studies reported that the bio-oil can phase separate into a low viscosity aqueous phase and a high viscosity organic phase (Oasmaa and Czernik, 1999; Diebold, 2000; Lu et al., 2008) (refer to Section 2.9.1).

Diebold, (2000) reviewed several general chemical reactions which are thought to take place during bio-oil aging in a mixture of over 400 organic compounds and reported that some of these reactions require a catalyst to take place, so depending on the amount of char (the inorganic content) found within the bio-oil can have a direct effect on the aging progress of bio-oil. Below is a list of the general chemical reactions thought to take place during bio-oil ageing as reported by Diebold, (2000):

- organic acids react with alcohols to form esters and water
- organic acids react with olefins to form esters
- aldehydes react with water to form hydrates
- aldehydes react with alcohols to form acetals and water
- aldehydes react with phenolics to form resins and water
- aldehydes react with proteins to form oligomers
- unsaturated compounds to form polyolefins
- air oxidation to form acids

There is no standard method for measuring stability of bio-oils, but a simple test has been developed that can be used to compare bio-oil sample stability (Diebold and Czernik, 1997; Sipilä et al., 1998; Elliott et al., 2012). In the test, 45 ml of bio-oil in a 50-ml bottle is kept at 80 °C for 24 hours as this is claimed to simulate one-year storage at ambient temperature. The increase in viscosity (measurement temperature at 40 °C) and water content is measured so that the stability of bio-oil can be determined. Special care has to be taken in handling, transportation, storage and bio-oil use due to its instability

2.11 Summary

This chapter has introduced the major constituents of MSW and their thermal decomposition behaviour under pyrolysis conditions. Different ash control methods used to reduce the inorganic content in MSW have been reviewed and explained. Pyrolysis allows the utilization of all carbon-containing materials both organic and inorganic as opposed to commonly used biological methods of waste disposal. Fast pyrolysis is more complicated, but the addition of inorganic waste (plastics, artificial textiles, tyres) results in improved product quality: gas contains more light hydrocarbons and less CO_2; liquid contains a lower aqueous fraction and a greater oil fraction and has a better heating value. The combination of organic and inorganic waste occurs in MSW; thus, pyrolysis is a favourable method for waste treatment. An extensive literature review has been undertaken on previous research into the pyrolysis behaviours of MSW and it was found from comparisons with previous research that even similar components of MSW can show a variation in composition. MSW has a heterogeneous nature which causes significant problems for EfW technologies.

This chapter has also explained in detail the process parameters and factors required for optimal operation of any fast pyrolysis process. The particle size of MSW has been found to be important and can have a significant effect on results. This has shown the importance of using a consistent particle size to aid comparison of the behaviours of different components of MSW. The moisture content of MSW has also been found to be an important consideration as it can have detrimental effects on the quality of the fuel and the efficiency of the process. The loss of mass of all MSW components has been found to vary significantly with the pyrolysis temperature and difference in component. The reduction in mass occurs over a wide temperature range of approximately 160 – 800 °C (Faravelli et al., 2003; Wu et al., 2003; Heikkinen et al., 2004; Ahmed et al., 2009; Skreiberg et al., 2011; Kumar et al., 2013; Chen et al., 2014; Chen et al., 2014). The pyrolysis temperature has also been found to have a significant effect on the pyrolysis products and the composition of the gas produced. The main gaseous products from the pyrolysis of MSW have been found to mainly consist of CO and CO_2 with smaller quantities of H_2, CH_4 and lighter hydrocarbons.

An increase in pyrolysis temperature has been found to lead to an increase in the production of CO and H_2 and in some instances a decrease in the production of CO_2 (Wu et al., 2003; Ahmed et al., 2009; Singh et al., 2012). The pyrolysis of plastics has been found to be complex and varied. The pyrolysis of HDPE produced no CO or CO_2 (Mastral et al., 2003) and the main gases produced from the pyrolysis of PVC were found to be hydrochloride and C_6H_6 (Zhou et al. 2014). The pyrolysis of mixed MSW showed that interactions of similar components such as paper, biomass and food waste were small (Skreiberg et al., 2011) but interactions between plastics and biomass or paper fractions were significant.

Pyrolysis gives ready-to-use fuels in an easy and safe way. Usually gas and/or char are used as a source of energy, because energy is the easiest product to utilize and sell. Liquid products from pyrolysis of MSW are very complex and usually contain water. However, the thermal decomposition of polymers produces oils with good qualities, which can be used both as a liquid fuel and as a source of chemicals. Additionally, after quality control and/or some improvement char can be used as activated carbon or fertilizer. A wide range of research has also been undertaken using laboratory scale pyrolyser. Comparisons between the results of these investigations can be difficult due to differences in the processes and equipment used however these investigations makes it easier to represent the heterogeneous nature of MSW as a fuel.

Following this literature review, it has been concluded that further research is necessary in order to optimise the fast pyrolysis processes using trommel fines as a fuel. The characteristics of the inert materials in trommel fines, particularly the particle size, brittleness and hardness, need to be considered to minimize the adverse effects on the fast pyrolysis process and products. This would lead to an increase in process efficiency and to maximise the calorific value of the produced products. In this study, an experimental investigation of the influence of temperature, moisture content and pre-treatment methods on the fast pyrolysis products of trommel fines has been undertaken. A laboratory scale bubbling fluidised bed fast pyrolysis rig was used to address a range of conditions.

3 Experimental Methods

This chapter gives an overview of the source and characterization of the MSW raw trommel fines feedstock used during this research. Due to its heterogeneous nature, a wide range of pre-processing techniques were employed to obtain appropriate sample sizes for analytical characterization of the physio-chemical properties of the feedstock. The details of the analytical techniques and procedure used for characterization of the raw feedstock, derived size-fractions and the fraction suitable for thermochemical processing are contained in this chapter. In addition, the 300 g h^{-1} bench scale bubbling fluidised bed fast pyrolysis reactor used for fast pyrolysis during this work is described as well as major modifications carried out on the system to enable the processing of MSW trommel fines. Lastly, methods used to characterise the fast pyrolysis products are also described. Results are presented in subsequent chapters.

3.1 Trommel fines feedstock

The sample used in this study was supplied by a UK-based commercial waste management company – Biffa Ltd from Leicester. The sample supplied was reportedly obtained from household waste after mechanical removal of most of the metals, glass, and plastics material, etc. The materials represent the ‘unders’ obtained after passing the shredded household waste through a 10 mm trommel screen installed in a rotary drum (Figure 3.1). Based on size range and apparent composition of various admixture of components of municipal solid waste, this feedstock has been classified as trommel fines (Fitzgerald, 2013; Pitchell, 2014).

The typical composition of trommel fines depends on the initial type and composition of MSW, the severity of mechanical processing of the MSW and the design of the trommel screens used. Thus, trommel fines can contain a wide variety of the characteristics of different components in the waste. To determine the suitability of the trommel fines feedstock for thermal recovery via fast pyrolysis, a range of process and analytical methods would be required. Due logistic issues, it was decided at the beginning of this work to prepare the trommel fines to meet the technical requirements of the feeding system and operation on an existing fluidised bed reactor in European Bioenergy Research Institute (EBRI).

Figure 3.1: Trommel fines feedstock as received (<10 mm size range).

3.1.1 Size distribution of ‘as-received’ trommel fines

Due to the variable sizes of particles in the trommel fines (<10 mm), initial work was carried out to determine its size distribution using a system of sieves (Figure 3.2). In the procedure, the ‘as- received’ trommel fines feedstock was dried, sampled (five replicate 0.5 kg samples) and sieved to determine the size distribution. Prior to sieving, the feedstock was dried in the oven at 60 °C for 24 h. The sieve analysis was carried out according to ASTM D 422 standards (ASTM, 2007) using a set of sieves of different aperture sizes (0 mm to 3.5 mm) and Powermatic Sieve Shaker to separate the sample into different size-fractions as follows: (<0.25 mm; 0.25 -1 mm; 1 – 2 mm, 2 -3.5 mm and > 3.5 mm.

Previous work using the existing fluidised bed reactor had indicated that the suitable size of feedstock for the feeding systems should be between the 0.25 – 2 mm range (Kalgo, 2011; Banks et al., 2014). Therefore, the focus of the sieving process was to quantify the size fraction (0.25 – 2 mm) and to determine the fractions that needed further physical processing (e.g. size reduction) as described in Section 3.2 for all size fractions greater than 2mm.

Figure 3.2: Powermatic sieve shaker with 0-3.5 mm sieve stack (Source: EBRI Biomass storage room)

A mass balance of the sieving process was calculated based on mass of dry trommel fines feedstock sieved and the sum of the wt.% of the different size fractions obtained. Table 3.1 below shows an example of experimental raw data for ‘as received’ sample size distribution analysis and the wt.% of each size fraction and mass balance was calculated using Eq. 3.1 and Eq. 3.2 below. The average and standard deviation (SD) are reported and discussed in subsequent chapters. A standard deviation greater than 5 from the same procedure, highlights the heterogeneous nature of the sample.

Table 3.1: Reproducibility data for as received sample size distribution analysis

Sample ID	**1.1**		**1.2**		**1.3**		**1.4**		**1.5**		**AVERAGE**		
Sieve Size (mm)	**wt (g)**	**wt. %**	**wt (g)**	**wt. %**	**wt (g)**	**wt. %**	**wt (g)**	**wt. %**	**wt (g)**	**wt. %**	**wt (g)**	**wt. %**	**Standard deviation**
3.5 Above	295.20	59	354.00	71	314.90	63	343.30	69	265.60	53	314.60	63	6
2 - 3.5	60.97	12	91.28	18	93.95	19	65.56	13	133.80	27	89.12	18	5
1 - 2	51.61	10	31.42	6	46.43	9	44.14	9	45.31	9	43.78	9	1
0.25 - 1	53.20	11	16.16	3	27.04	5	29.39	6	35.65	7	32.29	6	2
0 - 0.25	37.16	7	5.79	1	16.60	3	15.54	3	16.43	3	18.30	4	2
TOTAL	**498.1**	**100%**	**498.6**	**100%**	**498.9**	**100%**	**497.9**	**100%**	**496.8**	**100%**	**498.1**	**100%**	

$$\text{Size fraction [wt\%]} = \frac{\text{mass of size fraction}}{\text{total mass of feed used}} \text{ x } 100 \qquad \textbf{(Eq. 3.1)}$$

$$\text{Mass balance} = \sum \text{wt\% of different size fractions} \qquad \textbf{(Eq. 3.2)}$$

3.2 Feedstock preparation by size reduction and separation

The trommel fines sample came in different forms, shapes and sizes (Figure 3.1). It was necessary that the feedstocks be processed due to limitations of the feeding system of the fast pyrolysis unit (refer to section 3.5). It was also necessary for the feedstock particles to be of certain sizes for analytical studies. To ensure that the trommel fines sample met the particle size requirements of the fluidised bed reactor, the schematic flow diagram in Figure 3.3 was designed to prepare the sample for fast pyrolysis.

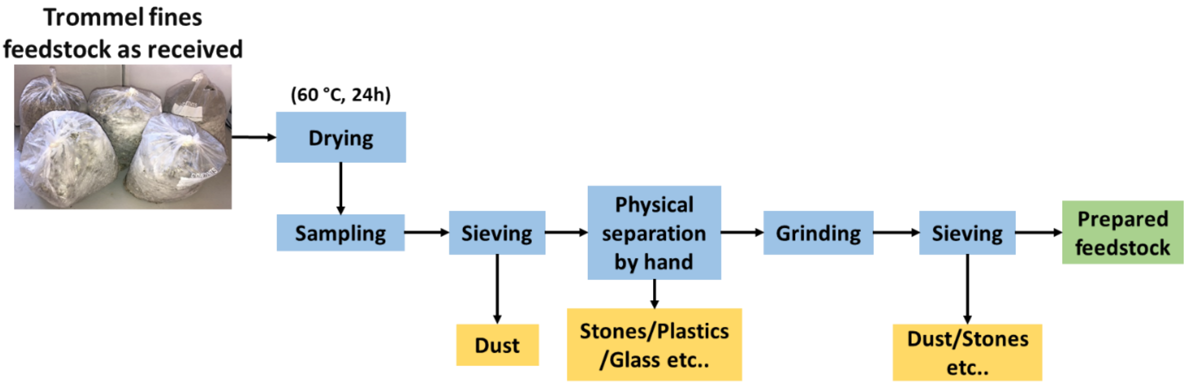


Figure 3.3: Block flow diagram for trommel fines physical pre-treatment feedstock preparation

3.2.1 Sampling

The heterogeneous nature of the feedstock could impact on the integrity of characterisation results and analytical pyrolysis involving small amounts of feedstock. The coning and quartering method (Gerlach et al., 2002) was used to obtain a 3 kg representative sample of the raw trommel fines feedstock and all the analyses were based on a sample batch (Figure 3.4). The method, which is used for sampling large quantities of material, consists of pouring the dried trommel fines into a conical heap upon a solid surface and dividing the heap by a cross. The two opposite corners are taken as the sample and the other two set aside. This sampling method reduces the deviation that may be caused when using a heterogeneous sample.

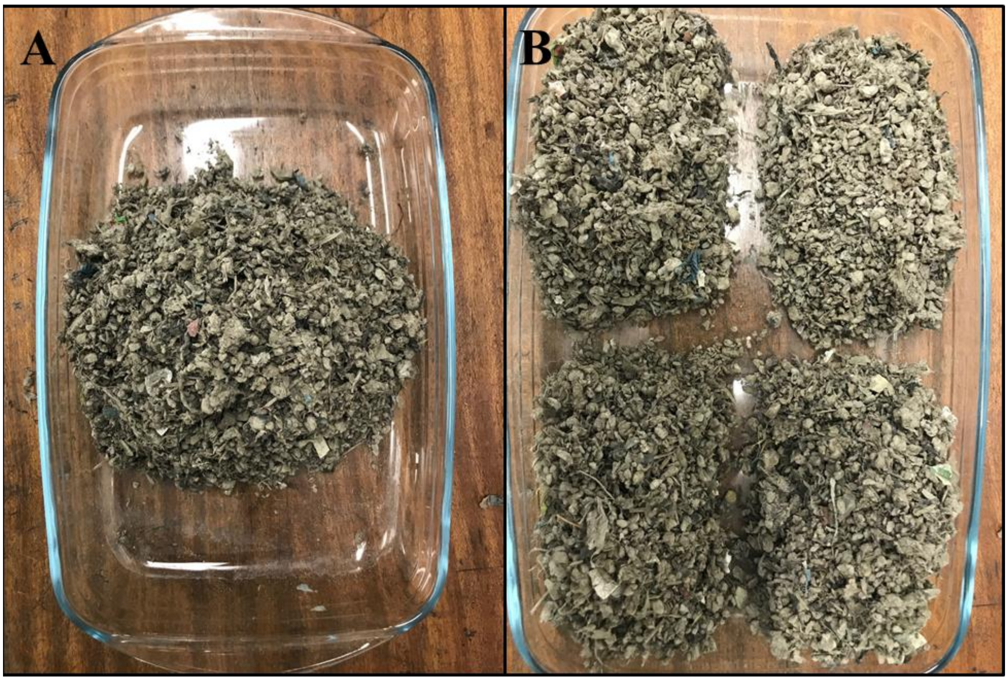


Figure 3.4: Photographs of trommel fines sampling; A: conning of trommel fines; B: quartering of trommel fines

3.2.2 Manual separation

In order to further make the experimental sample more representative of the bulk feedstock, the sampled feedstock was then subjected to size reduction via grinding. Preliminary grinding test of the feedstock proved a challenge as the inorganics, and plastics caused a blockage in the grinding mill as shown in Figure 3.5. To aid the grinding process a manual separation step was added to the feedstock preparation steps, which involved the removal, by hand, of visible glass, stones, metal and plastics from the feedstock fraction with size range > 2 mm. This step did not remove the entire inorganics and plastics present, but was found to be beneficial for the grinding process (Figure 3.6). Although this step can be achieved for a laboratory scale process, a more suitable method such as mechanical sorting would be needed for an industrial scale process. In such a situation, the recovered plastics and organic-based materials could be used for RDF production. The removal of hard materials (stones and concrete) would reduce the abrasive wear and tear of processing equipment (e.g. pyrolysis reactors or gasifiers) as well as the blocking of moving parts such as auger reactor feed systems.

Figure 3.5: Retsch SM 2000 grinding mill: - A: blockage to mill blade caused by inorganics and plastics. B: inorganics and plastics removed from grinding mill (Source: EBRI Biomass storage room)

Figure 3.6*:* Photographs of trommel fines after manual separation; A: trommel fines (<2mm) for grinding after manual separation of inorganics and plastics; B: manually separated plastics and textiles; C: manually separated glasses and large stones (inorganics)

A mass balance of the manual separation process was calculated based on mass of dry trommel fines feedstock used and the sum of the wt. % of the different fractions separated. The wt.% of each separated fraction was calculated using Eq. 3.3 and Eq.3.4 below.

$$\text{Separated fraction [wt\%]} = \frac{\text{mass of fraction}}{\text{total mass of feed used}} \text{ x } 100 \qquad \textbf{(Eq. 3.3)}$$

$$\text{Mass balance } = \sum \text{wt\% of separated fractions} \qquad \textbf{(Eq. 3.4)}$$

3.2.4 Grinding

The dried feedstock (Figure 3.6A) was ground with a Retsch Ltd., Germany, Heavy-Duty Cutting Mill, Type SM2000 with interchangeable screens of varying sizes (1-10 mm), after manual removal of large stones and glasses, textiles and plastics. The choice of screen was based on the feeding requirement of the fast pyrolysis reactor which are limited to <2 mm to prevent blockages and feeding problems during fast pyrolysis experiments and to bring the feedstock particles to the optimum pyrolysis temperature and minimize exposure to lower temperatures which favour the formation of char (Bridgwater, 2012). After grinding, random samples were taken from the feedstock particles. For analytical experiments and characterization methods requiring small amounts, up to 5 mg of the ground sample was obtained.

3.3 Ash content reduction by agitated washing and sedimentation

The inorganic content of trommel fines sample (stones, aggregates, glass and soil) has been shown to cause blockages to the grinding mill (refer to section 3.2.3) and represent to the ash content of the feedstock after grinding (refer to section 4.1.1). The inorganics in the trommel fines feedstock will lead to an increase in volume and weight of bed material in the pyrolysis process and can influence the yields of pyrolysis products. For example, depending on the chemical composition of the ash, it can promote the formation of solids and gas at the expense of pyrolysis liquid yield. (Hodgson et al., 2010; Teng et al., 1998; Varhegyi et al., 1989; Sekiguchi et al., 1984). The inorganics also tends to contaminate the liquid and solid fractions (Bernardo et al., 2010; Yuan et al., 2014; Gao et al., 2016a, b) thus, highlighting the need for a more plausible way to further separate the inorganics in the trommel fine feedstock at smaller size fraction to further reduce the ash content and increase the volatile content of the feedstock. The schematic flow diagram in Figure 3.7 was designed to involve a sedimentation process to recover inorganics from the feedstock and reduce the ash content of material for fast pyrolysis. The eventual prepared feedstock from this process was designated as physically-treated (PT) trommel fines.

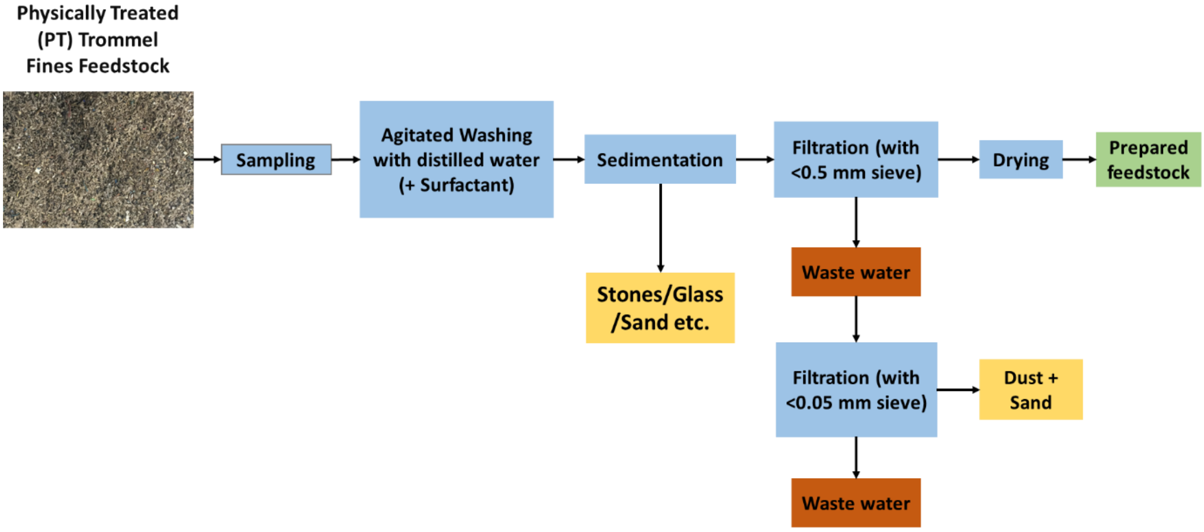


Figure 3.7: Block flow diagram for agitated washing and sedimentation pre-treatment feedstock preparation

3.3.1 Agitated washing and sedimentation

Using distilled water to wash solid waste materials can be used to reduce the ash content of a feedstock, thus can be applicable to trommel fines. Literature studies have shown, that the removal of majority of soluble alkali metals is simple to achieve with water-washing and are more efficient when the wash is agitated (Jenkins et al., 1996; Baxter et al., 1998; Fahmi et al., 2007). Ash content due to soil contamination can be expected to be removed even though it tends to be insoluble (Fahmi et al., 2007). Literature has also shown that the addition of a surfactant can further reduce the ash content of the feedstock (Ying et al 2002; Coulson and Bridgwater 2009; Jamur et al 2010).

Two different ash reduction methods were used based on the two solvents below:

1. 100% distilled water
2. 99 vol. % distilled water + 1.00 vol. % Decon Neutracon surfactant.

In the procedure, physically pre-treated (PT) trommel fines batches of 300 g (dry basis) were separately washed with 3 litres each of 100% water and the solution of water and 1.00 vol.% Decon Neutracon surfactant, respectively. The washing was carried by adding the PT trommel fines into a large laboratory bucket and then the solvent added. The mixture was stirred for 30 mins at room temperature with a metal bar. The batches were then left to sediment for 1 hour so that the heavy fraction of the inorganics (stones, glass, sand, etc.) present in the feedstock could settle at the bottom allowing for them to be separated (Figure 3.8A). To accumulate sufficient pre-treated feedstock material for a fast pyrolysis experiments, duplicate washings were carried for both washing methods and the feedstock materials were combined.

A code was assigned to each different ash reduction method:

AW – Agitated washing (100% distilled water)

AWS – Agitated washing with surfactant (99% distilled water + 1.00 vol. % Decon Neutracon surfactant)

3.3.2 Filtration

After the sedimentation process (Figure 3.8A) the batch was then filtered using a 0.5 mm sieve tray placed over an empty bucket and a bowl. The bowl was used to scoop the suspended feedstock particle from the batch and poured through the sieve tray to recover the trommel fines feedstock size range suitable for fast pyrolysis (0.5-2 mm) until the settled inorganics became visible in the batch (Figure 3.8B). The bucket was used to recover the waste water. The recovered trommel fines feedstock was air dried for 24 hours and then dried in a Swallow oven at 60 °C ± 1 °C for 48 hours.

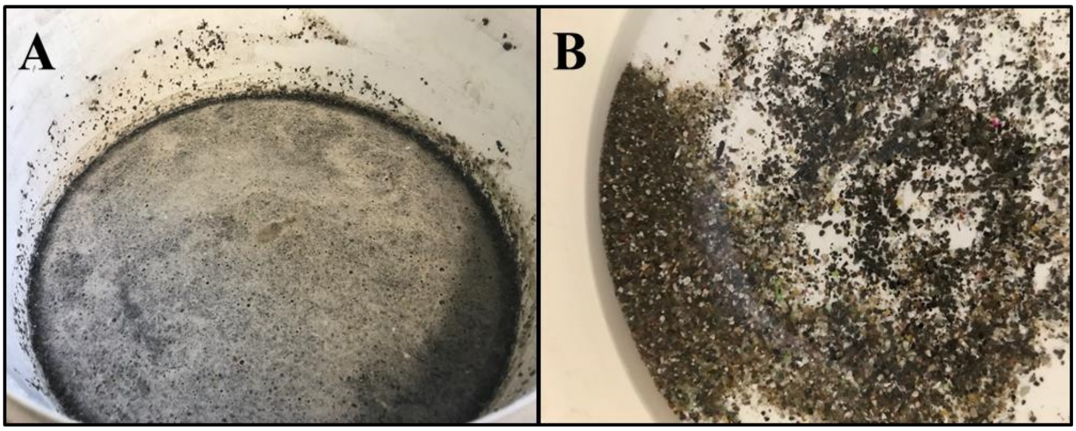


Figure 3.8: Photographs of sedimentation process; A: sedimentation of trommel fines feedstock (0.5-2 mm); B: inorganics after sedimentation and filtration.

3.3.3 Determination of suspended solids in waste water

The recovered waste water was further filtered using a 0.05 mm sieve tray to recover the suspended solids in the waste water (Figure 3.9). The recovered suspended solids were air dried for 24 hours and then dried in a Swallow oven at 60 °C ± 1 °C for 48 hours.

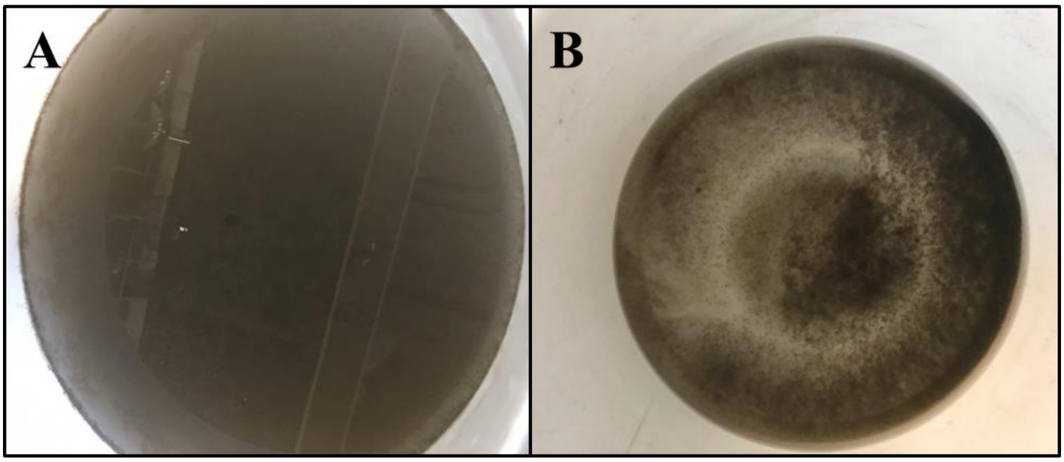


Figure 3.9: Photographs of recovered waste water; A: waste water before second filtration; B: recovered dust and sand from filtration of waste water

3.3.4 Determination of dissolved solids in waste water

Three different 100 ml samples of each of the waste water recovered after the second filtration and using the 0.05 mm sieve from the different method were evaporated using a water bath for 3 hours and then dried in a Swallow oven at 60 °C ± 1 °C for 24 hours. The aim was to quantify the amount of dissolved solid in the waste water.

A mass balance of the washing process was calculated based on mass of trommel fines feedstock used and the sum of the wt. % of the different fractions recovered. The wt. % of each recovered fraction was calculated using Eq. 3.5 and Eq. 3.6 below.

$$\text{Recovered fraction [wt\%]} = \frac{\text{mass of fraction}}{\text{total mass of feed used}} \text{ x } 100 \qquad \textbf{(Eq. 3.5)}$$

$$\text{Mass balance } = \sum \text{wt\% of recovered fractions} \qquad \textbf{(Eq. 3.6)}$$

3.4 Feedstock characterisation methods

The fast pyrolysis process is affected by the characteristics of the feedstock (Miskolczi et al. 2013). The moisture content of the feedstock is a major parameter that influences the product water and composition of the bio-oil product (Miskolczi et al. 2013). The particle size distribution influences the reaction times for complete thermal decomposition of the feedstock particles (Luo et al. 2010). The volatile matter content of the feedstock will influence the product yields of any pyrolysis process (Zhou et al. 2013). The ash content may impact side reactions and act as a catalyst for unwanted reactions that impact negatively on oil product quality and yields (Bernardo et al., 2010; Yuan et al., 2014; Gao et al., 2016a, b). For these reasons, it is important to characterise the feedstocks both physically and chemically so that reasonable conclusions can be drawn from experimental results. The 'as-recieved' trommel fines samples and the different size range fractions from the physical and aggitated washing and sedimentation pre-treatment procedures were analysed to determine their physico-chemical properties. Due to the heterogenous nature of the sample, the coning and quartering method (Gerlach et al., 2002) was used to obtain 100 g batch samples from the as received sample, physical pre-treated feedstock particle size fractions of <0.25 mm, 0.25 – 2 mm, 2 – 3.5 mm and 3.5 mm above, AW and AWS. Five replicate analyses were also carried out to account for sample varaiation, for which standard deviations were derived.

3.4.1 Proximate analysis

The proximate analysis of samples involved the determination of the moisture, ash, volatile matter and fixed carbon contents. The moisture contents were determined according to ASTM E1756-01 principles on a dry basis (ASTM, 2007b) and Eq. 3.7. The percentage weight loss on a dry weight basis of a pre-weighed sample heated at 105 °C to constant weight was recorded. Using the cone and quartering method, five aluminum boats with 4 – 5 g of the trommel fines sample were placed in an oven at 105 °C for 6 h. The samples were then cooled in desiccators and re-weighed. The process was repeated hourly for each sample until constant weight was achieved. The average of five samples was taken to further reduce the deviation. Table 3.2 below shows an example of experimental raw data for sample moisture content.

Table 3.2: Reproducibility data for moisture content determination in trommel fines sample

Sample ID	**Initial Boat wt. (g)**	**Boat + wet TF wt. (g)**	**Constant wt. @ 105 ° C (g)**	**Wt. of wet TF (g)**	**Wt. of dry TF (g)**	**Dry TF (wt. %)**	**Moisture Content (%)**
1.1	0.97	5.43	4.92	4.46	3.95	88.55	11.45
1.2	0.97	5.5	4.78	4.53	3.82	84.24	15.76
1.3	0.97	5.33	4.75	4.37	3.78	86.58	13.42
1.4	0.96	4.86	4.31	3.9	3.35	85.9	14.1
1.5	0.97	4.52	4.13	3.55	3.16	88.92	11.08
AVERAGE %							**13.16**
STANDARD DEVIATION							**1.93**
TF – Trommel fines							

$$\text{Moisture content} = \left(1 - \frac{\text{wt of dry TF}}{\text{wt of wet TF}}\right) \text{x } 100 \qquad \textbf{(Eq. 3.7)}$$

The ash contents were determined according to the ASTM E1755-01 method (ASTM, 2007c). Five crucibles and lids were put in a Carbolite AAF1100 furnace and heated to 900 °C for 3 h; crucibles were then removed from the furnace and cooled in a desiccator (Figure 3.10). The crucible weights were recorded and then approximately 4 - 5 g of dried feedstock was weighed into each crucible. The crucibles and samples with their lids placed at an angle were placed in a furnace and heated to 250 °C at 10 °C min^{-1} and held for 30 min, then increased to 575 °C for 5 h. After 5 h, the crucibles were removed and cooled in a desiccator for one hour. Each crucible was weighed to the nearest 0.1 g. Crucibles were replaced in a furnace and heated at 575 °C for 1 h periods until the crucible weigh was constant to within 0.3 g. The ash content was then obtained by dividing the weight of the samples by the pre-drying weight and expressed as a percentage of the original weight. The average of five samples was taken to further reduce the deviation. Standard deviation >5% highlights the heterogeneous nature of the sample. Refer to Table 3.3 below which shows an example of experimental raw data of a sample's ash content and Eq. 3.8 was used to calculate the ash content.

Table 3.3: Reproducibility data for ash content determination in trommel fines

Sample ID	**Mass of Crucible (g)**	**Mass of Crucible + Sample (g)**	**Mass of dry Sample (g)**	**Mass of Crucible + Sample After ashing (g)**	**Ash Content (g)**	**Ash Content (%)**
1.1	11.15	15.31	4.16	13.38	2.22	53.48
1.2	8.03	12.15	4.13	10.47	2.44	59.12
1.3	7.95	11.97	4.02	10.08	2.13	52.85
1.4	8.44	12.49	4.05	10.84	2.40	59.29
1.5	7.41	11.53	4.12	9.23	1.82	44.09
AVERAGE %						**53.77**
STANDARD DEVIATION						**6.20**

$$\text{Ash content [\%]} = \frac{\text{Ash content (g)}}{\text{Mass of dry sample (g)}} \text{ x } 100$$ **(Eq. 3.8)**

Volatile matter was obtained on a moisture free basis. Volatile matter is the weight loss resulting from heating the sample under controlled conditions. The volatile content of the sample is taken as the weight loss at 950 °C (ASTM D3175-89) for 7 min (ASTM, 1997). Five crucible weights were recorded and then approximately 4 to 5 g of dried feedstock was weighed into each crucible. The crucibles and samples with their lids fully sealed were placed in a Carbolite AAF1100 furnace and heated to 950 °C and held for 7 min (Figure 3.10). Upon completion the oven was turned off the crucibles were removed and cooled in a desiccator. Each crucible was weighed, and the average of five samples was taken to further reduce the deviation. Table 3.4 below shows an example of experimental raw data for a sample's volatile content and Eq. 3.9 was used to determine the volatile content. The fixed carbon value was obtained by difference.

Figure 3.10: Carbolite AAF1100 furnace, desiccator and crucibles used for proximate analysis during this research (Source: EBRI Industrial Laboratory 02)

Table 3.4: Reproducibility data for volatile matter determination in trommel fines sample

Sample ID	Mass of Crucible (g)	Mass of Crucible + Sample (g)	Mass of dry Sample (g)	Mass of Crucible + Sample After Heating (g)	Content left wt (g)	Volatile matter (%)
1.1	11.15	16.13	4.98	14.29	1.84	37.05
1.2	8.03	13.31	5.29	11.19	2.12	40.20
1.3	7.95	13.07	5.12	11.08	1.98	38.74
1.4	8.44	13.38	4.93	11.15	2.22	45.06
1.5	7.41	12.35	4.93	10.42	1.93	39.13
AVERAGE %						**40.04**
STANDARD DEVIATION						**3.03**

$$\text{Volatile matter } [\%] = \frac{\text{Volatile matter wt (g)}}{\text{Mass of dry sample (g)}} \text{ x } 100 \qquad \textbf{(Eq. 3.9)}$$

3.4.2 Elemental analysis

A Carlo-Erba 1108 Elemental Analyzer was used to determine the elemental composition of a sample in terms of carbon, hydrogen and nitrogen. Other elements sometimes included in the analysis include, sulphur and oxygen; oxygen is often determined by percentage difference (Aiken, DeCarlo and Jimenez, 2007). Using the cone and quartering method, five different 5 g samples were dried in the oven at 60 °C for 24 h prior to analysis and were ground using a coffee grinder. The cone and quartering method was used again to obtain about 1 g from each of the grounded samples for analysis. The results are reported on a dry basis to avoid reporting moisture as additional hydrogen and oxygen (Stahl et al., 2004). The average of five samples was taken to further reduce the deviation. Table 3.5 below shows an example of experimental raw data for a sample's ultimate analysis.

Table 3.5: Reproducibility data for ultimate analysis of trommel fines sample

Sample ID	**C (wt. %)**	**H (wt. %)**	**N (wt. %)**	**S (wt. %)**	**O* (wt. %)**
1.1	34.1	5.2	4.8	0.5	19.2
1.2	32.3	6.5	3.9	0.3	20.8
1.3	35.3	4.3	2.9	0.3	20.9
1.4	37.6	4.8	1.5	0.2	19.7
1.5	40.2	4.7	4.5	0.1	14.3
Average	**35.9**	**5.1**	**3.5**	**0.3**	**19.0**
Standard Deviation	**2.8**	**0.7**	**1.2**	**0.1**	**2.4**
C – Carbon; H – Hydrogen; N – Nitrogen; S – Sulphur; O – Oxygen; * Calculated by difference					

3.4.3 Calorimetry

The bomb calorimeter experiment is the standard method (ASTM D2015) used to determine the higher heating value for a sample (ASTM, 2000). Results obtained from the bomb calorimeter experiment indicate the samples higher heating value (HHV). Using the cone and quartering method five different 5 g samples were dried in the oven at 60 °C for 24 h prior to analysis. The cone and quartering method was used again to obtain approximately 1 g each from the 5 five different samples, which was burnt completely in an excess oxygen environment in a steel vessel, which is called a bomb using an IKA C1 calorimeter. The reaction takes place at constant volume (Figure 3.11). The average of five samples was taken to further reduce the deviation. Refer to Table 3.6 below which shows an example of experimental raw data for bomb calorimeter experiment.

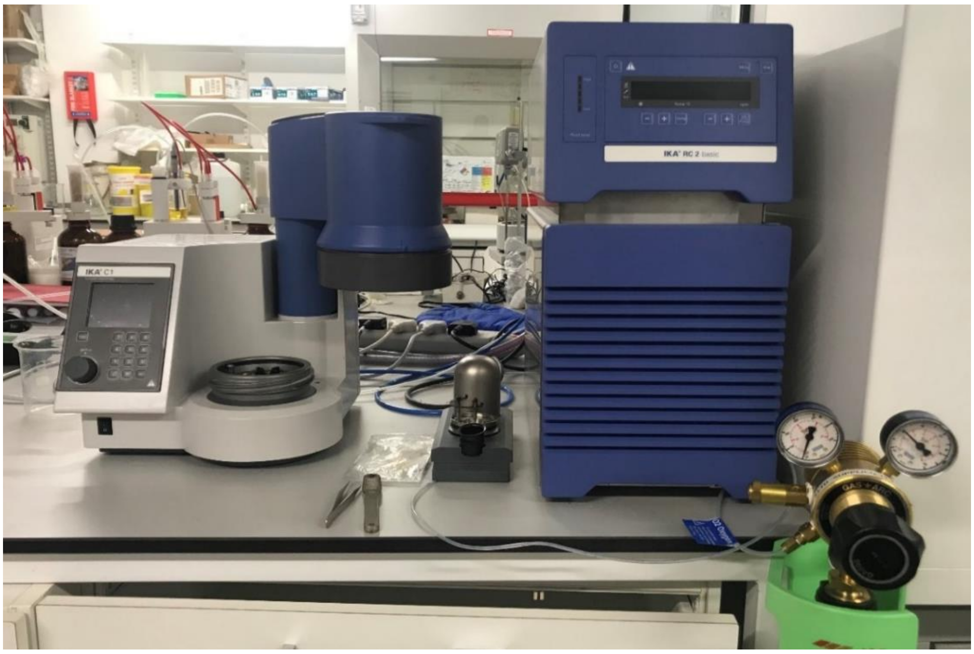


Figure 3.11: Bomb Calorimeter used during this research (Source: EBRI Syngas Laboratory)

Table 3.6: Reproducibility data for calorific value determination in trammel fines sample using bomb calorimetry

Sample ID	Mass of Sample (g)	Heating Value (MJ kg^{-1})
1.1	0.88	7.06
1.2	0.81	9.08
1.3	0.9	7.07
1.4	0.86	8.24
1.5	0.83	7.44
AVERAGE		**7.78**
STANDARD DEVIATION		**0.87**

In addition, a mathematical equation (Eq. 3.10) correlated from the proximate analysis of different biomass from the literature (Parikh, Channiwala and Gosal, 2004) was used to calculate the heating value on a dry basis. The calculated (Eq. 3.10) and experimental HHV would be displayed for comparison in the subsequent chapters.

$$\text{Feedstock HHV (dry)} = 0.3536\ \text{FC} + 0.1559\ \text{VM} - 0.0078\ \text{A}\ [\text{MJ/kg}] \qquad \textbf{(Eq. 3.10)}$$

Where: FC = fixed carbon, VM = volatile matter, and A = ash content.

3.4.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is recognised as useful tool for determining kinetic and physical properties of fuels (William et al., 1994). A thermogravimetric analyser can measure the weight change of a given substance as a function of temperature and time (William et al., 1994) and can be used to simulate pyrolysis conditions.

To study pyrolysis under dynamic heating for the trommel fines feedstock (PT), a PerkinElmer Pyres 1 thermogravimetric analyser was used. A pyrolysis heating rate of 10 °C min^{-1}, was used to heat from ambient temperature to 550 °C in nitrogen flow of 30 mL min^{-1}. Using the cone and quartering method, five different 5 g samples were dried in the oven at 60 °C for 24 h prior to analysis and were ground using a coffee grinder. The cone and quartering method was used to obtain about 2 -3 mg from each of the five different grounded samples which was placed on a ceramic crucible on the analyser tray. The sample crucible was placed in a sensitive thermo-balance. The sample was subjected to heat from an external furnace to pre-set temperatures and heating rate. The weight loss because of thermal degradation was measured and recorded on the program software. All pyrolysis TGA experiments were conducted in an inert atmosphere of nitrogen, to simulate pyrolysis conditions. Each analysis was repeated 5 times. Figure 3.12 below shows an example of experimental raw data for PT trommel fines TGA analysis.

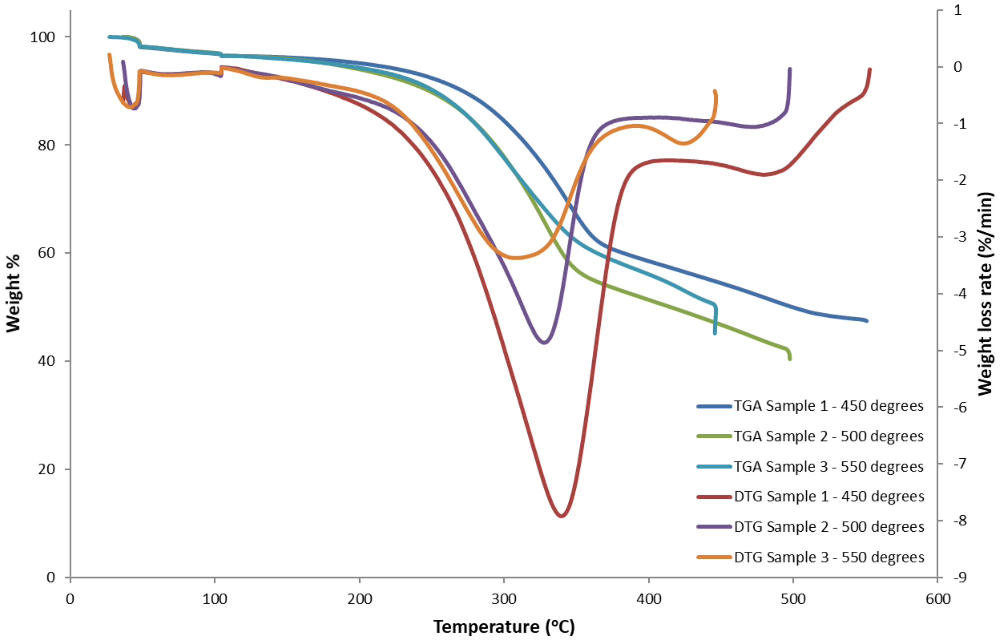


Figure 3.12: Reproducibility data for TGA and DTG curves of trommel fines

3.5 Fast pyrolysis rig

The fast pyrolysis experiments were carried out in a 300g h^{-1} continuous bubbling fluidised bed fast pyrolysis rig located in EBRI Industrial Laboratory 02. A flow sheet of the 300 g h^{-1} bubbling fast pyrolysis rig set-up is shown in Figure 3.13 and a photograph is shown in Figure 3.14 (Kalgo, 2011; Banks et al., 2014). The rig used for experiments is composed of three sections: the feeding system, the fast pyrolysis reactor and product collection. The feeding system used for this research is Ktron KT-20 gravimetric feeding system which consists of an air-tight hopper (Figure 3.13 - 1) with a nitrogen purge with a dual screw gravimetric feeding system with variable speed motor for feeding to the fast speed feed screw (Figure 3.13 - 2) which is water cooled at the feed point to minimise pre-pyrolysis. The feedstock feed rate can be adjusted using its computing system to adjust the speed of the feeding screw; the set feed rate is then displayed on the systems LED screen.

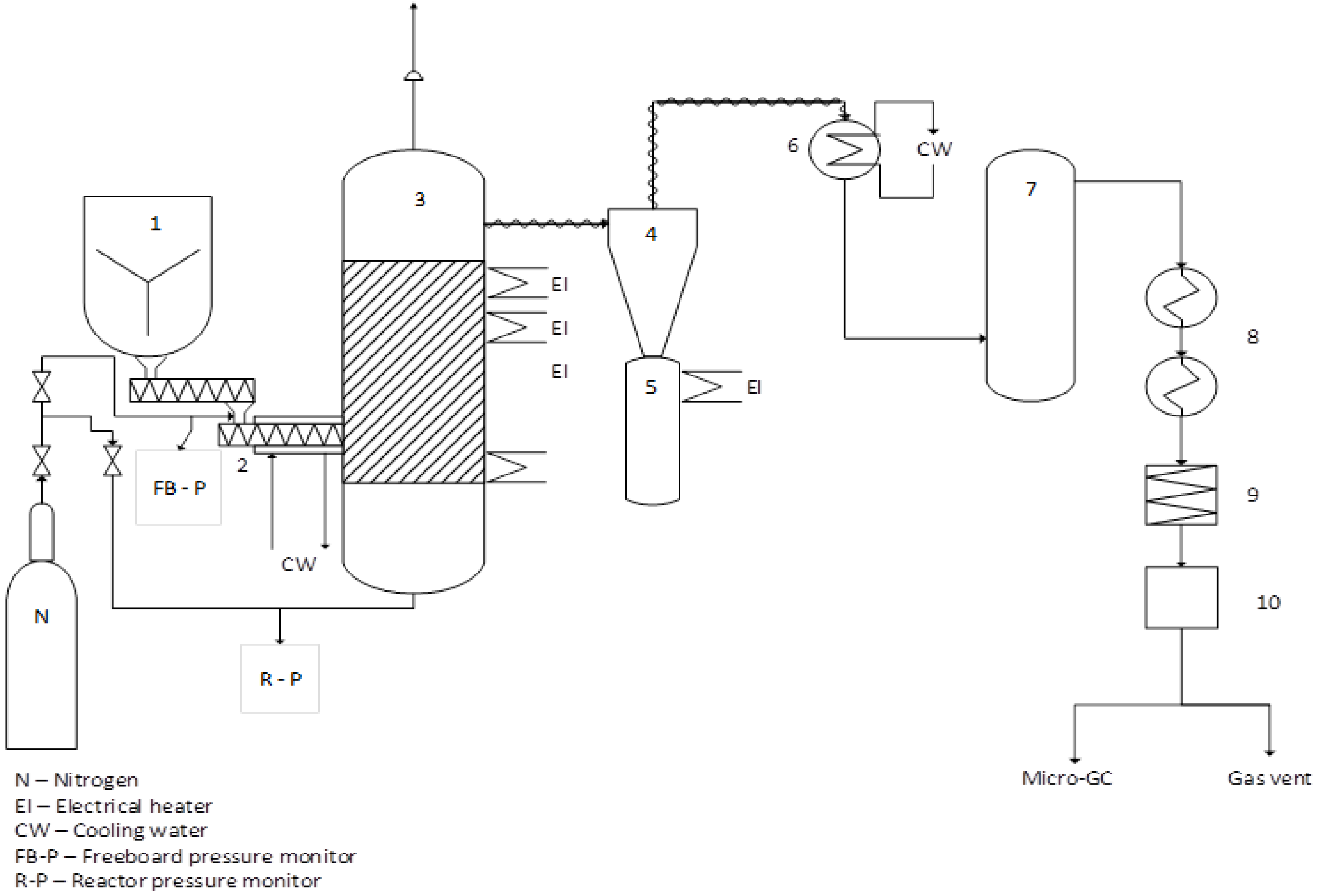


Figure 3.13: Schematic of initial set-up of the bench scale 300g h^{-1} bubbling fluidised bed fast pyrolysis rig

1 - feed hopper with twin screw feeder, 2 – fast screw, 3 – fluidised bed reactor, 4 – cyclone, 5 – charpot, 6 – water cooled condenser, 7 – Electrostatic precipitator (ESP), 8 – dry ice acetone condenser, 9 – cotton wool filter, 10 – gas meter

Figure 3.14: Photograph of 300 g h^{-1} fluidised bed fast pyrolysis unit at commencement of this research

The fluidised bed reactor is a steel tubular reactor (Figure 3.13 - 3), it has a height of 335 mm, and a diameter of 40 mm. The feed point is 41 mm above the distributor plate which has and average pore size of 0.1 mm. The reactor operates at a temperature of 500 – 700 °C and utilizes feedstock particle of 0.25 – 2 mm (Kalgo, 2011, Banks et al., 2014). The fluidised bed reactor has two inlets and one outlet. The first inlet supplies the feedstock particle into the reactor bed and the feed inlet is fitted with copper pipes used to pass cooling water to prevent pre-pyrolysis from occurring at the feed inlet. The second inlet into the reactor supplies nitrogen which serves as a fluidising agent and the outlet channels char and pyrolysis vapours out of the reactor.

The reactor bed material is 150 g of sieved quartz sand with a particle size between 500 – 600 µm. Silica sand was chosen as it is a very efficient heat transfer material due to its high solid density, it is also robust, thermally stable and cheap. Being thermally stable is important as the silica sand is burnt off after each experiment to remove char. The reactor was fluidised with three times the minimum fluidising velocity of sand (0.019 m s^{-1}) (Kalgo, 2011; Banks, 2014) with preheated nitrogen used on a single pass basis. A single pass basis was used so that the gas stream (nitrogen and product gas) can be analysed every 150 seconds, therefore the product gas composition can be studied at any point during a fast pyrolysis experiment.

Heat is supplied to the reactor using Watlow Starflow circulation heater capable of reaching 700 °C. The heating bands are fitted to the bottom and top sections of the reactor respectively to ensure even temperature distribution across the reactor. Temperatures were measured and recorded using three K-type thermocouples joined to a Microlink 751 ADC unit using Windmill data logging software. As the pyrolysis temperature needs to be regulated and controlled to a specific temperature range a few temperatures are monitored which include nitrogen pre-heater, fluidising gas before distributor plate, electric knuckle heaters (around the outside of reactor), bottom of reaction zone (T1) and middle of reaction zone (T2). System pressures are measured by analogue instrumentation at varying points, so that any blockages or leaks can be identified. The fluidised bed is also monitored to ensure it is operating suitably. The pressure differences were measured at the reactor outlet and freeboard in the reactor disengagement zone (FB). To minimise heat loss to the surrounding and prevent condensation of organic vapour that may cause blockage, the reactor as well as the metal transition pipe from the reactor outlet to the glass transition pipe inlet are properly insulated with fibre glass material. As the vapour and gas stream leaves the reactor it passes through a cyclone (Figure 3.13 - 4) where the char is separated into the char pot (Figure 3.13 - 5).

Following the cyclones, the vapours are condensed in a water-cooled condenser (Figure 3.13 - 6) where the pyrolysis vapour is quenched to form liquid. The water-cooled condenser is made up of concentric glass tubes, an inner one through which the hot gases pass, and an outer, "ported" chamber through which a cooling water passes, to reduce the gas temperature in the inner, to afford the condensation. An electrostatic precipitator (Figure 3.13 - 7) is used to collect liquid that remains in the vapour phase. It is made of Perspex, casing a stainless-steel plate that acts as appositive electrode within its wall. A high voltage wire (10 – 15KV) passed through the middle of the electrostatic precipitator serves as a negative electrode. The wire is held in place through the Perspex cover of the ESP. The aerosols upon entering the precipitator obtain a negative charge and are attracted to the positively charged stainless steel plate; the oil accumulates on the plate and eventually cascades to the oil collection tank aided by gravity. Majority of the liquid is collected in the electrostatic precipitator.

Following the electrostatic precipitator, the gas passes through two dry ice / acetone condensers (Figure 3.13 - 8) in series at -70 °C where lighter fraction oils are condensed which are later collected at the bottom of the condensers. The cotton wool filter (Figure 3.13 - 9) is used to trap lighter fraction and solids that might have escaped condensation in the water condenser and dry-ice condensers. After the cotton wool filter, the nitrogen carrier gas together with the non-condensable pyrolysis gases passes through the gas meter (Figure 3.13 - 10) where the volume of the exit gas is recorded. Then part of the gas mixture is pumped into an online Varian CP 4900 Micro-GC micro gas chromatograph with a thermal conductivity detector (TCD) and two columns (Varian CP-5A molsieve and CP-PortaPLOT) for interval analysis (every 150 seconds) of the non-condensable gases for each fast pyrolysis run and the excess gas are vented to the fume hoods.

3.5.1 Safety considerations prior to commissioning

Prior to commissioning the fluidised bed fast pyrolysis unit, it was essential to investigate, identify and familiarise myself with certain hazards associated with operating a fluidised bed fast pyrolysis unit. The operation of a fluidised bed fast pyrolysis unit can constitute hazards that may be categorised in to the following groups.

3.5.1.1 Toxic hazards

Fast pyrolysis units produce a certain number of hydrocarbons and other toxic compounds present in both the liquid and gaseous products. The product gas can contain high levels of carbon monoxide a colourless and odourless gas toxic to the human body in high proportions. The other gaseous components of the non-condensable pyrolysis gases such as hydrogen, carbon dioxide, nitrogen, and methane are less toxic than carbon monoxide but also pose risks to the human body if present in large enough quantities (Anon, 1971, 1975, 1987 and 1988). Other toxic hazards posed by products of the fast pyrolysis process come from the pyrolysis liquids and tars formed during the condensing of vapours. Certain compounds from the pyrolysis liquids have been directly linked to the cause of scrotum cancer (Anon, 1988).

Before running an experiment, the rig is purged with nitrogen to check for leaks. The liquid products produced are transferred into a sealed vessel and any sampling of the liquid are done in a fume cupboard with PPE worn always (refer to section 3.5.2.3). The non-condensable gases are transferred to the gas volume meter and then to the gas chromatograph used to analyse the composition of the gas products before they are sent to the nederman arm fume extractor through a pipe. The rig is surrounded by three nederman arm fume extractors.

3.5.1.2 Explosion and fire hazards

There is a fire and explosion risk associated with the fast pyrolysis process. The solid char products of the process are known to have the tendency to self-ignite if the conditions are suitable. This is particularly more likely if the char is of a finer nature. The presence of nitrogen as part of the gaseous products however reduces the risk of explosion and fire but does not completely mitigate the risk of occurrence.

An added fire hazard associated with the process is the presence and storage of the feedstock in the laboratory. The trommel fines feedstock are stored as directed on MSDS's in the freezer in Industrial Laboratory 01 located in the EBRI building. Only the required amount of feedstock is brought to the lab and removed directly after experiment (2 - 3 kg). This research does identify the risk of dust explosion although it can be said to be minimal. Dust is generated during grinding and sieving, and the quantities generated is not enough to pose the risk of an explosion. Feeding of the trommel fines can also generate dust but the feeder is mounted with a storage facility which is sealed and purged with nitrogen.

Pressure build up in the rig caused by feed blockage especially at the inlet to the reactor or pressure build up in the reactor can also lead to explosion and fire hazards. The reactor and the feed hopper are equipped with pressure monitors which are recorded every 5 minutes during an experiment and the reactor is also equipped with a bursting disc.

3.5.1.3 Hot surfaces

The fast pyrolysis rig is operated at temperatures of 400 °C and above which present a burn risk. Care needs to be taken to manage this risk. Heat resistant gloves are worn during experimental runs and no maintenance is done during runs. However, the reactor (Figure 3.13 - 3), cyclone (Figure 3.13 - 4), char pot (Figure 3.13 - 5), metal and glass transition pipes are all insulated using a BCTEX Fleece Mat 13 mm insulating material (max. operating temp.: 1000 °C) to reduce heat loss and keep external temperatures to a minimum.

3.5.1.4 Moving parts

The fast pyrolysis rig is fitted with a twin and fast screw which are constantly moving during experimental runs. Injuries can occur due to machinery becoming unreliable and developing faults or when machines are used improperly through inexperience or lack of training. No maintenance is done until all the moving parts have all come to rest and the whole system unplugged from the mains.

3.5.2 Safety precautions

Safety measures were taken in three categories to minimise the inherent dangers associated with a fast pyrolysis process. The precautions were introduced in three forms described below.

3.5.2.1 Incorporation of safety devices into the process

An assessment of the fast pyrolysis process areas most likely prone to pressure build up and blockages was undertaken. Based on this, relief valves are installed on the reactor and feed hopper. A relief valve was installed at the top of the reactor connected to the process vent line to vent any pressure build up in the reactor. Similarly, a relief valve was also installed on the feed hopper to vent any pressure that may build up if blockages occur anywhere across the pyrolysis rig.

The laboratory is equipped with a carbon monoxide alarm that sounds when the concentration of carbon monoxide in the lab rises above 50 ppm. As an added precaution however, a personal carbon monoxide alarm was worn during experiments. The idea of constructing a fume hood over the unit was also considered but the space and budget restrictions meant that the idea was dropped. The safety precautions around the system were considered sufficient.

3.5.2.2 Operational procedure

An operational procedure contained in Appendix 2 was written for the unit by the departmental safety officer for general use by other researchers.

3.5.2.3 Supporting laboratory equipment

As part of laboratory procedure, an added number of equipment and safety measures independent of the fast pyrolysis unit were already in place and they included

- Access: A clear path around the entire pyrolysis unit was maintained as a safety measure. A clear path between the fast pyrolysis units and the laboratory exits were also established and maintained to ensure the swift evacuation of the laboratory when the need arises.

- Personal Protective Equipment (PPE): To carry out experiments, personal protective equipment is required, and these include, dust mask, silicon gloves, laboratory coats, spectacles and occasionally thermal gloves.
- Feed Storage: The feedstock to be pyrolyzed were stored in plastic containers with tight lids to reduce any risk of ignition. Similarly, storage plastic bags present in the lab were used as storage for any produced solids from the process.
- Emergency procedures: It was also essential that the operator of the unit familiarised themselves with the laboratory and university safety procedures. This was undertaken prior to the commencement of any experiments. Emergency telephone numbers and evacuation paths and points were also noted.

3.5.3 Commissioning of individual sections of 300 g h^{-1} fluidised bed fast pyrolysis rig

The 300g h^{-1} fluidised pyrolysis rig located in EBRI Industrial Lab 02 has been used in the past to process various biomass feedstock (Diebold et al., 1997; Peacocke et al., 1997; Peacocke, 2007; Abdullah, 2005; Pattiya, 2007; Papadikis et al., 2009; Papadikis, 2009; Kalgo, 2011). However, fast pyrolysis of trommel fines using this system was new and as such, it had to be commissioned. The commissioning of the units happened in two separate phases. Cold and hot commissioning stages were carried out on the unit. The aims of the commissioning stages were to

- Test and observe the performance of individual units of the system.
- Test and observe the performance of the entire system.
- To make amendments and modifications if necessary to individual units based on the tests.
- To obtain and utilise data obtained for subsequent analysis of the system.

The commissioning of the sections happened in the following order.

- Feed System
- Reactor unit
- Condensing unit
- Complete Unit commissioning

The following section details the results from the commissioning phase of individual sections of the rig.

3.5.3.1 Cold commissioning tests

The cold commissioning phase involves the operation of individual pieces of equipment. The primary purpose was to ensure that sections of the unit performed satisfactorily. Other purposes were to calibrate the equipment and obtain the requisite experience required for purposeful operation and cold-feed the feedstock into the existing bubbling fluidised bed pyrolysis rig to monitor particle behaviour prior to actual pyrolysis tests. A summary of tests performed under the cold commissioning stage are presented in Table 3.7. The details of feed system commissioning are also described in full in the subsequent section.

Table 3.7: Summary of cold commissioning tests

Equipment	Purpose of test	Observation/modifications	Cross reference to detailed discussion
Twin and fast screw	Rotation speed, calibration	Twin screw connection to fast screw bent. Straightening required. Calibration undertaken	3.5.3.2
Feed hopper	Leak test	OK	
Flowmeters (entrain)	Calibration	OK	
Multizone temperature controller	Communication with thermocouples. Temperature control.	1 faulty thermocouple changed. Others fully functional	
Reactor joints, Band heaters	Leak test, Reactor heating	No leaks observed.	
Cyclone	Leak test, solid separation	No leaks. Successful separation of bed material.	
Char pot	Leak test	OK. No leaks found	
System pipework	Leak test	OK	
Water condenser	Leak test	OK	
Electrostatic Precipitator (ESP)	Leak test, Current and voltage in nitrogen atmosphere	No leaks found. Stable operation. Constant voltage and current.	
Dry ice condensers	Leak Test	OK	
Cotton wool filters	Leak Test	OK	
Gas meter	Leak Test, calibration checks	OK	
Reactor System	Cold feeding under pyrolysis conditions	Dust deposition (< 0.5 mm) observed at the bottom and entrance of the fast screw during the heating of the reactor sand. Modification made to feed particle size.	4.2

3.5.3.2 Feed system commissioning

The feed system commissioning involved feed rate tests on PT trommel fines samples relative to the twin-screw drive motor setting. The operational principle of the feeder unit was based on being able to control the feed rate via the motor attached to the twin-screw feeder.

To calibrate the feed system, a set-up was put in place as portrayed in Figure 3.15. The feed system calibration was carried out with the reactor detached from the face plate which holds it in place. A flow of nitrogen (10 L min^{-1}) was passing through the feed hop to mirror a real pyrolysis run. The calibration involved putting a pre-weighed collection vessel on a scale. By varying the twin-screw feeder set point the quantity of biogenic trommel fines conveyed through the fast screw from the twin-screw feeder into the receiving vessel over a fixed period was determined. The average of five trials for each set point was taken to further reduce the deviation. Table 3.6 shows the results of the feedstock tested at varying motor speeds. The results are also presented as a calibration curve in Figure 3.16. The results show a linear relationship between the twin-screw feeder set point and the average feed rate.

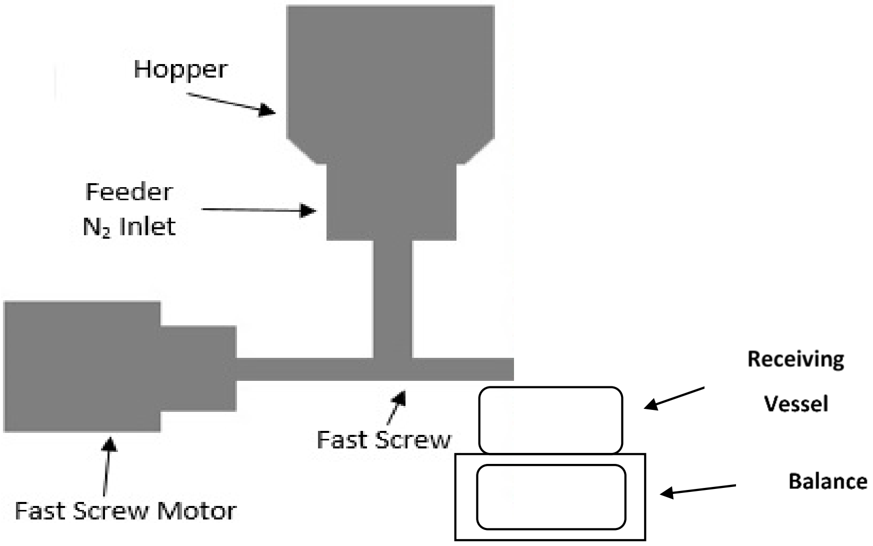


Figure 3.15: Schematic diagram of feed system calibration set up

Table 3.8: Calibration data for trommel fines feedstock

Exp. ID	Twin screw feeder set point (g h^{-1})	N$_2$ feeder rate (L/min)	Fast screw rate (RPM)	Time (min)	Mass fed (g)	Feed rate (g/hr)	Average (g h^{-1})	Standard deviation
1.1	5	10	100	10	11.6	69.6		
1.2	5	10	100	10	11.9	71.4		
1.3	5	10	100	10	10.8	64.8	**68.6**	**2.79**
2.1	10	10	100	10	18.3	109.8		
2.2	10	10	100	10	19.6	117.6		
2.3	10	10	100	10	19.5	117	**114.8**	**3.54**
3.1	20	10	100	10	63.5	381		
3.2	20	10	100	10	58.4	350.4		
3.3	20	10	100	10	53.9	323.4	**351.6**	**23.53**
4.1	30	10	100	5 *	50.7	608.4		
4.2	30	10	100	5 *	48.3	579.6		
4.3	30	10	100	5 *	44.1	529.2	**572.4**	**32.73**

*** Feed blockage after 5 minutes into feeding**

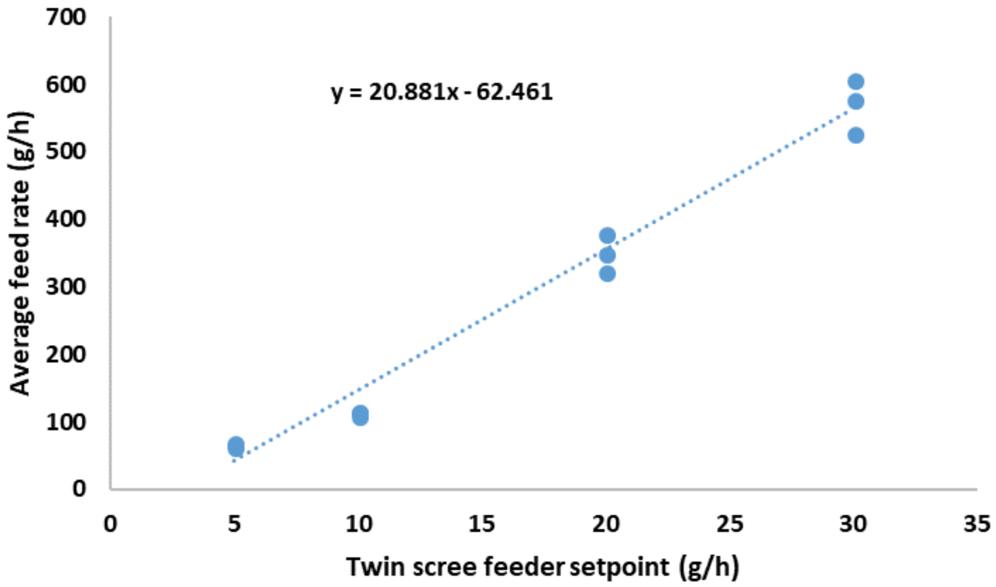


Figure 3.16: Trommel fines feed system calibration curve

3.5.3.3 Hot commissioning tests

The cold commissioning tests detailed in Table 3.7 though useful were limited in the kind of data they could provide. Performance of certain equipment could only be assessed under pyrolysis conditions. Equipment including the water condenser and dry ice condensers can be operated individually but an assessment of their efficiency and limits could only be determined under actual pyrolysis conditions; hence, the need for the hot commissioning tests. A summary of the hot commissioning test parameters is presented in Table 3.9.

Table 3.9: Summary of hot commissioning tests

Equipment	Purpose of test	Problems	Observation/Modification	Cross reference to detailed discussion.
Reactor heating	Get reactor to pyrolysis temperature (500 °C).	Short circuits/Tripping. Reactor heating takes 2-3 hours to reach pyrolysis temperature.	Unable to maintain pyrolysis temperature. Modification to heating system.	3.6.1
Condensing unit	Vapour quenching	Blockages.	Highly viscous liquid produced causing blockage to ESP. Modifications made to entire condensing unit.	3.6.2
Reactor system	Feeding under pyrolysis conditions	Inorganic separation of reactor bed	Inorganics unable to leave reactor	5.4

3.6 Modification of existing reactor for trommel fines fast pyrolysis

During the hot commission phase of the 300 g h^{-1} fluidised bed reactor to process trommel fines (refer to section 3.5.3.3), several operational problems were encountered on the unit. They included bridging in feed system, poor reactor heating and blockage in the condensing unit. The problems limited the operational range of the process, particularly in terms of reactor hydrodynamics, vapour quenching and more importantly, the organic liquid yield and mass balance closures. The problems and the modification made to the process are discussed in this section.

3.6.1 Feed system problems and modifications

Bridges were formed continuously in the connection between the hopper and fast screw that caused disruptions to continuous and steady operation of the feeding system. The severity of the bridging problem varied depending on the pre-treated trommel fines type being processed. The bridges could be collapsed by the application of an external force to the hopper walls.

However, this proved ineffective in some cases, as the feeding of AW and AWS feedstock formed bridges that were difficult to break. As a result of this, regular checking of feeding was carried out to minimize the formation of bridges in order to ensure continuous operation of the feeding system and the fast pyrolysis process.

To understand the bridging problem, the ‘flowability’ of bulk materials must first be defined. Marinelli and Carson, (1992) define flowability as the ability of granular and solid powders to flow. The flowability of the solid feedstocks, including pre-treated trommel fines, depends on the physical characteristics of each feedstock type (particle size, moisture, temperature and pressure), environmental conditions and storage conditions (Craik et al., 1958; Irani et al., 1959; Jenike, 1964; Clift et al., 1978; Johanson, 1978; Moreya et al., 1981; Mattsson, 1990; Marinelli and Carson, 1992; Brigg, 1994; Cuenca et al., 1995; Mattsson 1997; Yan and Barbosa, 1997; Prescott, 2000; Klausner 2001; Mattsson, 2001, 2002, 2003; Fitzpatrick et al., 2004; Marinelli, 2004). The bridging problem encountered during this research was aggravated by the flawed design of the feeding system for the 300 g h^{-1} fluidised bed fast pyrolysis rig. The connection between the Ktron KT-20 gravimetric feeding hopper and the fast screw has a conical cross section as depicted in Figure 3.17.

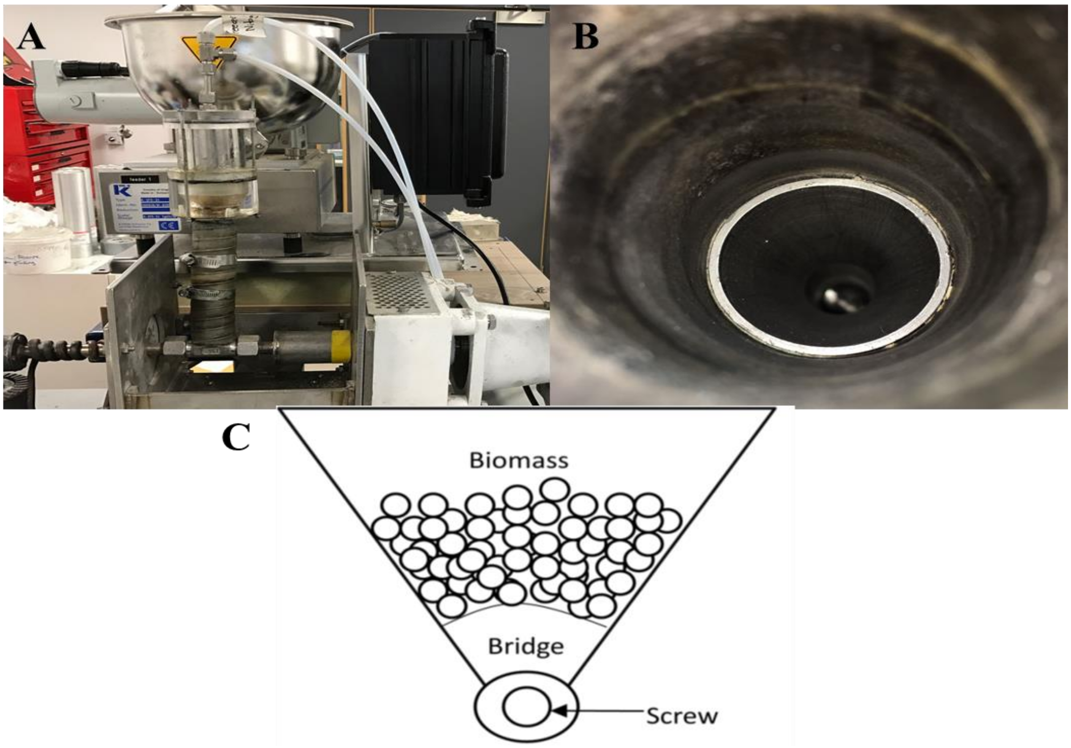


Figure 3.17: A: Photograph of Ktron KT-20 gravimetric twin screw feeding system connection to fast screw; B: Photograph of fast screw inlet; C: Schematic representation of bridging problem in feed system (Source: adapted from Maniatis, 1986)

Based on the discussions of flowability and its related parameters, the pre-treated trommel fines feedstock types, compacting and bridge formation arose (Figure 3.17 – C) because of packing characteristics and the storage vessel shape. Maniatis, (1986) reports a similar problem after construction of a feed system for a gasification process. When this happens, a feedstock arch is formed that can withstand considerable stress. Depending on the feedstock, the arch can transfer the load to the hopper walls. At that point, the kinematic coefficient of friction, F, which is a measure of coefficient of friction between the material and the wall of the hopper, becomes high and the result is a situation where a bridge is formed and continuous flow through the feed system is stopped. External force must then be applied to collapse the bridge and resume flow into the reactor. It is important to state at this point that the afore-mentioned physical parameters relate in complex ways with each other to contribute to flow of the prepared trommel fines (PT, AW and AWS). In effect, each of the parameters may play a single or cumulative part in the extent of flow or lack of it.

3.6.1.1 Bridging solution

Due to time constraints, it was not possible to physically modify the existing unit to provide a permanent solution to the bridging problem. Rather, a successful attempt was made at stopping the formation for bridges at the inlet of the fast screw (Figure 3.17) by reducing the feeding rate. During the hot commission phase of the fluidised bed rig, the feeding rate set point on the Ktron KT-20 was 20 g h^{-1}. However, decreasing the feeding rate of the pre-treated trommel fines (PT, AW and AWS) to 10 g h^{-1} managed to slightly reduce the bridging effect but also varied the amount of the pre-treated trommel fines feedstock that was processed within an hour of running the process (Table 3.10). The amount of pre-treated trommel fines sample fed into the reactor depended on the characteristics of the samples at the time of processing.

Table 3.10: Pre-treated trommel fines PT, AW and AWS processed after 1 hour of operation

	Twin screw feeder set point (g h^{-1})	
Type of feedstock	**10**	**20 ***
PT	153.3 ± 6.54	268 ± 25.4
AW	123.6 ± 4.27	237.4 ± 18.6
AWS	111.8 ± 5.13	205.4 ± 23.8

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon); * could not be processed for up to 1 hour

3.6.2 Reactor heating problems and modifications

One of the aims of the reactor commissioning tests was to successfully get the fluidised bed reactor to pyrolysis temperatures. The test also involved maintaining the reactor at the desired pyrolysis temperature (500 °C) for a duration of at least 1 hour for a typical experimental operation. The tests involved operation of the band heaters with the temperature controller already described in section 3.5 of this report. Several attempts were made using the 750 Watlow band heater shown in Figure 3.18, to achieve the desired temperature, which took about 3 hours (Figure 3.19) as shown by the gentle heating rate profile. In addition, the desired temperature could not be maintained for 60 min. The band heater was old and was prone to absorbing moisture from its surroundings when it was not in operation. Frequent short circuits were noticed with the Watlow Starflow circulation heater in the early parts of testing the rig as a result of the faulty band heater. Similar problems have previously been reported by Kalgo (2011), who used the same reactor set up to pyrolyse biomass. The first step taken to deal with the problem was to dry the band heaters in an oven at 105 ºC prior to operation. This step proved to be partially successful as the heater still failed after a couple of minutes of operation.

Figure 3.18: Original reactor band heater

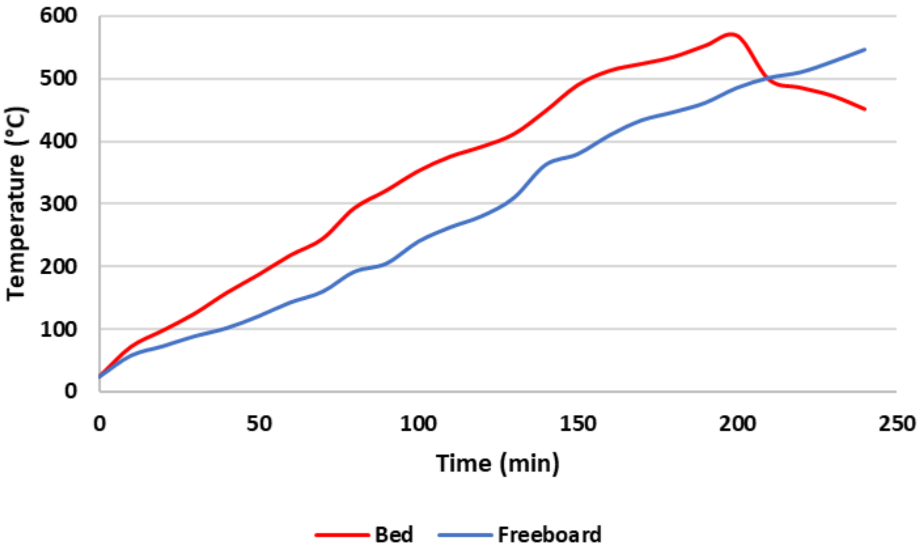


Figure 3.19: Initial reactor heating profile showing the heat-up time to reaction temperature

3.6.2.1 Modifications to reactor heating system

The original band heater though could get the reactor to pyrolysis temperature after 3 hours, it was not able maintain it even after numerous attempts. The decision was then taken to replace the band heater. A similar band heater (Watlow mineral insulated band heater 800W) was purchased, however, the band heater was thought not to be effective on its own (Figure 3.21A) so a nitrogen pre-heater (Figure 3.20) was also installed into the process.

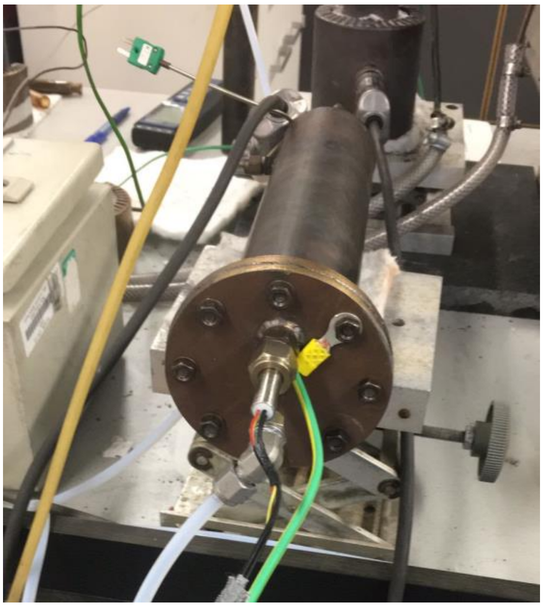


Figure 3.20: Photograph of nitrogen pre-heater installation into reactor inlet.

After installation of the new band heater and the nitrogen pre-heater, the modified heating system of the reactor was tested and operated successfully. Figure 3.21B shows that the reactor can reach pyrolysis temperature of 500 °C within 90 min from the commencement of heating. The heating rate was faster as shown by the steeper increase compared to Figure 3.19. A nitrogen flowrate of 10 L min^{-1} was passed through the reactor and the mass of fluidising sand for this test was 150 g. The pyrolysis bed temperature could be maintained for at least 60 min by setting the nitrogen pre-treated to 250 °C and setting the band heater to 50 °C higher than reactor temperature.

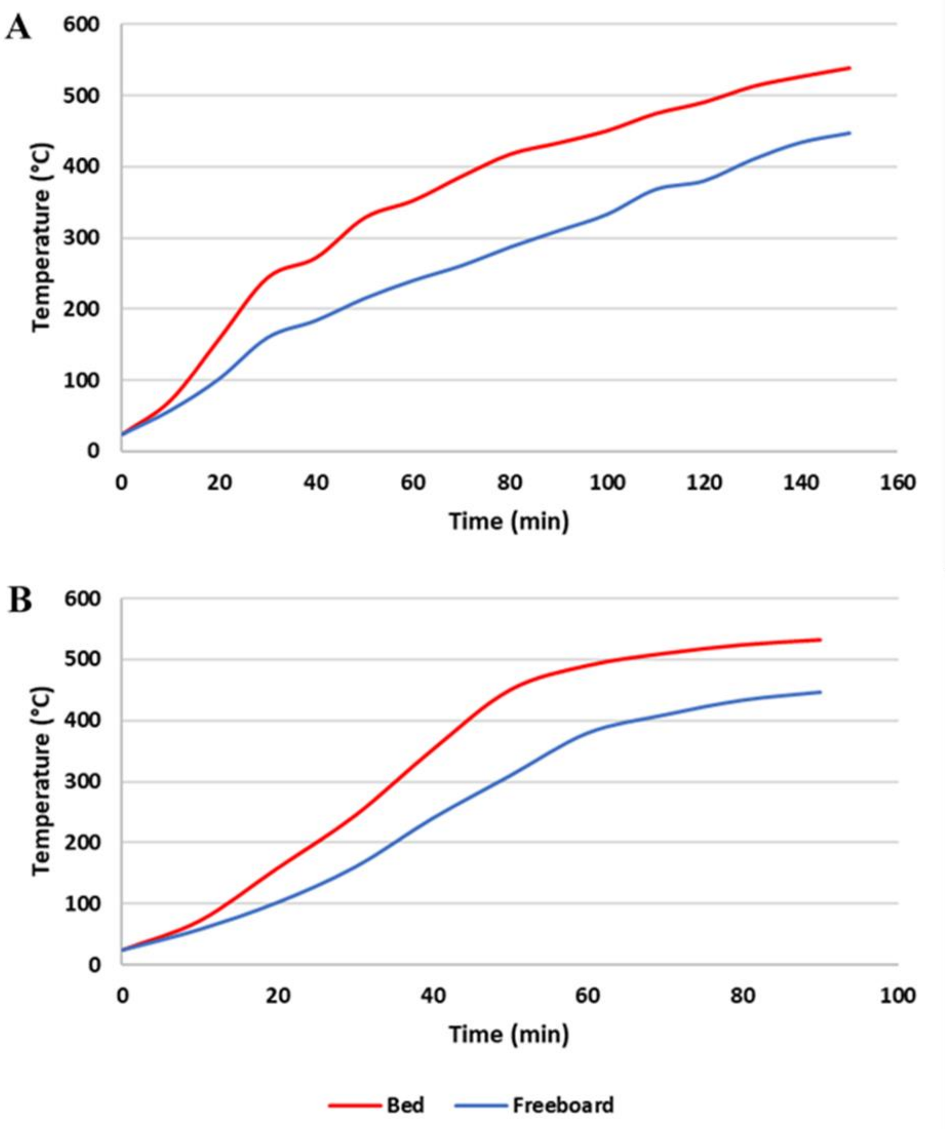


Figure 3.21: Reactor heating profile – (A) new electric heating band; (B) new electric heating band + nitrogen pre-heater

3.6.3 Condensing unit problems and modifications

The aim of the condensing unit commissioning was to:

- Observe the behaviour of the water condenser (Figure 3.13 - 6), electrostatic precipitator (ESP) (Figure 3.13 - 7) and dry ice condensers (Figure 3.13 - 8) under pyrolysis conditions.
- Develop a mass balance calculation method on the condensing unit.

The commissioning of the condensing highlighted some problems. Table 3.11 details the overall mass balance results from the condensing unit commissioning run (Exp. CR-300-001). During the commissioning phase of the condensing unit, the Gas Chromatograph was out of commission. The gases produced during this experiment were not analysed. The decision was taken to proceed with the commissioning anyway since the aim of the experiment was to observe the behaviour of the condensing unit in terms of oil product recovery and collection. The gases were obtained by difference. At the end of the commissioning run, it was observed that certain parts of the vapour delivery system to the condensing unit retained some of the liquids produced.

Table 3.11: Exp. CR-300-001 overall mass balance results for condensing unit commissioning run

PT feedstock used (g)	**158.91**
Char (g)	
Char in sand	11.8
Char pot	72.1
Metal transition pipe	0.1
Total char (g)	**84**
Liquid (g)	
Glass transition pipe	0.3
Water cooled Condenser	9
ESP	12.6
Oil pot 1	0
Dry Ice Con 1	3.2
Oil pot 2	17
Dry Ice Con 2	1.8
Oil pot 3	3.1
Cotton wool filter	9.9
Total liquid (g)	**56.9**
Closure (g)	**140.9**
Closure [a] (wt.%)	**88.66%**
PT – Physically pre-treated trommel fines; [a] excluding gas produced	

The liquid produced from PT trommel fines feedstock was of high viscosity, containing water, char and organic liquids. This invariably stuck to the walls of the ESP and blocked the exit point of the ESP into the oil pot 1 (Figure 3.22). Hence, why the amount of oil retained in the ESP stood at 12.6 g, nothing was recorded for oil pot 1 (refer to Table 3.11). The blockage in the ESP forced the rest of the gases to move towards the dry ice condensers and cotton wool filter. A total of 20.1 g of the liquids was collected in oil pots 2 and 3 and was a mixture of the heavy and lighter fractions (Table 3.11). The cotton wool filter recorded a weight increase of 9.9 g after the experiment, which was relatively high when compared to the weight increase of the dry ice condensers. Figure 3.23 show the photograph of the 300 g h^{-1} fast pyrolysis rig after the commissioning run Exp. CR-300-001.

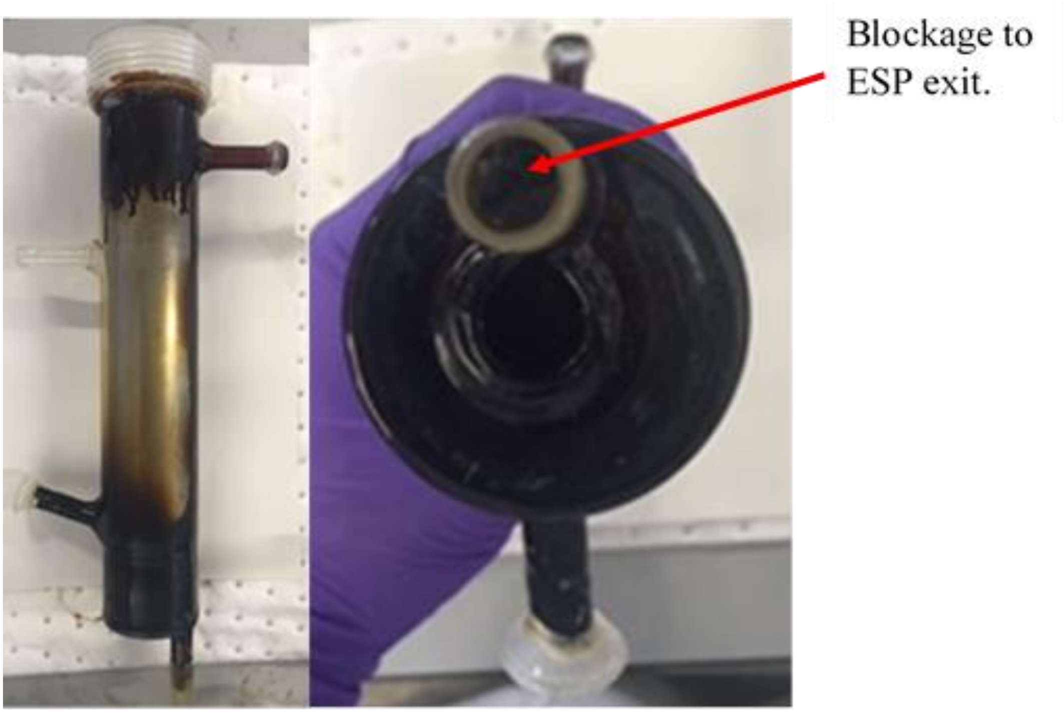


Figure 3.22: Photograph of blockage to electrostatic precipitator (ESP)

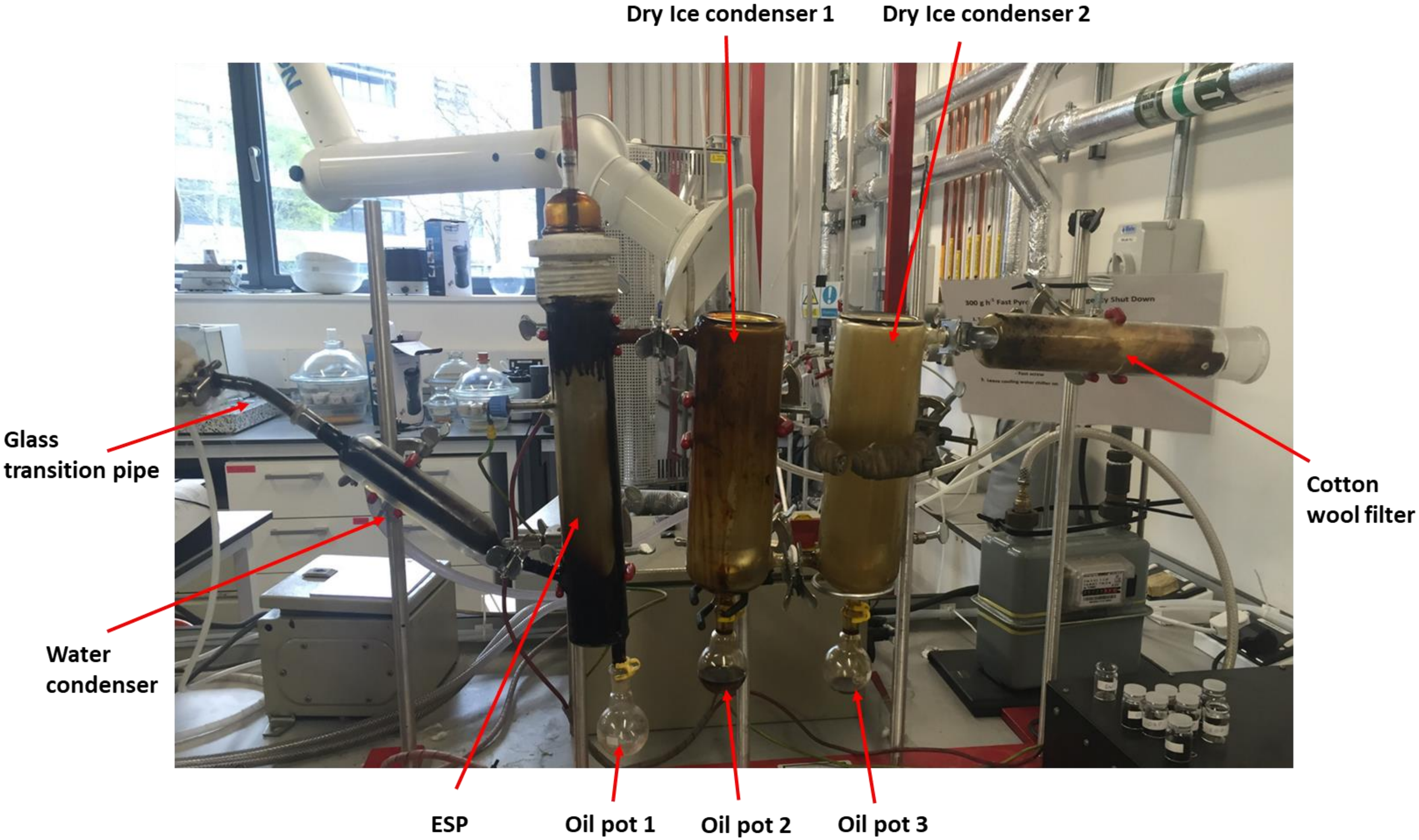


Figure 3.23: Photograph of 300 g h^{-1} pyrolysis condensing unit after commissioning run Exp. CR-300-001

3.6.3.1 Modifications to condensing unit

To reduce the likelihood of blockage, the decision was taken to replace the water-cooled condenser, ESP, oil pots (1, 2, & 3) and dry ice condenser (1 & 2) with three condensers (30 MM ID x 300 MM L) with side arms, and 14 MM OD glass tubes. A high temperature rubber connecting pipes were used as gas transition pipes between the condensers. The first condenser was dipped into a flask filled with water and ice, while the other two were dipped in to a flask filled with dry ice and acetone mixture. This facilitated easier collection of the liquid product, reduced the likelihood of blockage, and made it easier to clean the units. Figure 3.24 shows a photograph of the new condensing unit after modification and a flow sheet of the modified configuration of the 300 g h^{-1} bubbling fluidised bed fast pyrolysis unit is shown in Figure 3.25.

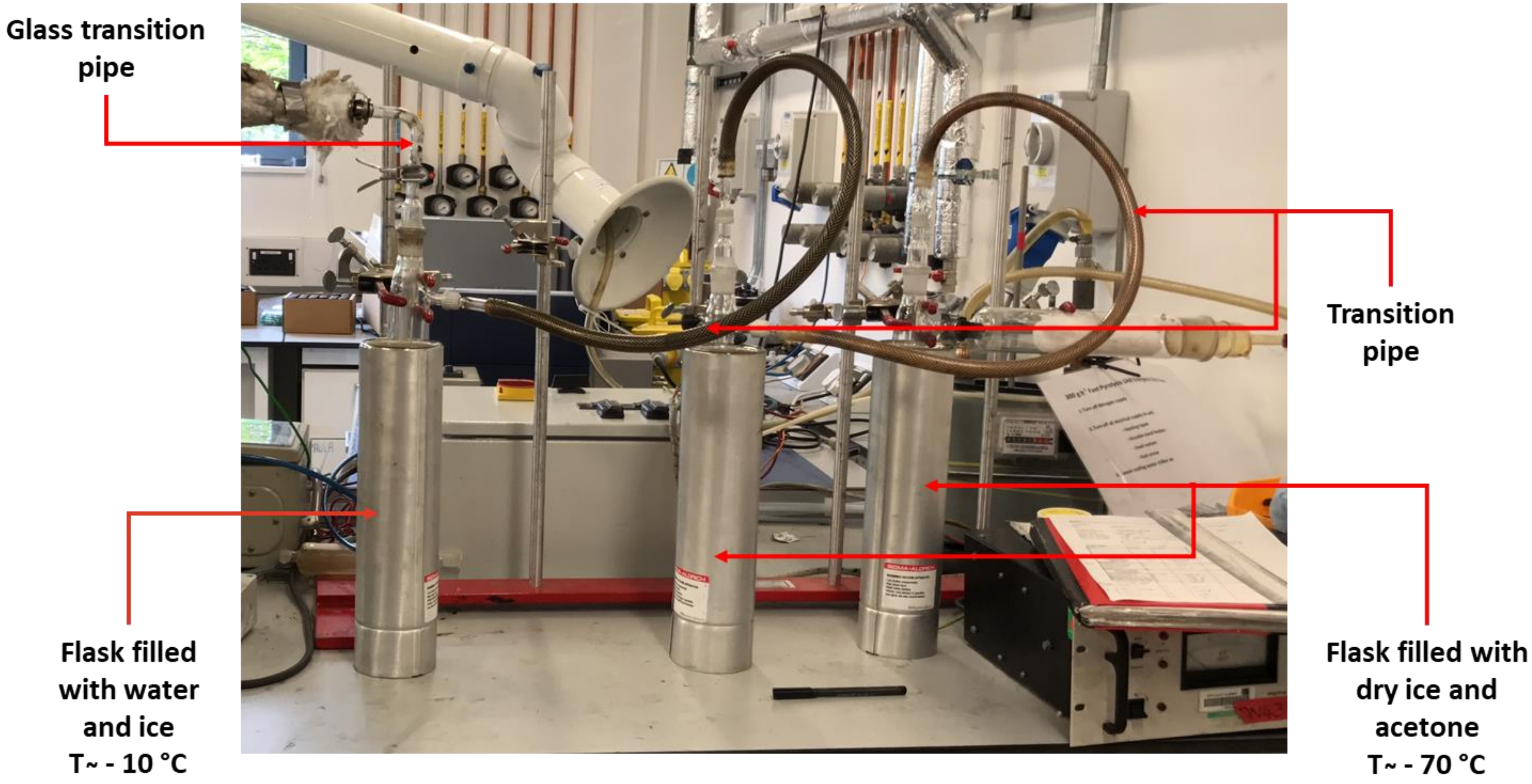


Figure 3.24: Photograph of modified 300 g h^{-1} fast pyrolysis rig condensing unit during operation

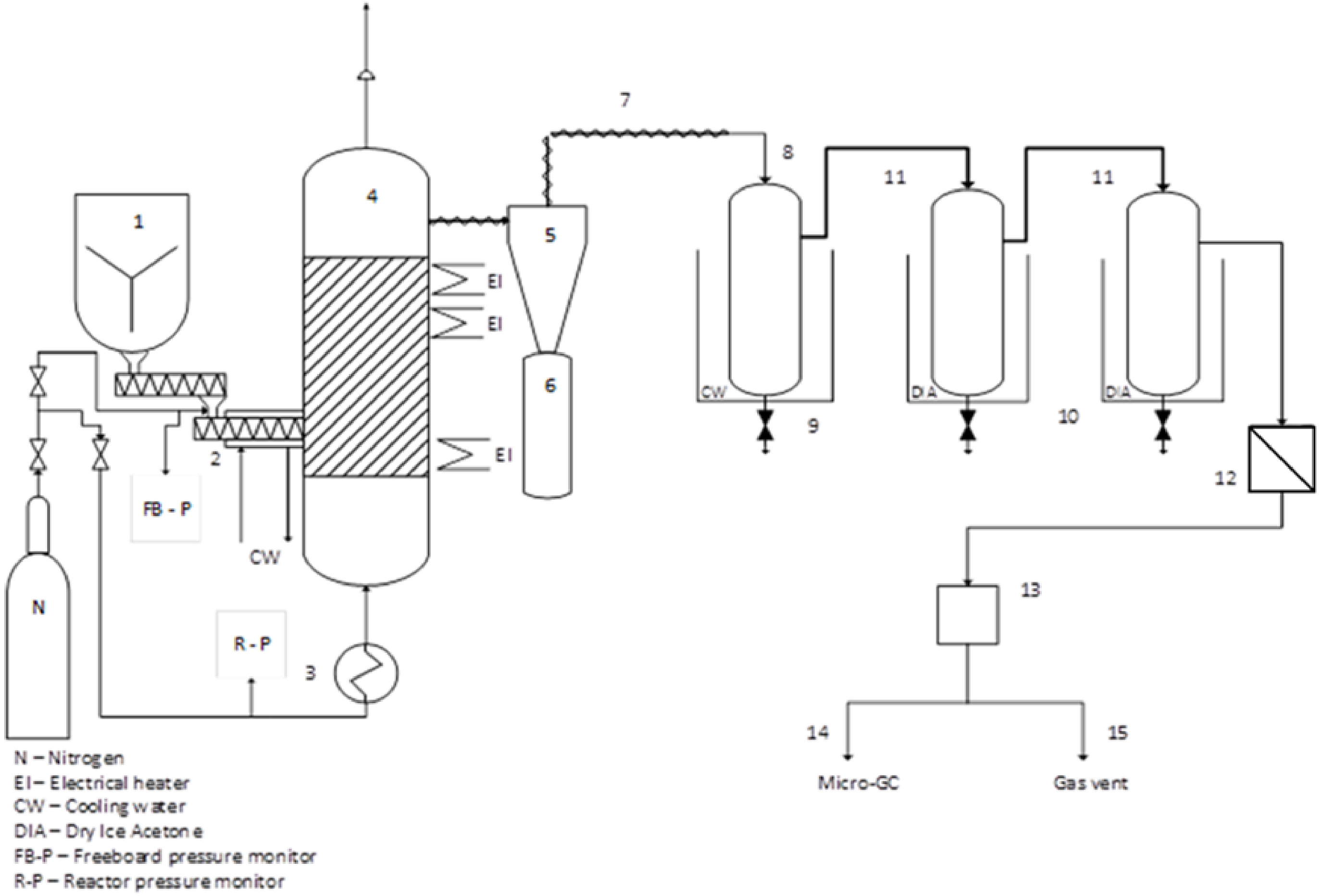


Figure 3.25: Bench scale 300g h^{-1} fluidised bed fast pyrolysis rig set-up after modifications.

1 - feed hopper with twin screw feeder, 2 – fast screw, 3 – nitrogen preheater, 4 – fluidised bed reactor, 5 – cyclone, 6 – charpot, 7 – metal transition pipe, 8 – glass transition pipe, 9 – water cooled condenser, 10 – dry ice acetone condenser, 11 – ruber tansition pipe, 12 – cotton wool filter, 13 – gas meter, 14 – micro-gc, 15 – gas vent

3.7 Parameters for investigation

The fast pyrolysis process is dependent on a number of process variables relating to the feedstock and process. In this section the process parameters investigated during this research are discussed, they are parameters shown by researchers to influence the fast pyrolysis process. The selected variables are discussed below.

3.7.1 Effect of pyrolysis temperature

The reaction temperature has been shown to be the key parameter that influences the pyrolysis process particularly in terms of product distribution ratios and yields (Wang et al., 2005b; Jiang, 2006; Buah et al., 2007; Velghe et al., 2011; Zhao et al., 2011; Pan, 2012; Zhou et al., 2013; Chen et al., 2014; Dong et al. 2016). As part of investigating the suitability of the physically pre-treated trommel fines feedstocks (PT) as raw materials for fast pyrolysis, the impact of temperature on process yields and distributions were to be studied. The aim was to investigate the effect of pyrolysis temperature on product distribution, liquid yields and gas compositions as well as to identify the optimum pyrolysis temperature for obtaining the highest organic yields on dry basis. The chosen target reaction temperatures were 400, 500, 600 and 700 ºC. A total of twelve experiments were conducted (3 each). A summary of the temperature investigation test parameters is presented in Table 3.12.

Table 3.12: Temperature investigation test parameters

Experiment ID	Feedstock type	Feedstock particle size (mm)	Feedstock moisture content (wt.%)	Temperature (°C)	Number of experiments
TIR-400	PT	0.5-2	< 3	400	3
TIR-500	PT	0.5-2	< 3	500	3
TIR-600	PT	0.5-2	< 3	600	3
TIR-700	PT	0.5-2	< 3	700	3
TIR-Temperature Investigation Run; PT - Physically pre-treated trommel fines					

3.7.2 Effect of feedstock moisture content

Literature studies have reported that feedstock moisture content can impact the pyrolysis process, as the moisture in the feedstock eventually ends up in the products of the process mainly the liquid product (Kelbon et al., 1988; Maniatis et al., 1988; Bridgwater and Peacocke, 2000). The investigation of the effects feedstock moisture content was to be carried out using the physically pre-treated trommel fines feedstock (PT) at optimum pyrolysis temperature. A total of six experiments were conducted at different feedstock moisture content ranging from bone dry (>3 wt. %) to 10 wt. %. The primary aim of these sets of experiments was to investigate the impact of moisture content on the yields and properties of fast pyrolysis products at the investigated optimum reaction temperature. The results from TIR-500 experiment is represented as MCR-01 in this investigation, as the PT feedstock moisture content was < 3 wt. %, thus not requiring further experiments to be conducted. A summary of the moisture content investigation test parameters is presented in Table 3.13.

Table 3.13: Moisture content investigation test parameters at 500 °C

Experiment ID	**Feedstock Type**	**Feedstock Particle size (mm)**	**Feedstock Moisture content (wt.%)**	**Number of Experiments**
MCR-01	PT	0.5-2	< 3	3
MCR-05	PT	0.5-2	5	3
MCR-10	PT	0.5-2	10	3
MCR-Moisture Content Run; PT - Physically pre-treated trommel fines				

3.7.3 Effect of feedstock pre-treatment method

The composition of the feedstock has been shown to be the key parameter that influences the process particularly in terms of product distribution ratios and yields (Luo et al., 2010; Miskolczi et al., 2013; Chen et al., 2014). As part of investigating the suitability of the trommel fines feedstocks as raw materials for fast pyrolysis, the impact of pre-treatment method on process yields and distributions were studied. The AW and AWS trommel fines were processed at optimum reaction temperature and conditions and the results were compared to the TIR-500 results, which is represented in this investigation as PT. A total of 3 fast pyrolysis experiments were performed for each feedstock type investigated (AW and AWS) (refer to section 3.6), because of previous parameter investigations (temperature and moisture content) yielding a reproducibility of <5% (refer to section 3.8), thus only requiring duplicate runs. A summary of the pre-treatment method investigation test parameters is presented in Table 3.14.

Table 3.14: Pre-treatment method investigation test parameters at 500 °C

Experiment ID	**Feedstock Type**	**Feedstock Particle size (mm)**	**Feedstock Moisture content (wt.%)**	**Number of Experiments**
PT	PT	0.5-2	< 3	3
AW	AW	0.5-2	< 3	3
AWS	AWS	0.5-2	< 3	3
PT - Physically pre-treated trommel fines; AW-sample from agitated washing of PT with 100% distilled water; AWS-sample from agitated washing of PT with distilled water + surfactant				

3.8 Fast pyrolysis product analysis

This section describes different fast pyrolysis product analysis techniques including GC-MS/FID, water content, elemental analysis and calorific value experiment. The procedure for each technique is explained in detail.

3.8.1 Liquid product

The liquid products produced from fast pyrolysis of trommel fines are made of organics, water and solid content. The properties studied include water and solids contents, bio oil analysis by GC-MS, basic elemental composition and heating value. Understanding the basic properties of the liquid products would be beneficial for identifying their appropriate applications and for upgrading them (Buah et al., 2007; Velghe et al., 2011; Zhou et al., 2013; Chen et al., 2014; Dong et al., 2016). It is important to emphasise that the liquid products produced in this work were initially in five fractions (refer to Table 3.13 in section 3.8). But only the contents in water cooled condenser (Figure 3.25 - 9 primary condensate) and dry ice/acetone condensers (Figure 3.25 – 10 secondary condensate) were used as the representative liquid samples as they contain majority of the liquid products produced. It is also imperative to be aware that the mixtures were dissolved in a solvent, which was absolute acetone at a ratio of 1 to 6. Consequently, properties such as water content, solids content, and elemental composition have been calculated after each analysis and reported on solvent free basis.

3.8.1.1 Moisture determination in liquid products

Volumetric Karl-Fischer (KF) titration (ASTM E 203-96; Chiaramonti et al., 2007; Banks et al., 2014) was used to determine the water content of all the fast pyrolysis primary and secondary condensate. The primary and secondary condensates were dissolved in a known weight of acetone (1:6) prior to analyses. All analyses were performed in triplicate with the water content reported visually after being calculated automatically by the KF and because the amounts of acetone in the liquids are known, the amounts of water present in these liquids can be calculated once obtaining their water and solid contents.

3.8.1.2 Solids determination in liquid products

Solids content in the primary condensate was determined using the vacuum filtration technique suggested by Oasmaa and Peacocke (2001). The primary condensate was filtered through a pre-dried and pre-weighed Whatman No. 2 qualitative filter paper with mean pore size of 8 µm. The primary condensate was then washed with excess amount of acetone until the filtrate was clear to ensure that there was no organic liquid left on the filter paper. The filter paper with the residue was air-dried for approximately 15 min and in an oven at 105 °C for around 30 min, cooled in a desiccator and weighed.

3.8.1.3. Elemental analysis of liquid products

The primary and secondary condensate mixed with a known amount of acetone (1:6) were subjected to CHN analysis using CE-440 and Carlo Erba elemental analysers with ±0.3% absolute accuracy (Fadeeva et al., 2007; Banks et al., 2014). After obtaining the carbon, hydrogen and nitrogen (CHN) contents of the primary and secondary condensate, the elemental analysis of the tar derived oil was calculated by subtracting the carbon, hydrogen and oxygen amounts of the known quantities of acetone and water to obtain the carbon hydrogen and nitrogen contents of tar derived oils on dry, solvent-free basis. In addition, the oxygen content of tar derived oils was calculated by difference.

3.8.1.4 Determination of calorific value of liquid products

Approximately 1 g of the bio-oil of the liquids sampled from the primary condensate (water cooled condenser (Figure 3.25 - 9) was analysed using the procedure previously described in section 3.4.3.

The higher heating values (HHV) of liquids (primary #9 and secondary #10 condensate) were also calculated for the primary and secondary condensate based on a correlation developed by Channiwala and Parikh (2002) as shown by the following equation:

$$\text{Liquid HHV (dry)} = 0.3491\text{C} + 1.1738\text{H} + 0.1005S - 0.10340\text{O} - 0.0151\text{N}\ [\text{MJ/kg}] \qquad \textbf{(Eq. 3.11)}$$

where C, H, S, O, N and A represent mass percentages on dry basis of carbon, hydrogen, sulphur, oxygen, nitrogen and ash contents of bio-oil (organics and solid fine particles) on water-free basis, respectively.

The lower heating values (LHV) were calculated from HHV and the hydrogen content by the following equation (ECN, 2005):

$$\text{Liquid LHV (dry)} = \text{HHV dry} - 2.442 \text{ x } 8.936\ (\text{H} / 100)\ [\text{MJ/kg}] \qquad \textbf{(Eq. 3.12)}$$

3.8.1.5 Liquid analysis by GC-MS

Analysis of bio-oil samples were performed using a PerkinElmer Clarus 680 GC-MS system (Kalgo, 2011; Banks, 2014; Banks et al., 2014). GC samples were prepared by mixing bio-oil with GC grade acetone (1:6 v v.$^{-}$1). 1 µl of the GC sample was filtered using a 0.2 µm pore size Sartorius filter, and was injected into the GC column via an injection port maintained at

300 °C, with 1:50 split ratio. The GC oven programme was as follows: held constant at 50 °C for 2 minutes, then ramped at 5°C min^{-1} to 275 °C and held at 275 °C for 3 minutes. The programme lasted 50 minutes. Helium was used as the carrier gas with a constant flow of 15 ml min.-1. A column splitter was used to enable simultaneous detection of compounds separated on the columns by MS and FID detectors at 250 °C. Mass spectra were obtained using 70 eV ionisation energy in the molecular mass range of m/z = 35 – 300, with a scan time of 0.35 seconds. Assignments of the main peaks were made from mass spectral detection (NIST05 MS library).

3.8.2 Solid residue analysis

3.8.2.1 Ash determination in solid residues

The ash contents were determined according to the ASTM D1762-84 method five crucibles and lids were put in a Carbolite AAF1100 furnace and heated to 900 °C for 3 h; crucibles were then removed from the furnace and cooled in a desiccator. The crucible weights were recorded and then approximately 4 - 5 g of solid residue was weighed into each crucible. The crucibles and samples with their lids placed at an angle were placed in a furnace and heated to 750 °C for 6 h. After 6 h, the crucibles were removed and cooled in a desiccator for one hour. Each crucible was weighed to the nearest 0.1 g. Crucibles were replaced in a furnace and heated at 750 °C for 1 h periods until the crucible weigh was constant to within 0.3 g. The ash content was then obtained by dividing the weight of the samples by the pre- weight and expressed as a percentage of the original weight. The average of five samples was taken to further reduce the deviation (refer to section 3.4.1 Table 3.2).

3.8.2.2. Elemental analysis of solid residues

The solid residue was subjected to CHN analysis using CE-440 and Carlo Erba elemental analysers with ±0.3% absolute accuracy to determine the elemental composition of a sample in terms of carbon, hydrogen and nitrogen. Other elements sometimes included in the analysis include, sulphur and oxygen; oxygen is determined by percentage difference (Aiken, DeCarlo and Jimenez, 2007).

3.8.2.3 Determination of calorific values of solid residues

Approximately 1 g of the solid product obtained from the char pot was analysed using the procedure previously described in section 3.4.3. The higher heating values (HHV) of the solid product obtained from the char pot were also calculated using the procedure previously described in section 3.7.1.4.

3.9 Mass balance calculation from pyrolysis experiments

Mass balances (wt. % on dry feed basis) were calculated based on mass of dry trommel fines processed and final fast pyrolysis products of liquid, solid residue and non-condensable gases. An extensive mass balance is performed so that good overall closures are achieved which allows for comprehensive conclusions to be made on product yields. Once a fast pyrolysis experiment was completed the rig was left to stand until reaching room temperature, at which point it was partially dismantled. Dismantling includes all metal pipework and transition pipes between reactor output and condensers, including the cyclone and char pot. The rest of the fast pyrolysis rig cannot be measured directly as dismantling is time consuming and certain parts are too heavy to achieve an accurate weight measurement. Table 3.15 shows how each aspect of the mass balance was achieved for input material and fast pyrolysis products.

Table 3.15: Mass balance for 300 g h^{-1} fast pyrolysis rig

Material	Equipment	Method
Input material:		
Biomass	Feed hopper (#1)	Difference in weight of biomass added to hopper and biomass left in hopper after experiment run.
Sand	Reactor (#4)	Difference in weight before experimental run and bed material after being burnt off.
FP liquid products:		
Primary condensate	Water cooled condenser (#9)	Difference in weight before and after experimental run
Primary condensate	Glass transition pipe (#8)	Difference in weight before and after experimental run
Secondary condensate	Dry ice / acetone condenser 1 & 2 (#10)	Difference in weight before and after experimental run
Secondary condensate	Pipework 1 & 2 (#11)	Difference in weight before and after experimental run
Secondary condensate	Cotton wool filter (#12)	Difference in weight before and after experimental run
FP solid products:		
Char and char coating sand	Reactor (#4)	Difference in bed material after experimental run and when bed material has been burned off
Solid residue	Char pot (#6)	Directly removed and weighed
Solid residue	Metal pipework (#7)	Directly removed and weighed
FP gas products:		
Pyrolysis gas	Varian micro GC and diaphragm gas meter	Pyrolysis gas mass measured by average gas composition and total gas volume

3.9.1 Input material

The trommel fines feedstock was weighed before being poured into the feed hopper and then re-weighed after the fast pyrolysis experiment; the difference between them was the amount of trommel fines processed (Eq. 3.13). The bed material (silica sand) in the reactor was weighed before and after each run. The bed material after experimental runs, includes solid residues and char from the pyrolyzed sample, which is deducted from the input mass balances (refer to section 3.9.3).

$$\text{Feed processed} = \text{wt of feed before exp.} - \text{wt of feed after exp.} \qquad \textbf{(Eq. 3.13)}$$

3.9.2 Fast pyrolysis liquid products

The total amount of pyrolysis liquids generated from the unit is the mass of liquid collected in the glass transition pipe (Figure 3.25 - 8), water cooled condenser (Figure 3.25 - 9), dry ice acetone condenser 1 and 2 (Figure 3.25 - 10), transition pipework 1 and 2 (Figure 3.25 - 11) and cotton wool filter (Figure 3.25 - 12). The main liquid fraction which is a brownish black tar derived liquid is collected at the bottom of the water-cooled condenser (Figure 3.25 - 9). The amount of liquid (water, solids and organic liquids) collected in the water-cooled condenser (Figure 3.25 - 9) during an experiment is determined by the difference between the mass of the condenser at the start of the run, and its mass at the end of the run. The mass increase of the glass transition pipe (Figure 3.25 - 8) which is determined by weight difference measurements before and after the experiments is assumed to be liquid of the same composition as the water-cooled condenser (Figure 3.25 - 9) and this is also considered during the mass balance calculations. The glass transition pipe and water-cooled condenser was taken as the primary condensate.

The second liquid fraction is collected at the bottom dry ice cooled condenser 1 and 2 (Figure 3.25 - 10). That liquid fraction usually contains more water. At the end of the experiment after the rig has cooled down, the acetone in the dry ice condensers is then emptied. The mass of the condensers is then obtained and the initial mass prior subtracted from the value to obtain the mass of any liquids collected. The mass increase of the transition pipework 1 and 2 (Figure 3.25 - 11) which is determined by weight difference measurements before and after the experiments is assumed to be liquid of the same composition as the dry ice cooled condensers and this is also considered during the mass balance calculations. The final liquid fraction is collected in the cotton wool filter. The amount of liquid collected in the cotton wool filter is usually small when compared to other sections of the unit. It is absorbed in the cotton wool and is determined by weight difference before and after experimental run. This liquid is assumed to be of the same composition as the fraction collected in the dry ice cooled condensers. Since this liquid is absorbed in the cotton wool, recovery is almost impossible, and analysis is not carried out on it. The dry ice cooled condensers 1 and 2, pipework 1 and 2 and the cotton wool filter were taken as the secondary condensate.

The yield of organics present in the liquid is determined after the liquid has been subjected to Karl Fisher titration to determine its water content. The difference in the mass of liquid and that of the mass of water in the liquid accounts for organics present in the liquid (Eq. 3.14). Before this however, the mass of initial moisture in the feed is obtained and subtracted. The mass balance is reported on a dry basis. Thus, the initial feedstock moisture content must be discounted. The amount of solid in the liquid is also subtracted after the solid content of the liquid fractions have been determined (Kalgo, 2011; Banks, 2014).

$$\text{Organic liquid yield [wt\%]} = \left(\frac{(\text{total liquid} - \text{moisture content} - \text{solid content})}{\text{total mass of dry feed used}}\right) \text{x } 100$$

(Eq. 3.14)

3.9.3 Fast pyrolysis solid products

Most of the solid residue produced is collected before the condensing unit. The amount of solid residue produced, is determined by the mass increase in the char-pot (Figure 3.25 - 6) and metal transition pipe (Figure 3.25 - 7). Any mass increase in all the components listed is solely attributed to solid residue (Eq. 3.15). This is because the operational temperatures are not expected to favour any condensation prior to the condensing unit. Coarse char and char coating the sand within the reactor (Figure 3.25 - 4) was also included in the char products. This was calculated by weighing the overall bed material after a fast pyrolysis run, the bed material was then placed in an oven and heated to 600 °C for 2 hours which burns off the char. The bed material was left to cool to room temperature and reweighed; the difference was concluded to be solid product. Since the amount of solid from the liquid fractions has already been quantified, they are added to the process solid yields (Kalgo, 2011; Banks, 2014).

$$\text{Solid yield [wt\%]} = \left(\frac{\text{char pot (\#6)} + \text{metal transition pipe (\#7)} + \text{char in reactor sand (\#4)}}{\text{total mass of dry feed used}}\right) \text{x } 100$$

(Eq. 3.15)

3.9.4 Fast pyrolysis gas products

The accuracy of mass balances is hugely dependent on the accuracy of gas measurements. The mass of gases is however obtained from the gas composition obtained from the micro GC and the total volumetric throughput of the experiments. A Varian Star Chromatography

Workstation 6.0 was used for quantification of non-condensable gases produced during the fast pyrolysis run. The pyrolysis gas products were sampled every 150 seconds exactly. The CP-PortaPLOT column was used for separation of carbon dioxide, ethane, ethene, propane, propene and n-butane. The molecular sieve CP-5A column was used for separation of carbon monoxide, hydrogen, oxygen, nitrogen and methane. A range of BOC gas mixtures of known compositions of non-condensable gases were used to calibrate the columns prior to all pyrolysis runs. A diaphragm gas meter was used to measure the total gas output. By using the total gas output and the Varian Star Chromatography Workstation 6.0 the mass of the gas can be calculated (Eq. 3.16). The total gas yield was calculated using Eq. 3.17. (Kalgo, 2011; Banks, 2014).

$$\text{Mass of Gas proucded (H, CO, etc..)} = \frac{\text{MPV}}{\text{RT}} \qquad \textbf{(Eq. 3.16)}$$

Where: M - Gas molar mass; P - Pressure; V- Volume of gas produced; R - 8.314; T - Temperature

$$\text{Gas yield [wt\%]} = \left(\frac{\text{total mass of gas produced}}{\text{total mass of dry feed used}}\right) \text{x } 100 \qquad \textbf{(Eq. 3.17)}$$

3.9.5 Errors/Losses

Losses in the mass balance are mostly due to unidentified and undetected product gas components. However, entrainment of the finer particles of trommel fines samples in the fluidising gases and the losses in taking some representative liquid samples for water and solids contents analyses also contributed.

Gas detection was limited to the calibrated gases and the pyrolysis product gas is diluted in fluidising nitrogen. Pyrolysis product gas can account for as little as 5% of the overall analysed gas stream. Therefore, small errors in analysis of the fast pyrolysis gas products can have a large knock-on effect on the overall mass balance.

3.10 Reproducibility of fast pyrolysis experiments

Three fast pyrolysis experiments were performed for each parameter investigated (refer to section 3.6). The same fast pyrolysis temperature, feed hopper feed rate set point and reaction time were used for all three experiments to ensure results could be compared accurately. The resulting mass balances were compared to see how similar the results were to each other. Reproducible results are defined as yields of liquid, solid and gas being within a 5% range. If yields are outside this range it would show that processing the same feedstock would produce different results and therefore an average of yields would be taken from the multiple runs, and if the yields are within the 5% range, the highest mass balance closure will be reported and the rest of the results from the other two experiments will be represented as standard deviations. Mass balance closures are acceptable above 95% (Kalgo, 2011; Banks, 2014).

3.11 Fast pyrolysis process conversion efficiency

To determine whether trommel fines samples can be used for energy recovery via fast pyrolysis, with significant reduction in mass and volume of the original waste, the fast pyrolysis process conversion efficiency (η) was calculated based on the ratio of the energy content in the product to that in the feedstock. This was obtained by using the higher heating values (HHV) and the mass of each component (m) as follows:

$$\eta\,[\%] = \frac{(\mathrm{m\,HHV})\mathrm{solids} + (\mathrm{m\,HHV})\mathrm{liquids} + (\mathrm{m\,HHV})\mathrm{permenent\ gas}}{(\mathrm{m\,HHV})\mathrm{feedstock}} \ \mathrm{x}\,100 \qquad \textbf{(Eq. 3.18)}$$

The results of the process conversion efficiency calculations are used to evaluate the integration of the pre-treated trommel fines fast pyrolysis process and energy production systems with consideration of technical and economic aspects. The methodology and results are presented in chapter 7.

3.12 Summary

The trommel fines feedstock used in this research has been introduced along with the various approaches used to obtain representative samples for analyses, feedstock and pyrolysis product characterisation techniques used. The techniques introduced in this chapter have all been used during this research as will be seen in later chapters. This chapter also reported the operational problems discovered in the fast pyrolysis rig including the bridging in the feeding system, poor reactor heating profile and inappropriate condensing unit limitations during the hot commissioning phase of the 300 gh^{-1} bubbling fluidised bed reactor. The causes of all the major problems were identified and the modifications made to resolve the main problems have been discussed.

At this stage of the research, one of the primary objectives of the study had been met with the commissioning of the individual sections of the fast pyrolysis unit. The feed system, reactor system and liquid collection unit had all been put in working order and they can operate under fast pyrolysis conditions. The feed system has been commissioned and a calibration method for the feed system has also been developed. Mass balance calculation methods have been developed for all the processes involved in the preparation and fast pyrolysis of the trommel fines. All analytical techniques have provided acceptable reproducible results as shown by standard deviations (<10%) for a highly heterogeneous feedstock such as trommel fines.

4 Results and Discussions: Sample preparation and characterization

This chapter reports the results of the characterisation studies undertaken on the trommel fines feedstock used in this research. It employs some of the techniques introduced in Chapter 3 of this thesis.

4.1 Size distribution of 'as-received' trommel fines

Figure 4.1 below shows the photographs of size fractions and Figure 4.2 shows the average particle size distribution by wt.% for five replicate 0.5 kg samples of the dried trommel fines feedstock before any physical pre-treatment (refer to section 3.2).

The average particle size distribution show that only about 17.6 wt.% of the 'as-received' trommel fines feedstock was initially within the size range that could be used for fast pyrolysis with an existing bubbling fluidised bed reactor (refer to section 3.5). The 17.6 wt.% comprised of fractions with particle sizes of 1 - 2 mm range accounting for an average of 11.5 wt.% and 0.25 - 1 mm size range, which accounted for 6.13 wt.% of the total weight of the as received trommel fines sample, respectively. However, these fractions also contained a high content of sand as well as few tiny pieces of plastics, glasses and stones (Figure 4.1C & D).

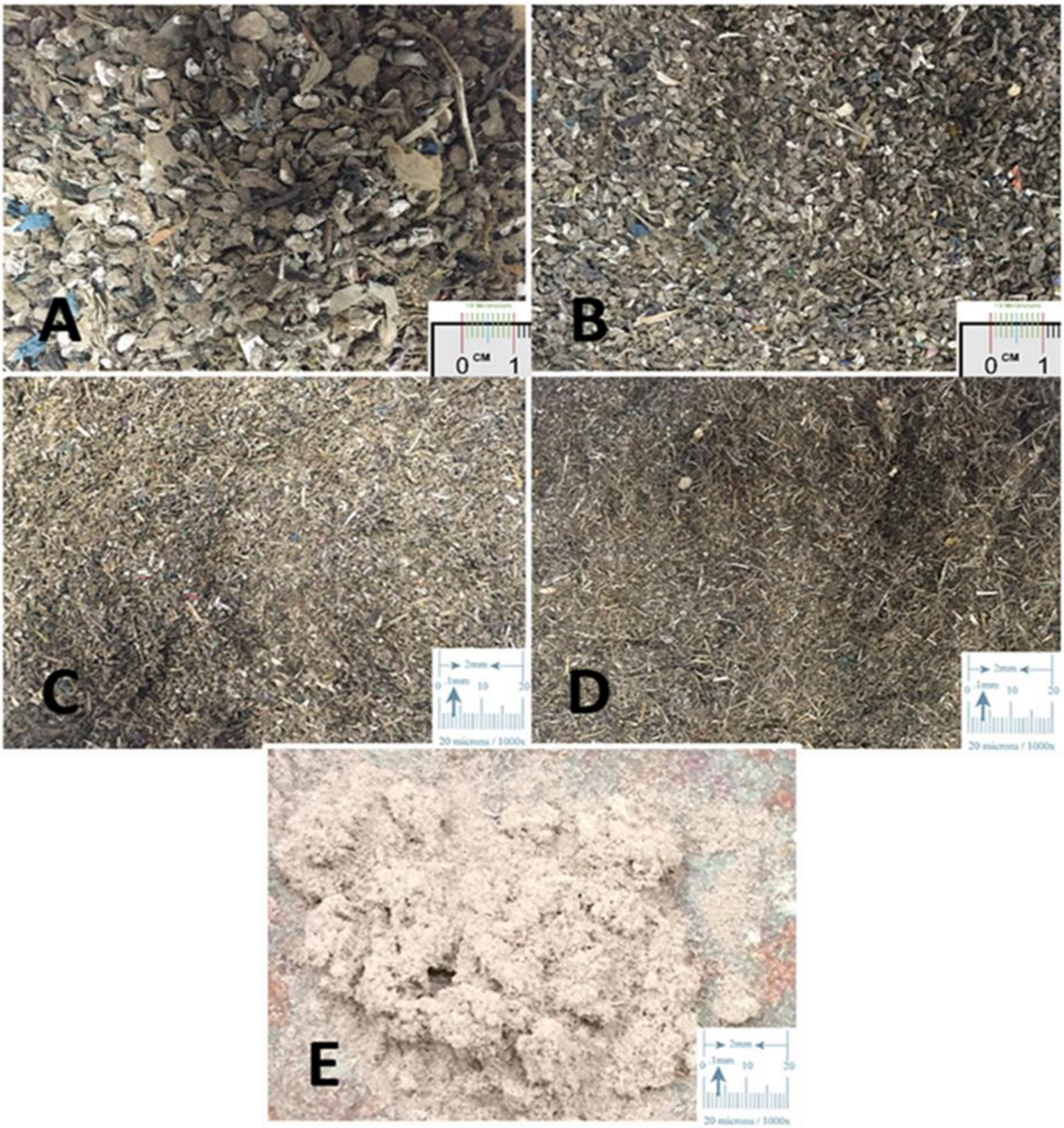


Figure 4.1: Photographs of fractions of dried raw trommel fines sample showing the size distribution

A: >3.5 mm; B: 2 – 3.5 mm; C: 1 – 2 mm D: 0.25 – 1 mm; E: <0.25 mm

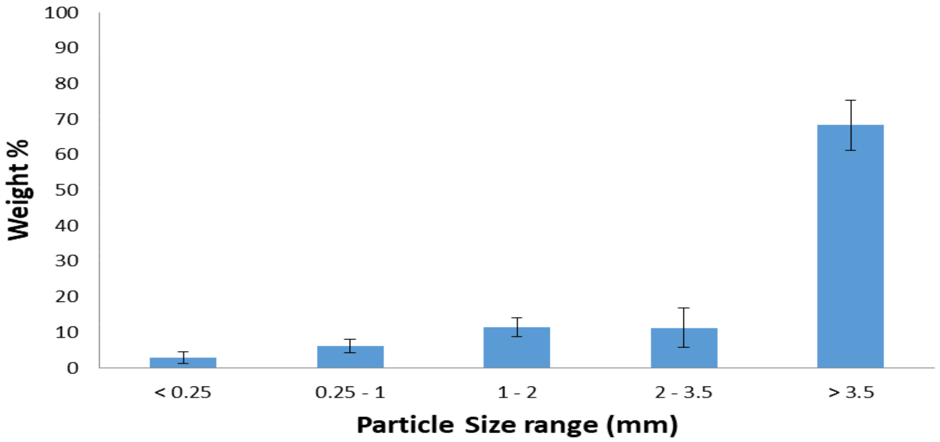


Figure 4.2: Average particle size distribution of dried trommel fines sample before preparation (5 replicates)

A small fraction, accounting for 2.8 wt.% was obtained with <0.25 mm particle size range and classified as dust (Figure 4.1E), while 79.5 wt.% needed to undergo further processing. On average, the fraction with particle sizes >3.5 mm accounted for 68.2 wt.% of the trommel fines. This size range comprised of mostly paper pellets, plastics, glass, stones, bones, miscellaneous wood, textile and metals (Table 4.1; Figure 4.1A & B). In addition, the fractions with particle sizes >2 mm would require size reduction to enable feeding into the fast pyrolysis equipment.

By physical visual observation, the prominent items found in each weight fraction was documented and the results of this observation are presented Table 4.1. Visual observation showed that the combined size ranges from 0.25 – 2 mm were similarly made up of wood, paper/cardboard and textile materials. Therefore, could be suitable for energy recovery by fast pyrolysis, due to the potential calorific value of these materials (refer to Table 4.2) and the feeding limitations to the existing fast pyrolysis reactor. While the size fractions >2 mm contained significant proportions of thermally degradable materials, a size reduction process would be required to make them suitable for the fast pyrolysis equipment.

Table 4.1: Physically observed contents of dried trommel fines fractions

OBSERVATIONS				
< 0.25 (mm)	**0.25 - 1 (mm)**	**1 - 2 (mm)**	**2 - 3.5 (mm)**	**> 3.5 (mm)**
Dust (Ash)	Paper, cardboard	Paper, cardboard	Paper, cardboard	Paper, cardboard
	Miscellaneous Plastics	Miscellaneous Plastics	Miscellaneous Plastics	Miscellaneous Plastics
	Miscellaneous Glass	Miscellaneous Glass	Miscellaneous Glass	Miscellaneous Glass
	Stones	Stones	Stones	Stones
	Miscellaneous Wood	Miscellaneous Wood	Miscellaneous Metals	Miscellaneous Metals
	Textile Material	Textile Material	Miscellaneous Wood	Miscellaneous Wood
	Sand	Sand	Bones (Food)	Bones (Food)
			Textile Material	Textile Material

4.1.1 Physio-chemical characterization of trommel fines particle size fractions

The properties of solid pyrolysable materials can have a huge impact on the process of fast pyrolysis. Particle size, moisture content and volatile content can all influence the main process mechanisms such as rate of reaction as well as influencing the reactions taking place. Table 4.2 shows the results of the proximate analysis of the trommel fines feedstock in different size ranges on a dry basis. The data in table 4.2 also reports the calculated HHV as well as the average of those obtained using a bomb calorimeter. The proximate analysis data is relevant in determining the suitable quantity and thus the feeding rate for fast pyrolysis processing, which depends on the proportion of volatile matter in the feedstock and the rate of its thermal degradation. Also, the analysis offers a preview on the mass balance of the system.

The moisture content of the feedstock prior to processing was found to be 46.0 ± 3.23 wt.% on a dry basis, therefore requiring drying before processing to aid the grinding and sieving process. After oven drying at 60 °C the moisture content decreased to less than 13.5 wt.% for all fractions. However, the 2 – 3.5 mm fraction was found to retain the most moisture, possibly due to its high organic content, which enhanced moisture retention.

Table 4.2: Results of average proximate analyses and heating values of trommel fines in relation to size ranges. (5 replicates)

ANALYSIS	**As received**	**< 0.25 (mm)**	**0.25 - 2 (mm)**	**2 - 3.5 (mm)**	**3.5 Above (mm)**
Ash content ^{a} (wt.%)	43.30 ± 4.81	53.77 ± 6.20	42.14 ± 3.41	34.87 ± 3.56	31.51 ± 2.08
Volatile Matter ^{a} (wt.%)	46.61 ± 3.53	40.04 ± 3.03	49.71 ± 6.50	56.74 ± 3.28	60.12 ± 4.65
Fixed Carbon (wt.%) ^{b}	11.09	6.20	8.15	8.39	8.38
Moisture content ^{a} (wt.%)	46.04 ± 3.23	9.56 ± 1.01	12.51 ± 3.04	13.20 ± 0.75	12.46 ± 0.92
Bomb Calorimeter ^{a} (MJ kg^{-1})	11.61 ± 2.59	7.78 ± 0.87	11.78 ± 0.27	13.20 ± 0.59	12.46 ± 0.41
HHV $_{dry}$ (MJ kg^{-1}) ^{ac}	10.70	8.01	10.30	11.54	12.09

^{a} dry basis; ^{b} calculated by difference; ^{c} Eq. 3.10

The moisture in the trommel fines feedstock will eventually end up in the fast pyrolysis products, mainly in the liquid product. This is because the moisture in the feed must be evaporated before the thermal degradation of the particle will begin. The presence of water has also been shown to cause secondary reactions in some cases, especially in gas-phase reactions (Gray et al., 1985; Kelbon et al., 1988; Maniatis et al., 1988; Bridgwater and Peacocke, 2000; Westerhof et al., 2007; He et al., 2009). As water is an unwanted compound in fast pyrolysis bio-oils, due to its lowering effect on the heating values, however, a moderate amount of moisture is known to impact positively on the viscosity of the oil product. Bridgwater et al. (2000) recommends that the moisture content for biomass for fast pyrolysis processes be around 10 wt.% and this would be applicable to a biogenic-rich waste feedstock. Therefore, further drying may be required before the prepared feedstock could be used; however, the energy required for this step may be provided via combustion of dusty fraction and char in the solid residues.

There was a clear indication of variation of ash content between the size fractions as seen in Table 4.2. The ash content decreased with increasing size fraction. The ash content of all the samples were between 31 – 54 wt.% on a dry basis and it shows significant difference between the size ranges. The inverse pattern was observed with the volatile matter contents, which increased with particle size. There was no apparent trend with the fixed carbon with respect to particle size. From these results, there was an indication that different fractions of the trommel fines can have significant differences in thermochemical properties. The high ash content in the feed was obviously due to the presence of high amounts of fine inorganics as the ash content is known to be dependent on the inorganic components of the feedstock (Teng et al., 1998; Hodgson et al., 2010). The high inorganics in the feed could arise from a number of reasons, such as the source of the feedstock and the technique used to separate the waste streams. The high ash content will lead to an increase in volume and weight of bed material in a fluidised bed pyrolysis process. Research has shown that inorganic compounds present in a feedstock promote the formation of char and gas at the expense of pyrolysis liquid yield. An increase in char and gas yield at the expense of bio-oil due to the presence of ash during pyrolysis was observed in a number of studies (Sekiguchi et al., 1984; Varhegyi et al., 1989; Teng et al., 1998; Hodgson et al., 2010). The reduced volatiles may be due to the size reduction process during the initial handling of MSW at recycling facilities (refer to section 3.2). For instance, the size reduction process might have aided the degradation of the feedstock as well as eliminating certain materials (rubber, textile, and plastics) that would have improved the volatile content of the feed. The reduced volatiles in this feedstock were an early indicator of low liquid and gas yields from fast pyrolysis.

The experimental heating values for all the samples were between 7.8 – 13.8 MJ kg^{-1}, on a dry basis with the heating value increasing with increasing size fraction. This was an indication that pyrolysis liquids and bio-fuels with moderately high-energy content may be obtained from this feedstock. The experimental results compared well with the theoretical heating values (Table 4.2) as they were observed to be similar and increasing with size fraction.

4.2 Physical preparation of trommel fines for fast pyrolysis

As mentioned earlier, due to the limitations of the feeding system (limited to < 2 mm), it was decided to test-feed the reactor with the combined fractions with particle size ranges covering between 0.25 – 2 mm. These initial tests revealed serious problems of dust entrainment and deposition throughout the downstream parts of the pyrolysis system (condensers and filters) as shown in Figure 4.3. Apparently, the amount of dust (< 0.5 mm) produced during the feeding increased due to the vibration of the fast screw rotating at a pre-set rate of 100 rpm. This dust was easily transported through the rig via the nitrogen gas connected to the feeding system and the fluidizing nitrogen in the reactor (Figure 4.3). This could easily pose significant problems during the operation of the pyrolysis equipment. Firstly, the dust could settle along narrower pipes and cause blockage which would in turn lead to build up of pressure in the rig. Such pressure build-up could lead to explosion and loss of containment. Secondly the dust, which still contains combustible organic matter may be susceptible to dust explosion with serious consequences. Thirdly, the dust would contaminate the condensable pyrolysis products downstream, cause blockage to the fast screw when feeding and affect the safe operation of the rig. The solution to this challenge was to reduce the content of the fine dust particles by physical separation via sieving. Hence, when the feed particle size was adjusted to 0.5 – 2 mm, the dust deposition and transportation through the rig stopped as shown in

Figure 4.4. Although, this would decrease the fraction obtained for energy recovery via fast pyrolysis, the safety of operation was deemed of much higher importance than a few losses.

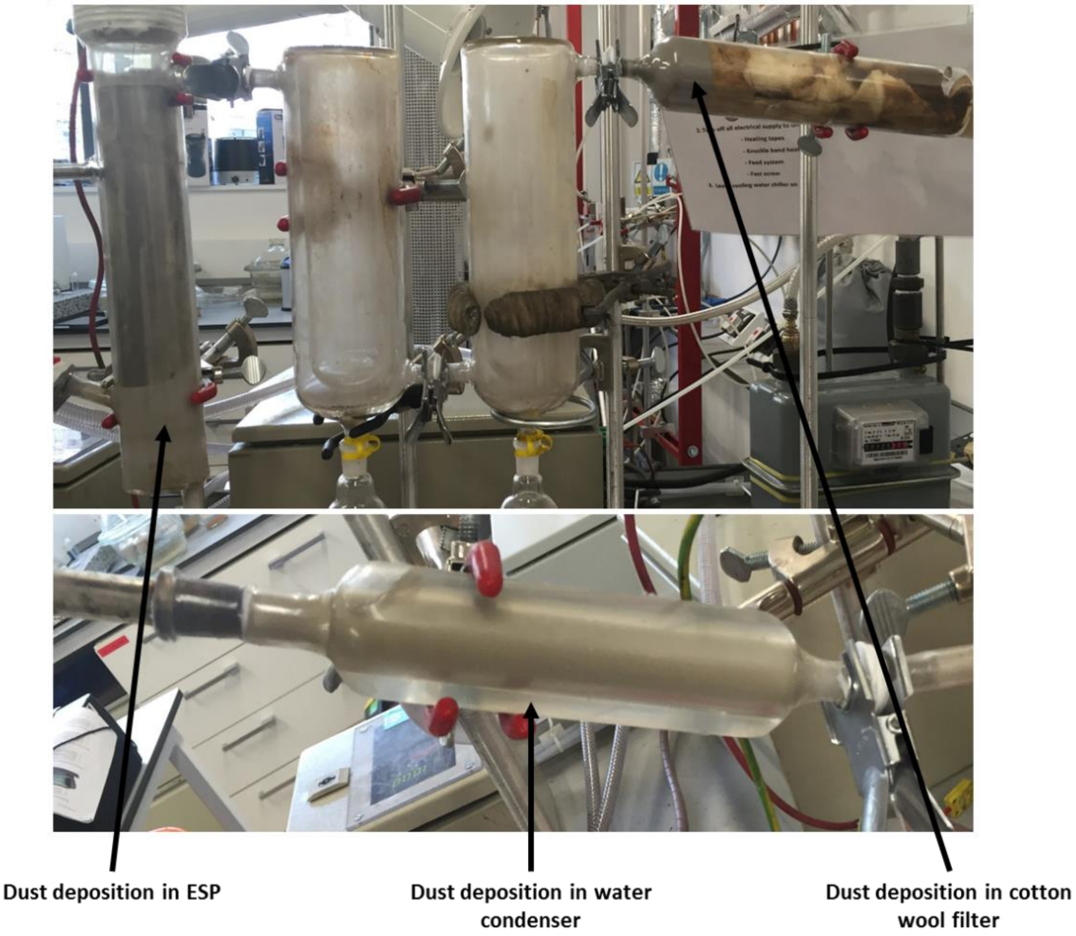


Figure 4.3: Accumulation of dust in downstream parts of a fast pyrolysis rig during feeding trial of 0.25 – 2mm trommel fines

Figure 4.4: Downstream parts of a fast pyrolysis rig during feeding trial after modification to feedstock particle size (0.5 – 2mm)

Hence, a new particle size range (0.5 – 2 mm) was considered for the fast pyrolysis of the trommel fines, following the sample preparation protocol depicted in Figure 4.5. As shown in Figure 4.5, a 3 kg batch of trommel fines was used directly for the sample preparation involving physical separation by hand, grinding and seiving. Table 4.3 shows the results of the preparation protocol. After feed preparation, 69.4 wt.% of the 3 kg trommel fines batch was obtained with a suitable particle size range for the fast pyrolysis process (0.5 – 2 mm). Overall, some 10.8 wt.% (<0.5 mm) comprised of mainly dust (ash) and some organics, which was eliminated. This fraction could be burnt in an industrial process to provide heat for the pyrolysis process as it had an appreciable heat content (7.78 MJ kg^{-1} as seen in Table 4.2). The physical separation by hand yielded 12.9 wt.% and 6.8 wt.% of plastics and inorganics (stones, bone, etc.), repectively. On an industrial scale, the plastics and textiles could be recycled for RDF, while the inorganics (glass and stones) can be used in construction.

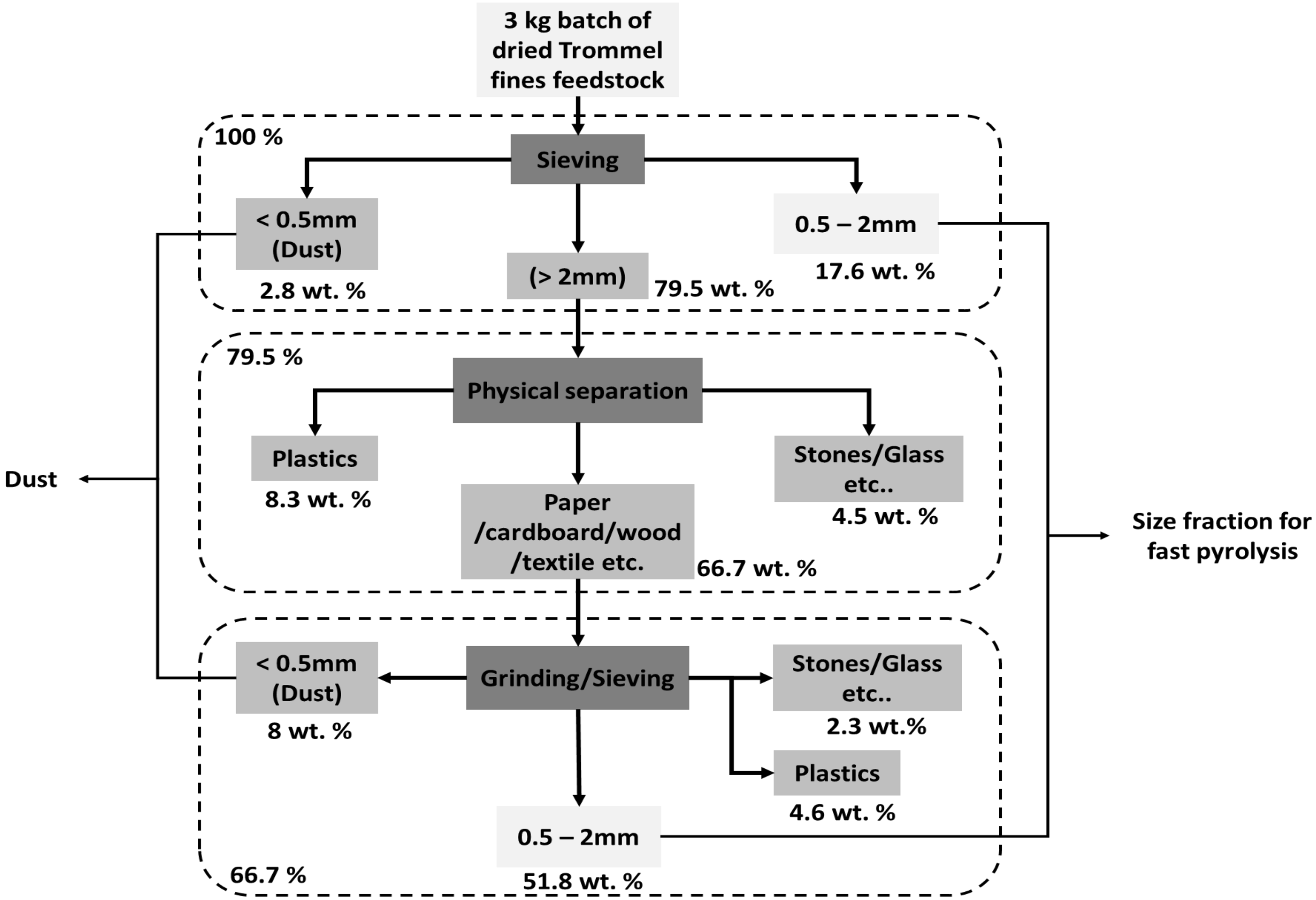


Figure 4.5: Detailed scheme for trommel fines feedstock physical pre-treatment preparation

Table 4.3: Updated summary of trommel fines main components after feedstock preparation

Fractions	**Weight %**
< 0.5 mm	10.8
0.5 - 2mm*	69.4
Stones/Glass etc.	6.8
Plastics	12.9
TOTAL	**99.9**
*** Size fraction for fast pyrolysis**	

4.2.1 Detailed characterization of 0.5 – 2 mm particle size range deemed for fast pyrolysis

An enlarged photograph of the prepared sample fraction deemed suitable for fast pyrolysis is shown in Figure 4.6. This obtained sample would be referred to in this thesis as the dry physically pre-treated trommel fines (PT). Table 4.4 shows the results of the proximate analysis of the PT trommel fines feedstock on a dry basis. The data in the table also reports the calculated HHV as well as the average of those obtained using a bomb calorimeter. PT, the particle size range of (0.5 – 2 mm) deemed for fast pyrolysis has an ash content of 36.2 ± 1.85 wt.% which is slightly lower when compared to the as received sample and the initial size fraction (0.25-2 mm) that was initial deemed suitable for fast pyrolysis (Table 4.2). The volatile and fixed carbon content were 56.3 ± 1.50 and 7.52 wt.% respectively (Table 4.4). The calorific value (HHV) of the fraction for fast pyrolysis (PT) was determined to be 13.8 ± 0.32 MJ kg^{-1}. This value is slightly higher to the value for the 0.25 – 2 mm fraction, indicating that the removed dusty fraction composed of mostly inert materials.

Figure 4.6: Photograph of prepared trommel fines fraction (0.5 – 2 mm size range) for fast pyrolysis

Table 4.4: Average proximate analyses and heating values of the 0.5 - 2 mm size range PT trommel fines. (5 replicates)

ANALYSIS	**PT (0.5 - 2 mm) [b]**
Ash content [a] (wt.%)	36.2 ± 1.85
Volatile Matter [a] (wt.%)	56.3 ± 1.50
Fixed Carbon (wt.%) [c]	7.52
Bomb Calorimeter [a] (MJ kg^{-1})	13.8 ± 0.33
HHV $_{dry}$ (MJ kg^{-1}) [a d]	11.1

[a] dry basis; [b] prepared size fraction for fast pyrolysis experiments; [c] calculated by difference; [d] Eq. 3.10; PT – Physical pre-treated Trommel Fines

The ultimate analysis, on dry, ash-free basis, of the PT trommel fines feedstock (size range 0.5 - 2 mm in Table 4.5) shows elemental compositions similar to literature data for a refused derived fuel from municipal solid waste (MSW) as reported by other authors (Efika, Wu and Williams, 2012; Blanco et al., 2012; Materazzi et al., 2015). The prepared trommel fines feedstock have a lower carbon content of 34 wt.% when compared to literature data range of 43 - 62.1 wt.% for RDF. The oxygen contents of the feedstock also differ with this feedstock having lower oxygen content of 17.06 wt.% when compared to literature, which stands at between 26.52 and 37.9 wt.%. These differences could be attributed to the source and composition of the waste. One clear observation was that the feedstock has a significantly high nitrogen content of 2.75 wt.% when compared with other MSW literature data of 0.1 - 1.82 wt.% (Efika, Wu and Williams, 2012; Blanco et al., 2012; Materazzi et al., 2015). The nitrogen contents also serve as an indication of the possibility of NOx compounds forming during the oxidative thermochemical processing of the feedstock (Diebold, 2002). This is undesirable in terms of environmental considerations. The feedstock showed sulphur contents like those reported for MSW in literature (Materazzi et al., 2015).

Table 4.5: Ultimate analysis of the 0.5 - 2 mm size range PT trommel fines (5 replicates)

Elements (wt.%)	**PT**
Nitrogen	2.75 ± 3.16
Carbon	33.71 ± 6.93
Hydrogen	4.62 ± 0.92
Sulphur	0.26 ± 0.20
Oxygen	17.06 ± 8.21
***remainder was classified as ash**	

Thermal degradation rate of solid fuels is very important in the design of a fluidised pyrolysis system. Fundamental to the degradation rate are the rates of bond breaking, formation and devolatilization of small stable molecules. The TG and DTG curves of the prepared trommel fines feedstock are shown in Figure 4.7. Three major weight loss steps are evident from the DTG curve. The initial weight loss step, which accounted for the removal of moisture from the feedstock, occurred between 40 and 106 °C. The second weight loss step happened between 110 and 390 °C. The second step was the major pyrolysis process and the inflection point of this step was at 350 °C and that showed the temperature at which weight loss was at its maximum. This loss can be attributed to the degradation of components such as hemicellulose, cellulose and lignin of the sample. The third weight loss step occurs between 400 and 523 °C. The small weight loss with a maximum degradation temperature of about 500 °C may be attributed to the small amount of fine plastic particles remaining in the sample. The total weight loss as can be seen on the TG curve of the trommel fines feedstock stands at about 54% between 40 ºC and 550 ºC, which is similar to the upper limit sum of VM and moisture contents of the sample (53.7 wt%).

Clearly, Figure 4.7 confirms the high ash content of the prepared trommel fines sample, but it also shows that the feedstock contains a significant proportion of volatile matter from which energy can be obtained via fast pyrolysis. Recovery of this energy will be important to meet landfill disposal requirements in terms of the loss on ignition (LOI) limits and for sustainable waste management (Official Journal, 1999). The results of the ash content analysis of the feedstock, suggest that about 50% of the feedstock can be used for energy recovery and diverted from landfill. In addition, the seemingly inert ash product may be used in construction. This will reduce the amount of landfill tax an operator that produces 40 tonnes a day would pay from over £1,000,000 to less than £60,000. This estimate takes into consideration the reduction in mass and volume of waste due to energy recovery as well as the reduced tariff applicable to the landfilling of ash-rich, low LOI-bearing solid residues (Official Journal, 1999).

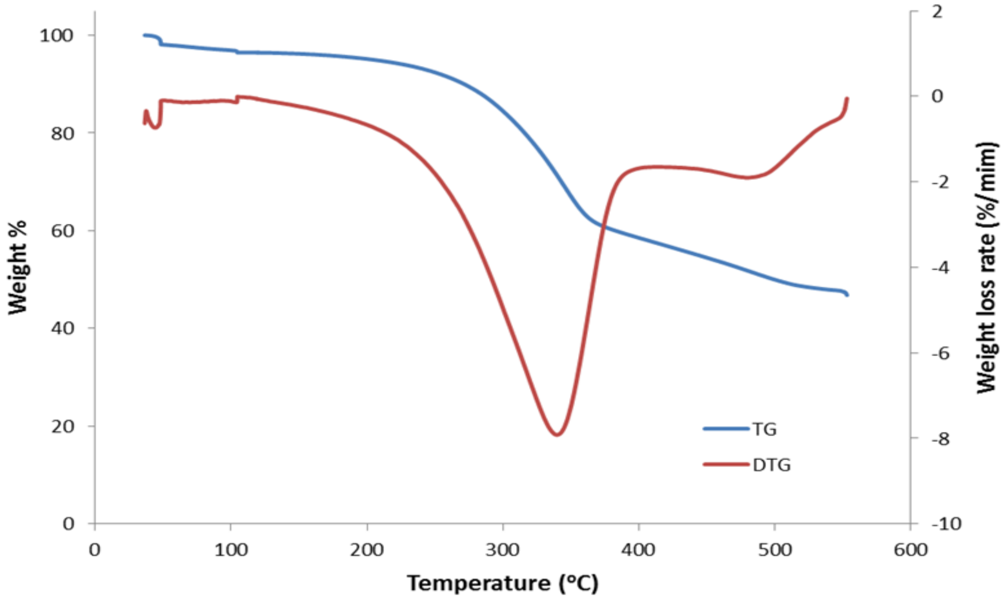


Figure 4.7: TG and DTG curves of PT trommel fines 0.5 - 2 mm size range

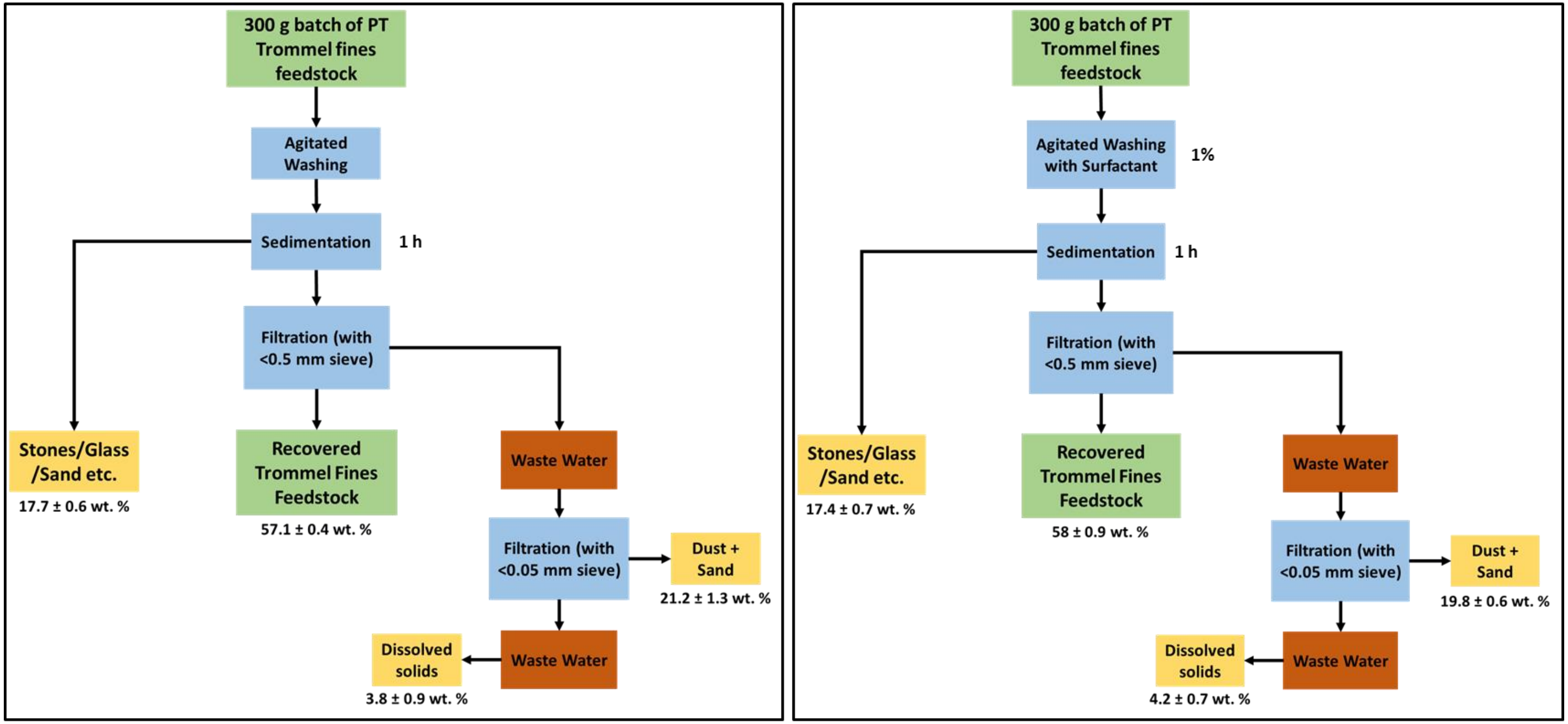
4.2.2 Conclusion on dry physical pre-treatment

A sample of trommel fines obtained from a UK Waste Management company showed a wide range of particle sizes and contained mixtures of different materials from plastics, paper and cardboard to stones and bricks. The increasingly tight regulations for disposal of trommel fines in landfills, especially in terms of LOI limits, have necessitated the need to investigate alternative processes for its management. Thermochemical process via fast pyrolysis looks like a plausible solution however, the physical characteristics of trommel fines would need to be adjusted to meet the requirements of fast pyrolysis. Initial results of proximate analyses showed that different size fractions of trommel fines have differences in properties. Ash, volatile content and heating values varied in relation to the range of particle sizes. However, the removal of glass, metals and inert materials such as stones etc., which do not contribute to the energy content of the waste, is highly recommended to reduce the volume of waste and minimize reactor damage which can be done via physical separation. Although, manual separation appears plausible for a lab scale process, an appropriate pre-treatment method tailored for inorganics recovery at small size fractions (<2 mm) is required for a large batch of waste (refer to section 4.3). In addition, dust formation is a potential hazard during the feeding for fast pyrolysis of trommel fines, but this can be minimized by using the appropriate particle size range after size reduction via screening, grinding and sieving. This preliminary work suggests that appropriate feedstock preparation is needed to make thermal recovery of energy possible from heterogeneous and complex waste materials such as trommel fines. Fast pyrolysis tests using the fluidised bed reactor will be carried out of the PT fraction in future to investigate its suitability to handle this type of sample.

4.3 Agitated aqueous washing and sedimentation of trommel fines for fast pyrolysis (wet physical pre-treatment)

The primary aim of the agitated washing pre-treatment procedure was to attempt to reduce the ash content of the physically pre-treated trommel fines feedstock by separating the inorganics (glass, stones, sand etc. present in the feedstock (refer to section 3.3). As shown in the schematics in Figure 4.8, a 300 g batch of trommel fines was used directly for the sample preparation involving agitated washing, sedimentation and flitration to recover the trommel fines feedstock and further separate inorganics from the feedstock. Table 4.6 shows the results of the preparation protocol for both agitated washing and agitated washing with surfactant (refer to section 3.3). Each sample preparation method was peformed twice and the recovered trommel fines samples were combined and dried for fast pyrolysis experiments.

According to Figure 4.8 and Table 4.6 after feed preparation, aproximately 58 wt.% of the 300 g trommel fines batch was obtained with a suitable particle size range for the fast pyrolysis process (0.5 – 2 mm). The sedimentation process yielded about 18 wt.% of inorganics (stones, glass, etc.) which was eliminated (Figure 4.9A). On an industrial scale, the inorganics (glass and stones) can be recycled and used in construction.



A: Agitated Washing (AW) **B: Agitated Washing with Surfactant (AWS)**

Figure 4.8: Detailed scheme for agitated aqueous washing pre-treatment trommel fines feedstock

Table 4.6: Updated summary of trommel fines main components from wet preparation procedure

Fractions	**AW (wt.%)**	**AWS (wt.%)**
Recovered trommel fines feedstock	57.1 ± 0.4	58 ± 0.9
Stones/Glass etc	17.7 ± 0.6	17.4 ± 0.7
Dust (ash) etc.	21.2 ± 1.3	19.8 ± 0.6
Dissolved solids	3.8 ± 0.9	4.2 ± 0.7
Total	**99.8 ± 0.3**	**99.4 ± 0.5**
AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)		

Overall, some 22 wt.% solid recovered from further flitration of the waste water, comprised of mainly dust (ash), soil and sand, which was eliminated (Figure 4.9B). Aproximately 4 wt.% of the 300 g dissolved in the washing water. From the results obatined, the addition of a surfactant (Decon Neutracon) to the pre-treatment procedure, did not affect the amount of inorganics separated from the feed. Nevertheless, though the agitated washing pre-treatment methods could further separate 43 wt.% of inorganics which can be recycled or landfilled, it is important to note that, not all the inorganics in the trommel fines feedstock was separated. The lighter fractions of the inorganics such as aluminium sheets were not separated because they were suspended together with the organic fraction of the trommel fines during the sedimentation process, thus was filtered out together with the recovered trommel fines feedstock. An enlarged photograph of the prepared sample fraction deemed suitable for fast pyrolysis from both AW and AWS are shown in Figure 4.10. From visual observations, there is no difference between the two washed samples.

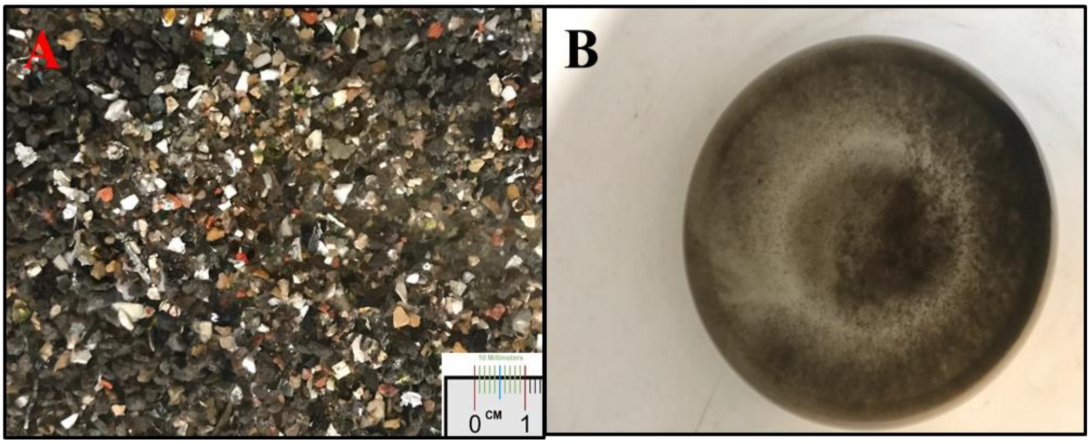


Figure 4.9: Photographs of sedimentation products; A: recovered inorganics; B; recovered dust and sand from filtration of waste water.

A: Agitated Washing (AW)

B: Agitated Washing with Surfactant (AWS)

Figure 4.10: Photographs of recovered trommel fines (0.5 – 2 mm size range) after the aqueous washing process

4.3.1 Characterization of wet pre-treated trommel fines feedstock

Table 4.7 shows the results of the proximate analysis of the wet physically pre-treated trommel fines feedstock on a dry basis. The data in the table also reports the calculated HHV as well as the average of those obtained using a bomb calorimeter. The ash content of the AW and AWS trommel fines sample were 23.1 and 22.3 wt.% respectively, which were both high when compared to other MSW and RDF samples from literature (Lyngfel et al. 1999; Winter et al. 1999; Zevenhoven et al. 1999; Guilin et al. 2000; Werther et al. 2000; Onay et al. 2001; Saenger et al. 2001; Sørum et al. 2001; Patumsawad et al. 2002; Demirbas, 2004; Michaël, 2007). The high ash content still in the wet physically pre-treated sample could be due to a number of reasons, such as the light inorganic components (aluminum sheets, etc.) still in the feed, which do not contribute to the energy content of the feedstock. However, the ash content of the AW and AWS samples, can further be reduced by mixing the pre-treated waste with another type of waste (refer to section 2.3) with low ash content (sludge, plastic waste, forestry biomass, etc). This would potentially lead to an increase in pyrolysis liquid yields and further decrease in solid yields (Vassilev et al., 2010). This recommendation is a subject for future research.

The volatile content of the AW and AWS trommel fines feedstocks were similar at 69.7 ± 1.92 and 70.8 ± 0.44 wt.% respectively and fixed carbon contents were 7.28 and 6.40 wt.% respectively (Table 4.7). The calorific value (HHV) of the AWS trommel fines feedstock was determined to be 16.1 ± 0.32 and MJ kg^{-1} and this value is slightly higher than the value for AW trommel fines feedstock (15.7 ± 0.41). This was an indication that pyrolysis liquids and bio-fuels with moderately high-energy content may be obtained from these pre-treated feedstocks. The experimental results compared well with the theoretical heating values (Table 4.7) as they were observed to be similar.

Table 4.7: Results of average proximate analyses and heating values of pre-treated trommel fines. (5 replicates)

ANALYSIS	AW	AWS
Ash content (wt.%) [a]	23.1 ± 0.46	22.8 ± 0.69
Volatile Matter (wt.%) [a]	69.7 ± 1.92	70.8 ± 0.44
Fixed Carbon (wt.%) [b]	7.28	6.40
Bomb Calorimeter (MJ kg^{-1})	15.7 ± 0.41	16.1 ± 0.32
HHV $_{dry}$ (MJ kg^{-1}) [c]	13.3	13.1
[a] dry basis; [b] calculated by difference; [c] Eq. 3.10; PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)		

The ultimate analysis, on dry, ash-free basis, of the wet physically pre-treated trommel fines feedstock (AW and AWS) are reported in Table 4.8 below. The AW and AWS trommel fines samples have a lower carbon content of 36.4 and 39.4 wt.% respectively when compared to literature data range of 43 - 62.1 wt.% for RDF and MSW. The oxygen contents of the AW and AWS trommel fines samples (33.1 and 29.1 wt.% respectively) were comparable to literature, which ranges from 26.52 - 37.9 wt.%. (Ruth et al. 1998; Zevenhoven et al. 1999; Guilin et al. 2000; Patumsawad et al. 2002; Rogaume et al. 2002; Tchobanoglous 2002; Michaël, 2007). The nitrogen contents of the AW and AWS trommel fines samples (1.54 and 1.89 wt.% respectively) were also comparable to literature data of 0.1 - 1.82 wt. % (Rogaume et al. 2002; Tchobanoglous 2002; Michaël, 2007; Efika, Wu and Williams, 2012; Blanco et al., 2012; Materazzi et al., 2015). However, the AW and AWS trommel fines samples showed higher Sulphur contents those reported for MSW in literature (Zevenhoven et al. 1999; Patumsawad et al. 2002; Rogaume et al. 2002; Materazzi et al., 2015).

Table 4.8: Ultimate analysis of pre-treated trommel fines (5 replicates)

Elements (wt.%)	**AW**	**AWS**
Nitrogen	1.54 ± 0.92	1.89 ± 0.52
Carbon	36.4 ± 3.03	39.4 ± 3.56
Hydrogen	5.27 ± 0.75	6.22 ± 0.84
Sulphur	0.58 ± 0.24	0.54 ± 0.18
Oxygen [a]	33.1 ± 4.65	29.1 ± 4.32

[a] Oxygen calculated by difference; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)

The TG and DTG curves of the wet physically pre-treated trommel fines samples (AW and AWS) are shown in Figure 4.11. Three major weight loss steps are evident from the DTG curve for the AW and AWS trommel fines samples. The initial weight loss step, which accounted for the removal of moisture from the feedstock, occurred between 40 and 103 °C for both samples. The second weight loss step occurred between 110 and 405 °C for the AW sample and between 110 and 410 °C for AWS sample.

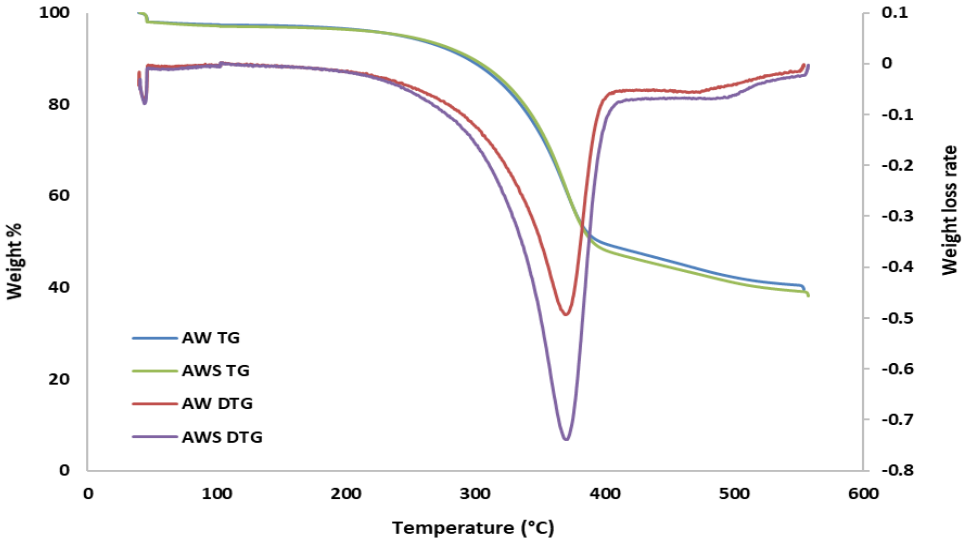


Figure 4.11: TG and DTG curves of wet physically pre-treated trommel fines sample

The second step was the major pyrolysis process and their inflection points of this step was at 374 °C and 370 °C respectively which showed the temperature at which weight loss was at its maximum. This loss can be attributed to the degradation of components such as hemicellulose, cellulose and lignin of the sample. The third weight loss step occurs between 407 and 554 °C for the AW sample and between 415 and 557 °C for AWS sample. The small weight loss with a maximum degradation temperature of about 473 °C and 502 °C respectively may be attributed to the small amount of fine plastic particles remaining in the sample. The total weight loss as can be seen on the TG curve of the wet physically pre-treated trommel fines samples (AW and AWS) stands at about 60.6% between 40 ºC and 554 ºC for the AW sample and 61.9% between 40 ºC and 557 ºC.

4.3.2 Conclusion on (wet physical pre-treatment) agitated washing and sedimentation

The ash, volatile content and heating values varied after agitated washing and sedimentation. However, although the removal of glass, stones etc., which do not contribute to the energy content of the waste, was plausible via the sedimentation process, the addition of a surfactant (Decon Neutracon) had no effect on the process. This preliminary work suggests that the agitated washing and sedimentation pre-treatment process is an effective process to further separate inorganics from the feedstock at smaller size fractions which can either be recycled or landfilled. This method would further help make the trommel fine feedstock suitable for fast pyrolysis thus making thermal recovery of energy possible from heterogeneous and complex waste materials such as trommel fines. Fast pyrolysis tests using the fluidised bed reactor will be carried out of the AW and AWS fraction in future to investigate its suitability to handle these types of samples.

4.4 Comparison of trommel fines pre-treatment methods

The effect of pre-treatment methods on the proximate analysis and heating values of all the pre-treated trommel fines feedstock can be seen in Table 4.9. There was a clear indication of variation of ash content between the pre-treatment methods as seen in Table 4.9. The ash content decreased after agitated washing and sedimentation from 36 to 23 wt.%, but the addition of a surfactant (Decon Neutracon) had no effect on the ash content. The decrease in ash content was solely due to the elimination of the inorganics recovered after sedimentation process. The inverse pattern was observed with the volatile content and the volatile content increased after agitated washing and sedimentation because of the eliminated inorganics.

There was no apparent trend with the fixed carbon with respect to pre-treatment method. From these results there was an indication that different pre-treated trommel fines samples can have significant differences in chemical properties. The reduced ash content after agitated washing and sedimentation would lead to a decrease in solid yield produced after fast pyrolysis process. The experimental heating values for all the pre-treated trommel fines feedstock were between 11.61 – 16.1 MJ kg^{-1}, on a dry basis with the heating value increasing after agitated washing and sedimentation (Table 4.9). The AWS trommel fines feedstock has the highest heating value (16.1 MJ kg^{-1}) because of reduced ash content.

Table 4.9: Comparison of average proximate analyses and heating values of pre-treated trommel fines.

ANALYSIS	**PT**	**AW**	**AWS**
Ash content (wt.%) [a]	36.2 ± 1.85	23.1 ± 0.46	22.8 ± 0.69
Volatile Matter (wt.%) [a]	56.3 ± 1.50	69.7 ± 1.92	70.8 ± 0.44
Fixed Carbon (wt.%) [b]	7.52	7.28	6.40
Bomb Calorimeter (MJ kg^{-1})	13.8 ± 0.33	15.7 ± 0.41	16.1 ± 0.32
HHV $_{dry}$ (MJ kg^{-1}) [c]	11.1	13.3	13.1
[a] dry basis; [b] calculated by difference; [c] equation 3.9; PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)			

There was a clear indication of variation of ultimate analysis on dry, ash-free basis, between the pre-treatment methods as seen in Table 4.10 below. The AW and AWS trommel fines samples have a higher carbon content of 36.4 and 39.4 wt.% respectively when compared to the PT trommel fines sample (34 wt.%). The oxygen contents of the feedstock also differ with this AW and AWS trommel fines samples having higher oxygen content of 33.1 and 29.1 wt.% respectively when compared to PT trommel fines sample (17.06 wt.% as seen in Table 4.10). One clear observation was that the AW and AWS trommel fines samples have a lower nitrogen content of 1.54 and 1.89 wt.% respectively when compared to PT trommel fines sample of (2.75 wt.% as seen in Table 4.10), indicating the possibility of reduced NOx compounds forming during the processing of the feedstocks (Diebold, 2002). The AW and AWS trommel fines samples showed higher sulphur contents (0.58 ± 0.24 and 0.54 ± 0.18 wt.% respectively) than the PT trommel fines sample (0.26 ± 0.20 wt.%), which may indicate that the sulphur content in the feedstock was retained even after washing. This would result to increase in SOx compounds forming during the processing of the feedstocks.

Table 4.10: Comparison of ultimate analysis of pre-treated trommel fines

Elements (wt.%)	**PT**	**AW**	**AWS**
Nitrogen	2.75 ± 3.16	1.54 ± 0.92	1.89 ± 0.52
Carbon	33.71 ± 6.93	36.4 ± 3.03	39.4 ± 3.56
Hydrogen	4.62 ± 0.92	5.27 ± 0.75	6.22 ± 0.84
Sulphur	0.26 ± 0.20	0.58 ± 0.24	0.54 ± 0.18
Oxygen	17.06 ± 8.21	33.1 ± 4.65	29.1 ± 4.32
***remainder was classified as ash;** PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)			

4.5 Summary

A detailed characterisation of the ‘as received’ trommel fines feedstock was carried out to ascertain its physico-chemical properties. Size fraction analysis revealed that only a small proportion of the MSW feedstock could be used for experimental studies on an existing fast pyrolysis reactor system. Hence, three feedstock pre-treatment methods were designed to improve the characteristics of the MSW feedstock towards it thermal recovery via fast pyrolysis. These methods included size reduction and adjustment to meet the feeding requirements of the pyrolysis reactor (0.5 – 2mm) as well as two aqueous washing procedures in an attempt to reduce the high ash load of the sample. Further characterisation studies have been conducted on the dry and wet physically pre-treated trommel fines feedstocks to be processed via fast pyrolysis. The thermal degradation behaviours of all the pre-treated trommel fines feedstocks have also been studied using thermogravimetric analysis at temperatures similar to pyrolysis. Results show that fast pyrolysis is a potential technology to process the pre-treated trommel fines feedstocks.

5 Results and Discussion - Pyrolysis of prepared samples

This chapter reports the results of 3 sets of fast pyrolysis experiments. The first investigates the influence of reaction temperature on product yields and conversion efficiency from the physically pre-treated trommel fines sample (PT). The second series of experiments investigates the effect of PT moisture content on the pyrolysis process at optimum reaction temperature. With the first two sets of experiments, the optimum conditions for the fast pyrolysis of trommel fines were determined. In the final set of experiments, the impact of feedstock pre-treatment methods on product yields at optimum processing conditions was explored.

5.1 Effect of pyrolysis temperature

Table 5.1 details an overview of the process parameters, product yields, product distributions and mass balance closure results obtained from the temperature investigation experiments (TIR) using the dry physically pre-treated trommel fines feedstock (PT). The primary aim of this set of experiments was to investigate the influence of temperature on the yields of fast pyrolysis products from trommel fines in order to determine the optimum pyrolysis temperature range for maximum total liquid and organic yields from the feedstock. Each experiment was conducted three times and averages reported. The resulting mass balances were compared to establish similarities between results. Reproducibility was less than 5%, so the highest mass balance closure obtained were reported and the rest are presented as standard deviations (Kalgo, 2011; Bank, 2014).

Table 5.1: Mass balance summary for temperature investigation (TIR) experiments using dry physical pre-treated trommel fines (PT)

Parameter	**TIR-400**	**TIR-500**	**TIR-600**	**TIR-700**
Set Temperature (°C)	**400**	**500**	**600**	**700**
Average Exp. Temperature (°C)	**426.3**	**525.0**	**640.0**	**737.0**
Feed Moisture before exp. (wt.%)	3.02 ± 0.25	2.69 ± 0.07	2.45 ± 0.84	2.95 ± 0.34
Run duration (minutes)	60	60	60	60
Average Feed rate (g h^{-1})	126.8 ± 5.10	158.9 ± 13.8	114.4 ± 4.21	120.8 ± 5.11
Total Liquid (wt.%) [a, b]	**25.3 ± 0.04**	**32.6 ± 0.56**	**17.4 ± 0.37**	**12.8 ± 0.05**
PC Organics	5.84 ± 0.0	12.5 ± 0.40	3.79 ± 0.30	2.37 ± 0.08
SC Organics	6.05 ± 0.21	7.07 ± 0.72	7.14 ± 0.06	6.63 ± 0.32
Reaction Water	13.4 ± 0.25	13.0 ± 0.56	6.49 ± 0.04	3.78 ± 0.35
Solid Residue (wt.%) [a, c]	**64.9 ± 0.04**	**52.1 ± 1.23**	**51.5 ± 0.60**	**48.6 ± 0.03**
Gas (wt.%) [a]	**7.29 ± 0.69**	**12.9 ± 0.02**	**18.8 ± 135**	**24.6 ± 1.42**
Hydrogen	0	0	0.01	0.01
Carbon dioxide	0.04	0.08	0.10	0.09
Methane	0.21	0.52	0.82	1.51
Carbon dioxide	5.48	8.82	10.87	13.56
Ethylene	0.07	0.25	1.50	3.33
Ethane	0.1	0.24	0.38	0.48
Propylene	1.21	2.45	2.68	1.94
Propane	0.12	0.41	1.68	2.32
n-Butane	0.05	0.16	0.76	1.33
Closure (wt.%) [a]	**97.5 ± 0.67**	**97.6 ± 0.69**	**87.8 ± 0.38**	**85.9 ± 1.50**

TIR: Temperature Investigation Run; [a] dry basis; [b] ash free; [c] including oil solid content; PC: Primary condensate; SC: Secondary condensate; Exp: Experiment

As it can be seen from the Table 5.1 above, the mass balance closures were above 95% for TIR-400 and TIR-500, which showed acceptable accounting for the mass flows. However, the mass balance closure decreases with increasing temperature with TIR-700 having the lowest mass balance closure due to some losses. The losses could be related to the unidentified and undetectable components of the gas products, but not neglecting the small amount of trommel fines samples and the losses in taking some representative liquid samples for water and solids contents analyses. The unidentified gases were observed from the presence of certain extra peaks, which could not be identified by the GC as seen in Figure 5.1. It is therefore suggested for future work that the gases should be sampled for GC/MS analysis to identify the extra peaks such as NOx, Sox and chlorine.

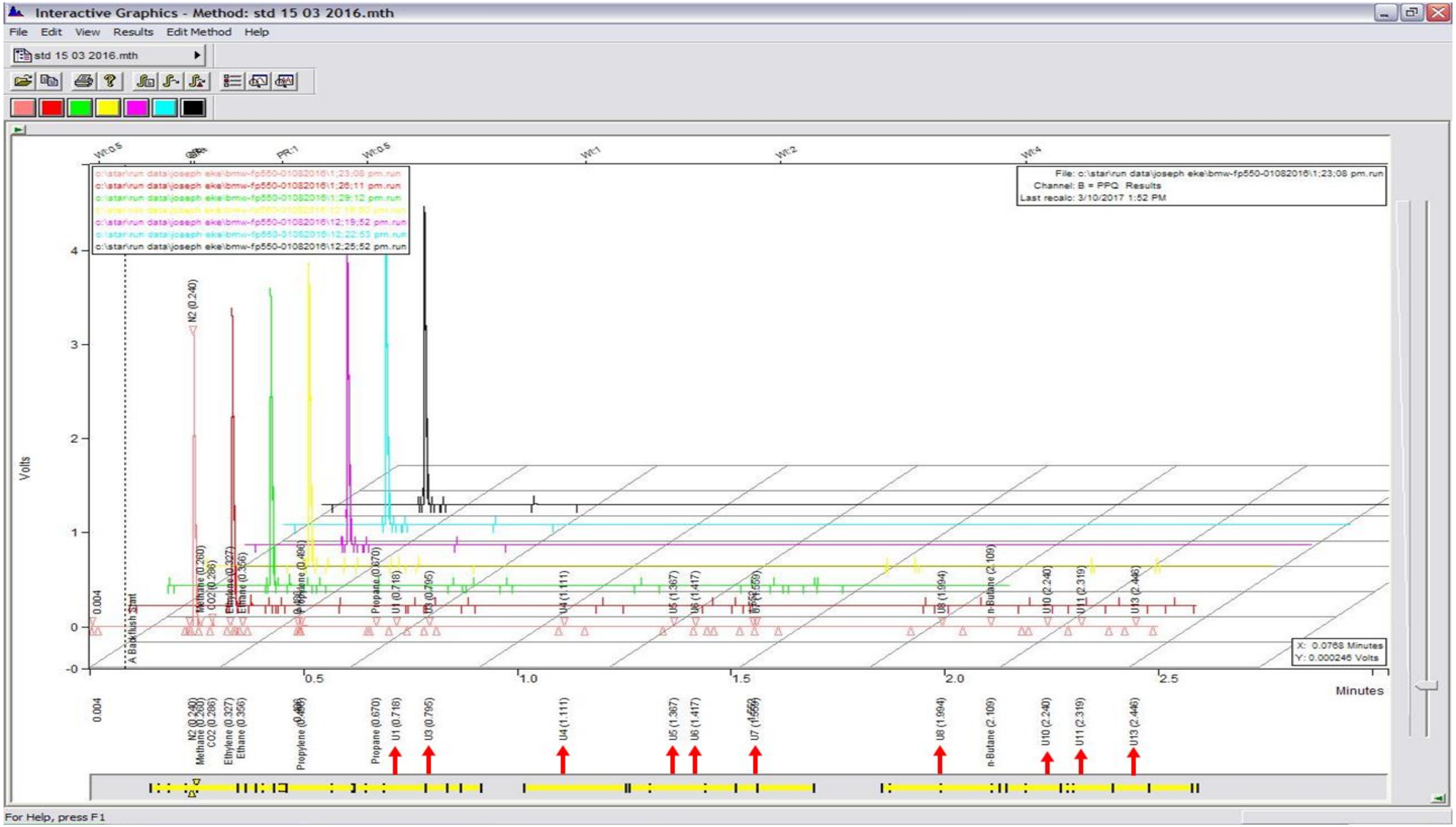


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Figure 5.1: GC outlines from the analysis of gas products from fast pyrolysis of trommel fines, showing unidentified peaks

Two sets of data for product gases have been included in Figure 5.2. One set of data represent the actual yields obtained from GC analysis, while the other set of data was obtained by difference after considering the yields of liquids and solids. Figure 5.2 therefore shows that there was a good agreement between two sets of data at the lower temperatures, with significant differences at higher temperatures. In fast pyrolysis, the liquid product is generally regarded as the main product, while solid products and permanent gases may be valuable by-products. Typically, liquid products contain some amount of water (Czernik and Bridgwater, 2004). This water is derived from the moisture in the feedstock and the water produced during fast pyrolysis reaction, which is called "reaction water". In Table 5.1, only the reaction water is reported, and the non-aqueous part of bio-oil is then referred to as "organics", which is the desirable product. With regards to the total liquids yields, the pyrolysis temperature has a dominant effect on the liquid product yield. In general, the yields of total liquid increased with increasing pyrolysis temperature from 475 °C to 550 °C and then decreased at higher temperatures (Figure 5.2). The highest liquid yield was observed at TIR-500 (32.6 wt.% dry basis) with a primary condensate organic yield of 12.5 wt.% (daf) and secondary condensate organic yield of 7.00 wt.% (daf). When compared to literature on pyrolysis of RDF, MSW and its components due to the similarity in composition with the trommel fines feedstock, the organic yield obtained was smaller (Mohan et. al 2006; Velghe et al., 2011; Zhou et al., 2013; Chen et al.,2014; Ding et al., 2016). In addition, the reaction water yields were found to decrease with increasing temperature, indicating the possible consumption of the produced water in the chemical processes occurring during fast pyrolysis at higher temperatures than 500 °C (Chen et al.,2014; Ding et al., 2016).

The solid residues gave the highest yield of products obtained from fast pyrolysis of trommel fines, with a range of 48 – 65 wt.% dry basis (Figure 5.2). This result is consistent with the high ash content (36.23 wt.% dry basis) of the feedstock, resulting in high solid yields. When considering the effect of pyrolysis temperature on product yields, it can be observed that increasing temperature from 400 °C to 700 °C led to a slight decrease from 64.9 to 48.6 wt.% in solid product yield, while gas yields increased from 7.29 to 24.6 wt.%. This result agrees with previous studies (Horne and Williams, 1996; Beis et al., 2002; Sensoz and Can, 2002; Lee et al., 2005; Luo et al., 2004; Sensoz et al., 2006; Asadullah et al., 2007a, b; Tsai et al., 2007), despite the different feedstock types (rice husk, rice straw, olive bagasse, pine etc.) and pyrolysis reactor systems applied. The reduction of solid product yield with increasing temperature could be due to the greater primary decomposition of the feedstock at higher temperature and/or secondary thermal decomposition of the solid formed before being entrained out of the reaction zone. The increase of gas yields with increasing temperature from 400 °C to 700 °C is possibly due to a combination of secondary thermal cracking of the evolved pyrolysis vapours and the secondary decomposition of solid residues via gas-solid reactions at elevated temperatures (Scott et al., 1988).

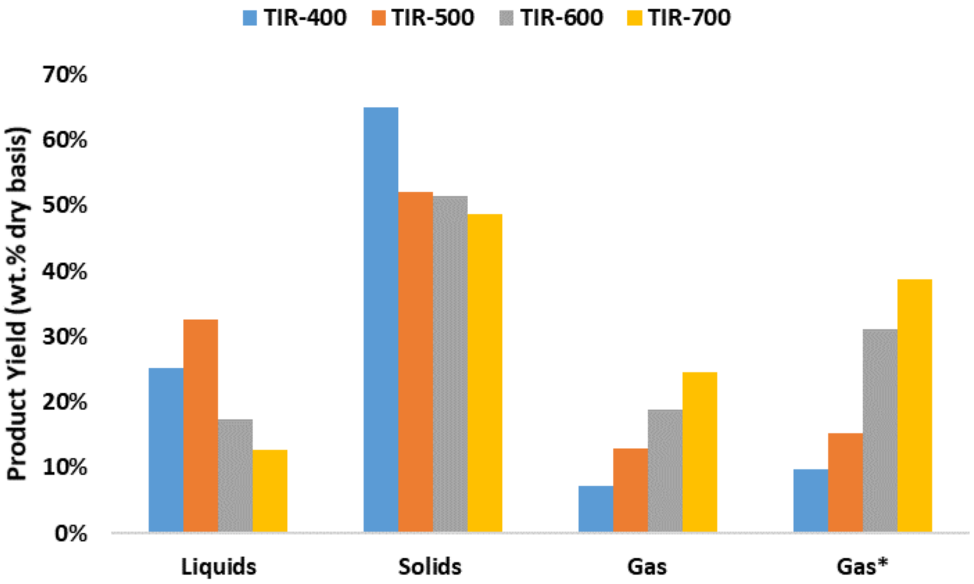

Figure 5.2: Yield of products obtained from TIR experiments

Gas* - Gas calculated by difference to achieve a 100% mass balance closure

According to Table 5.1, the gaseous products contain mainly of carbon dioxide and propylene with small quantities of C_1–C_4 hydrocarbon gases. Most of the gases identified, increased in their mass yields with increasing temperature. Moreover, Figure 5.3 presents the gas compositions in volume %. It can be noticed from the graph that increasing pyrolysis temperature led to a decrease in CO_2 proportion (Figure 5.3). This could be mainly because most of the CO_2 was already generated by carboxyl release at a relatively low temperature (Luo et al., 2004). In addition, the secondary thermal cracking of pyrolysis vapours produced CO and hydrocarbon gases rather than CO_2. Hydrogen (H_2) and carbon monoxide (CO) mass yields and proportions as noticed from Table 5.1 appeared to be small within the temperature range studied. This could be due to traces of these gases being below the detection limit of the online analyser (GC instrument) for these gases.

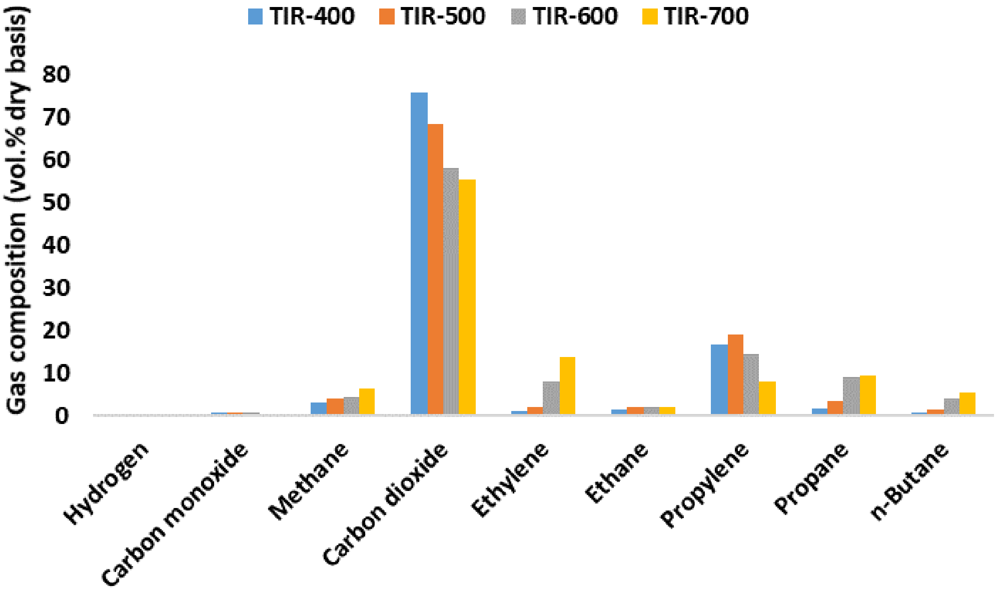

Figure 5.3: Composition of gaseous products obtained from TIR experiments

5.1.1 Effect of pyrolysis temperature on liquid product characteristics

The water content of the liquid products is one of the factors affecting their quality and use. In Section 5.1 above, the yields of reaction water in both the primary condensate (PC) and secondary condensates (SC) on dry basis were discussed. Certainly, the higher the reaction water yields, the higher the water content in the liquid products. The water in the liquid products also comes from original moisture in the trommel fines feedstock. The presence of water in the liquid products can be disadvantageous and advantageous. It reduces the heating value, especially the LHV and flame temperature and on the other hand, it improves bio-oil flow characteristics by reducing the viscosity (Czernik and Bridgwater, 2004).

The water contents of liquid products produced from trommel fines at different pyrolysis temperature are summarised in Table 5.2. Figure 5.4 shows the photographs of the primary and secondary condensates produced from fast pyrolysis of PT trommel fines with different reaction temperature. It can be seen from the table that operating temperatures had some influence on the water contents of liquid products; they seemed to be higher at lower temperature especially in the secondary condensate. This agrees with a study by Lee et al., (2005) where fast pyrolysis of rice straw at different temperatures was investigated. The total water contents of trommel fines liquid products (primary and secondary condensate) were in the range of 50–78 wt.%, which is higher than those of typical wood bio-oils and may need to be reduced prior to use. A promising route to lowering the amount of water in bio-oils has been proposed by Oasmaa et al. (2005b). The method was primarily developed for improving the storage stability of bio-oils without significantly decreasing their flash point. The technique includes the removal of water together with light reactive volatiles by increasing the condenser temperature to 50 ± 4 °C followed by the addition of alcohol (usually isopropanol) to improve the viscosity and stability of the bio-oils.

The solids contents entrained in the liquid products produced at different pyrolysis temperatures are presented in Table 5.2. The solid content in the trommel fines liquid products increased with increasing temperature. They fluctuated in the range of 0 – 16.2 wt.% which is a higher range than those reported in literature (Bernardo et al., 2010; Gao et al., 2016a; 2016b; Miskolczi et al.,2013). One explanation for this, apart from the fact that the feedstock has a high ash content, was that the solid contents measured in this work included those of the sticky liquid on the wall surface of the water condenser after vigorous washing with acetone solvent to get all organic fractions. It was also observed at the entrance of the water condenser that there was a significant amount of solid deposited. This solid did not look like normal char particles, but rather looked like sticky solid grease.

Solids in bio-oils are usually composed of char fines entrained out of the cyclone and the secondary char formed by secondary reactions of pyrolysis vapours such as repolymerisation and recondensation. In addition to these, the oils from trommel fines also contained inorganic materials (sand and glass fines) from the ash. The reasons why the solids can escape the cyclone are due to their very small particles (less than about 10 µm in diameter) and the gas stream velocity in the cyclone, which is not high enough to separate these small solid particles. The problem cannot be efficiently solved by increasing the carrier gas velocity as doing this would require more energy to heat up the gas and would be more difficult to condense the pyrolysis vapours. Once the solids are in the liquid products, it is difficult to remove by liquid filtration because of the highly viscous nature of the primary condensate. Literature has shown that, by introducing a hot vapour filter prior to condensation units, the amounts of solids in liquid products can substantially be reduced (Chen et al., 2011; Pattiya and Suttibak, 2017). The solids present in in the liquid product can cause erosion and blockages to equipment such as nozzles, valves and pumps, (Oasmaa et al., 2005a). Additionally, the inorganic compounds present in the solids are important to bio-oils ageing promoters as they appear to catalyse polymerisation reactions during storage, leading to viscosity increases and growth in the apparent diameter of the suspended char (Diebold, 2000). Accordingly, liquids with lower solids content are generally preferred. However, the solids content of liquid product may not be an important issue, if the product is a mixture of bio-oil and solid char in the form of slurry. This slurry which can contains up to 90% of energy from the feedstock and could be used as a feedstock for gasification process to produce syngas or producer gas. In fact, the slurry is commercially known as Bio-Oil Plus™ from Dynamotive Energy Systems Corporation, which can be used as fuel in boilers.

The elemental compositions of both the primary and secondary condensate liquids are listed in Table 5.2. The percentages of carbon for both primary and secondary condensate increased with increasing temperature until reaching a maximum. With regards to nitrogen contents, increase in temperature led to an increase in nitrogen content for both the primary and secondary condensate and are higher than typical wood bio-oil. The higher nitrogen content would be due to the high nitrogen content in the original trommel fines feedstock. The presence of textile materials such as those made from polyamides may have significantly increased the nitrogen contents of the trommel fines; which leave nitrogen in the oils after pyrolysis. The presence of nitrogen compounds can be a drawback when burning the liquids because of the high potential for NOx emissions. This problem may be prevented by pre-treatment such as the washing of the feedstock with distilled water prior to pyrolysis (Lee et al. 2005). The pre-treatment has shown to also remove some alkali metals such as sodium and potassium that are known to have adverse catalytic effect during fast pyrolysis reactions (Lee et al. 2005).

The heating values of the primary and secondary condensate liquids are also shown in Table 5.2. It was found that the heating values increased with increasing temperature until reaching a maximum then further increase led to slight decrease for both the primary and secondary condensate with TIR-500 liquids having the highest values for both the primary and secondary condensate 32 MJ kg $^{-1}$ and 17.45 MJ kg $^{-1}$ (dry basis) respectively. The HHV of the primary condensate was found to be slightly higher when compared to literature on pyrolysis of biomass (Diebold, 2000; Czernik and Bridgwater 2004; Oasmaa et al., 2004; Putun et al. 2004; Lee et al. 2005 Oasmaa & Meier, 2005) and has potential for energy recovery. The fractional plastic content of the trommel fines feedstock may be responsible to the high heating value.

Table 5.2: Water content, solids contents, elemental composition and heating value of liquid products produced from temperature investigation (TIR) experiments.

LIQUID/TAR PRODUCTS	**TIR-400**	**TIR-500**	**TIR-600**	**TIR-700**
Average Reaction Temperature (°C)	**420**	**525**	**640**	**737**
Primary Condensate (wt.%)				
Water content	5.14 ± 0.30	5.8 ± 0.56	3.69 ± 0.26	4.19 ± 0.17
Solid content	nd	3.58 ± 0.85	8.62 ± 0.80	16.2 ± 0.40
Elemental Analysis (wt.%) [a]				
Nitrogen	3.92	2.91	5.42	5.83
Carbon	65.6	72.9	63.7	66.7
Hydrogen	7.62	8.75	6.74	6.30
Sulphur	0.17	0.10	0.33	1.17
Oxygen [b]	22.7	15.3	23.8	20.0
Bomb Calorimeter (MJ kg^{-1})	30.5 ± 0.34	32.4 ± 0.09	26.9 ± 0.74	23.6 ± 0.62
HHV dry (MJ kg^{-1}) [a, c]	25.6	31.2	22.3	22.9
LHV dry (MJ kg^{-1}) [a, d]	15.7	22.5	12.0	11.5
Secondary Condensate (wt.%)				
Water content	72.8 ± 1.31	67.9 ± 2.78	55.4 ± 0.89	50.3 ± 1.27
Elemental Analysis (wt.%)				
Nitrogen	5.10	6.36	7.76	8.93
Carbon	51.8	54.7	52.3	53.5
Hydrogen	6.43	6.63	7.26	7.54
Sulphur	0.99	1.47	1.41	1.45
Oxygen [b]	35.7	30.9	31.3	28.6
HHV dry (MJ kg^{-1}) [a, c]	17.0	17.5	15.9	15.9
LHV dry (MJ kg^{-1}) [a, d]	8.33	8.89	8.74	8.99

TIR- Temperature Investigation Run; [a] dry basis; [b] calculated by difference; [c] Eq. 3.10; [d] Eq. 3.11

nd = not detected

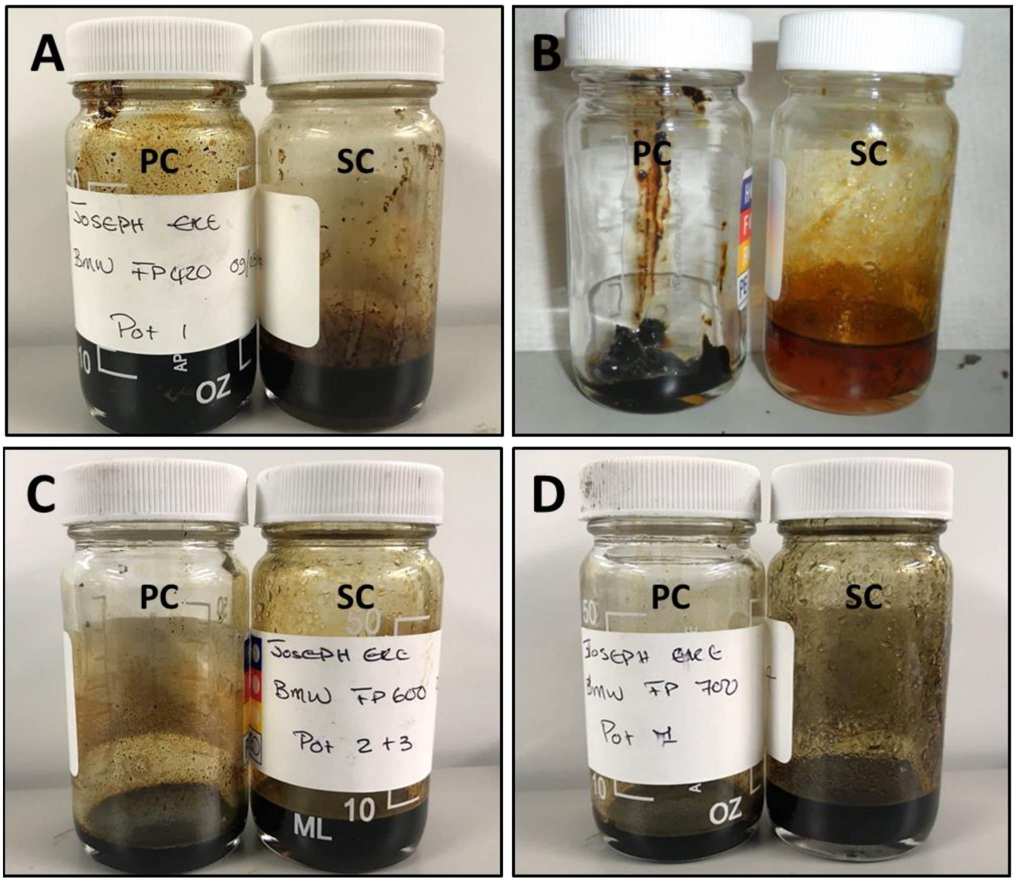

Figure 5.4: Liquid/tar products from TIR experiments

A - TIR-400; B - TIR-500; C - TIR-600; D - TIR-700; PC - Primary Condensate; SC - Secondary Condensate

5.1.2 Effect of pyrolysis temperature on organic liquid product

The organic liquid products (primary and secondary condensate) produced from pyrolysis temperature investigation are composed of differently sized molecules, which are derived primarily from the de-polymerization and fragmentation reactions of the organic components of the original feedstock, mainly cellulose, hemicellulose and lignin (Mohan et al., 2006). The chromatograms of the primary and secondary condensate liquids from fast pyrolysis are shown below in Figure 5.5 and 5.6 respectively. The major organic compounds along with their retention time, structure name, and molecular formula for the primary and secondary condensate are shown in Table 5.3 and 5.4 respectively. The molecular chains of complex compounds in the trommel fines have been broken, generating compounds in the organic liquids with a carbon number range of mainly 3 to 22.

Overall the main components were furans, aromatic hydrocarbons and phenols. GC-MS analysis of the primary condensate from fast pyrolysis of trommel fines shows the presence of phenolic compounds such as phenols, methoxy phenols and dimethoxy phenols derived from the pyrolysis of the lignin constituent of the feedstocks (Table 5.3). An increase in the temperature increased the intensity of the phenol groups in the primary condensate (Figure 5.5). The intensity of the peaks in the secondary condensate (Figure 5.6) seemed to also increase with increasing temperature. Possibly the increase in temperature led to further cracking of the compounds to produce lighter fractions. The secondary condensate liquid fraction collected from the dry ice condensers showed the presence of nitrogen-containing organic compounds (Table 5.4). These compounds were in the form of pyridines and their derivatives. This finding is in line with the result of the elemental analysis of the secondary condensate liquid which shows an increase in nitrogen content with increasing temperature (Table 5.4).

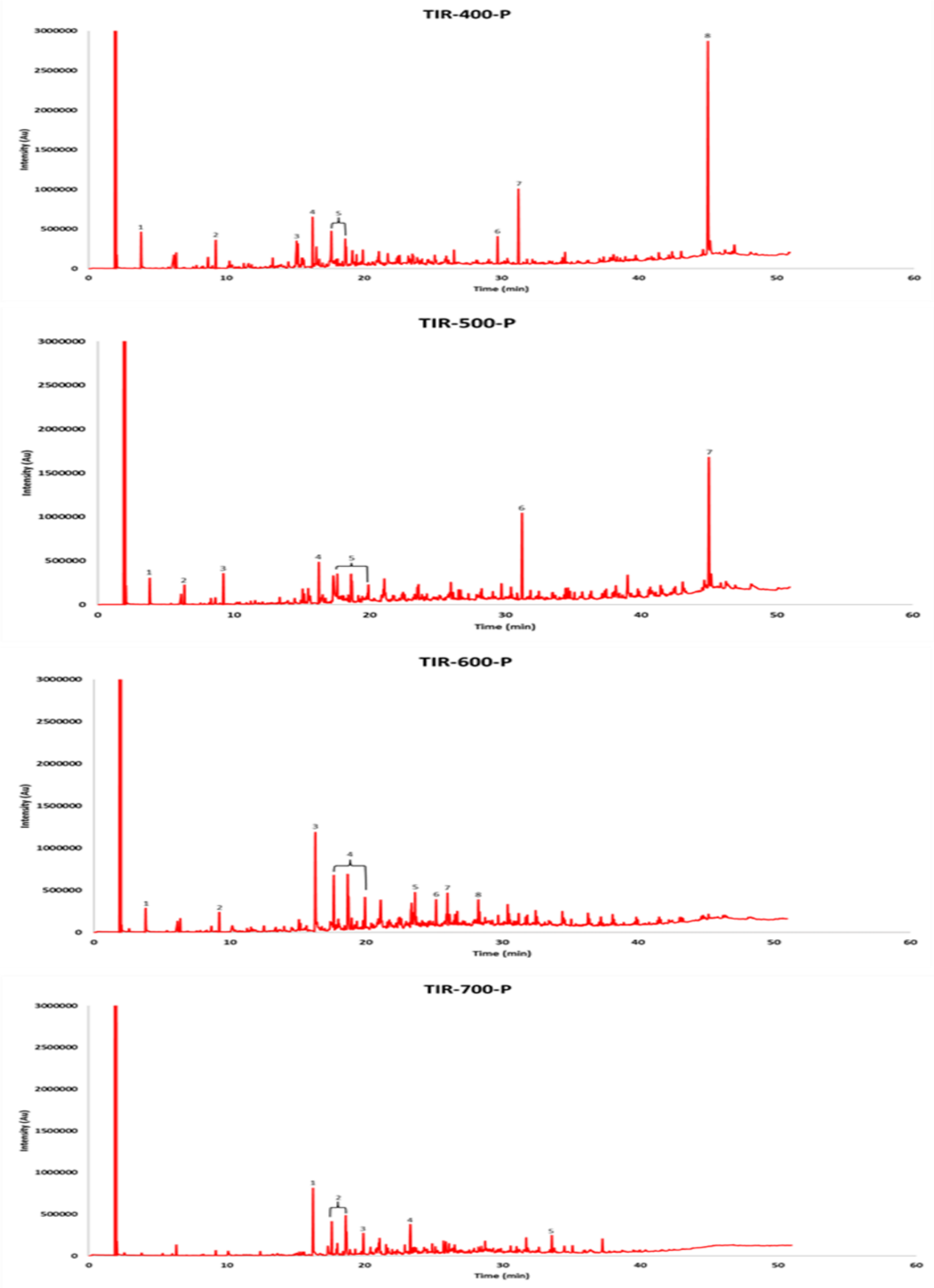

Figure 5.5: GC–MS spectrum of the primary condensate liquids from TIR experiments.

TIR- Temperature Investigation Run; PC – Primary condensate

Table 5.3: Main components of the primary condensate liquids from TIR experiments identified by GC–MS.

Peak ID	Retention Time (min.)	Structure name	Formula	Peak Area % of Total
TIR-400-PC				
1	3.81	Glycerin	$C_3H_8O_3$	3.63
2	9.24	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	2.75
3	15.21	4-Methyl-5H-furan-2-one	$C_5H_6O_2$	2.37
4	16.28	Phenol	C_6H_6O	5.05
5	17.64	Phenol, 3-methyl-	C_7H_8O	3.68
	18.66	Phenol, 4-methyl-	C_7H_8O	2.67
6	29.73	Benzene, 1,1'-(1,3-propanediyl) bis-	$C_{15}H_{16}$	2.76
7	31.24	Benzene, 1,1'-(1-butenylidene) bis-	$C_{16}H_{16}$	7.38
8	45.02	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl) bis-	$C_{16}H_{16}$	28.05
			Total	**58.33**
TIR-500-PC				
1	3.81	Glycerin	$C_3H_8O_3$	3.23
2	6.37	3-Penten-2-one, 4-methyl-	$C_6H_{10}O$	2.28
3	9.24	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	3.69
4	16.27	Phenol	C_6H_6O	5.11
5	17.63	Phenol, 2-methyl-	C_7H_8O	2.89
	18.64	Phenol, 4-methyl-	C_7H_8O	3.96
	18.71	Phenol, 3-methyl-	C_7H_8O	2.74
	19.92	Phenol, 3,4-dimethyl-	$C_8H_{10}O$	1.32
6	31.24	Benzene, 1,1'-(1-butenylidene) bis-	$C_{16}H_{16}$	11.13
7	45.00	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl) bis-	$C_{16}H_{16}$	20.06
			Total	**56.42**
TIR-600-PC				
1	3.82	Glycerin	$C_3H_8O_3$	1.51
2	9.22	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	1.19
3	16.29	Phenol	C_6H_6O	7.17
4	17.65	Phenol, 2-methyl-	C_7H_8O	3.27
	18.67	Phenol, 3-methyl-	C_7H_8O	4.06
	18.74	Phenol, 4-methyl-	C_7H_8O	2.05
	19.94	Phenol, 2,4-dimethyl-	$C_8H_{10}O$	2.29
5	23.62	7-Tetradecene	$C_{14}H_{28}$	2.22
6	25.17	Benzofuran, 2,3-dihydro-2-methyl-	$C_9H_{10}O$	1.86
7	26.00	1-Eicosanol	$C_{2}0H_{42}O$	2.01
8	28.27	1-Docosanol	$C_{22}H_{46}O$	1.65
			Total	**29.28**
TIR-700-PC				
1	16.27	Phenol	C_6H_6O	8.19

Peak ID	**Retention Time (min.)**	**Structure name**	**Formula**	**Peak Area % of Total**
2	17.64	Phenol, 2-methyl-	C_7H_8O	4.38
	18.64	Phenol, 3-methyl-	C_7H_8O	5.70
	18.71	Phenol, 4-methyl-	C_7H_8O	3.04
3	19.92	Phenol, 2,3-dimethyl-	$C_8H_{10}O$	2.85
4	23.33	Phenol, 4-ethenyl-, acetate	$C_{10}H_{10}O_2$	5.70
5	33.59	Anthracene	$C_{14}H_{10}$	2.26
			Total	**32.12**

TIR- Temperature Investigation Run; PC – Primary condensate

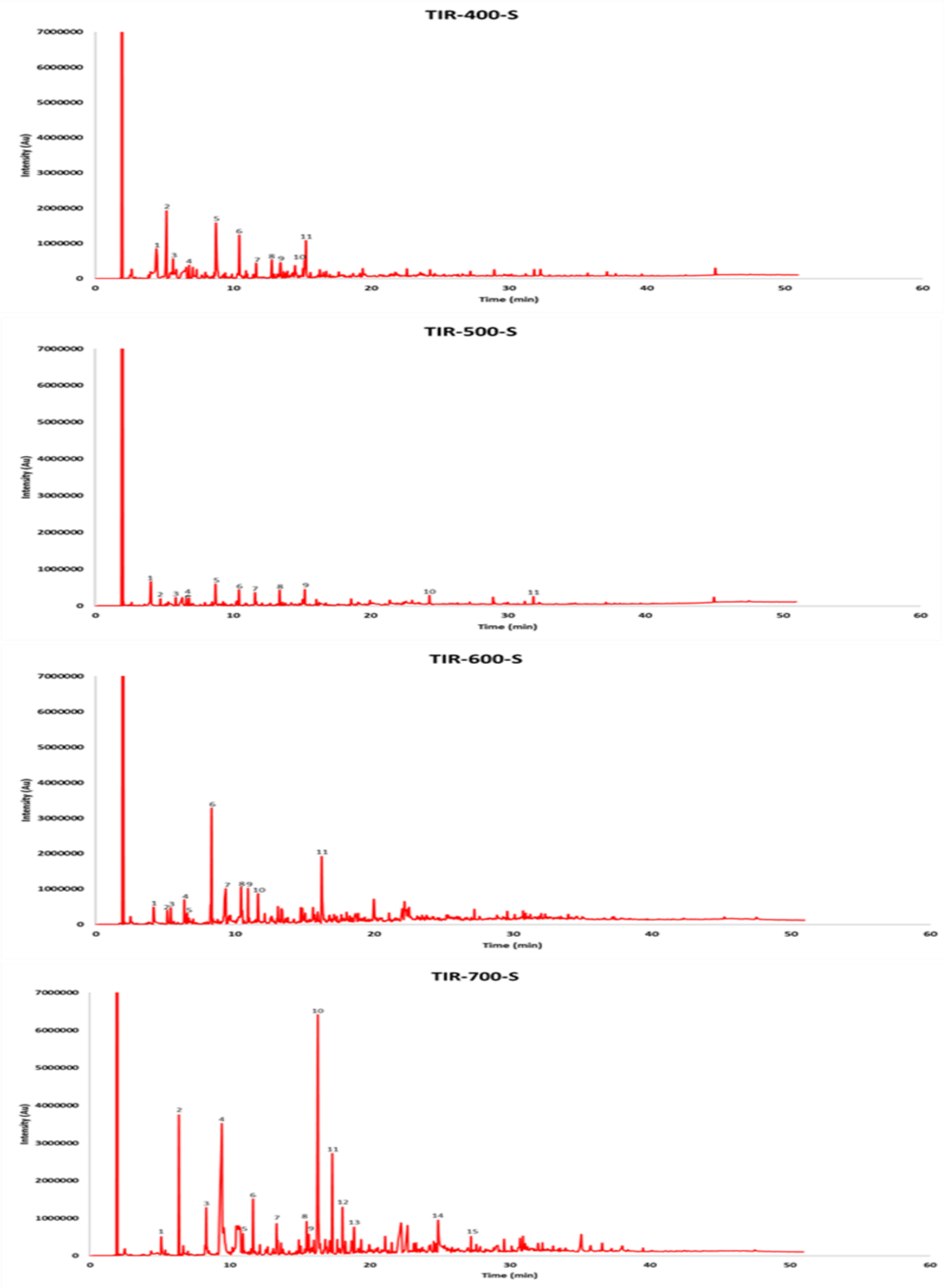

Figure 5.6: GC–MS spectrum of the secondary condensate liquids from TIR experiments.

TIR- Temperature Investigation Run; SC – Secondary condensate

Table 5.4: Main components of the secondary condensate liquids from TIR experiments identified by GC–MS.

Peak ID	Retention Time (min.)	Structure name	Formula	% of Total
TIR-400-SC				
1	4.44	Glycerin	$C_3H_8O_3$	7.31
2	5.18	Propane, 1,1,3,3-tetramethoxy-	$C_7H_16O_4$	13.15
3	5.65	Pyridine	C_5H_5N	2.37
4	6.82	Cyclopentanone	C_5H_8O	1.74
5	8.76	2-Cyclopenten-1-one	C_5H_6O	15.04
6	10.45	2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	5.35
7	11.68	2-Propen-1-amine, N-2-propenyl-	$C_6H_{11}N$	2.48
8	12.81	Propanoic acid, 2-hydroxy-	$C_3H_6O_3$	3.08
9	13.45	2-Cyclopenten-1-one, 3-methyl-	C_6H_8O	4.06
10	15.19	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	2.91
			Total	**57.48**
TIR-500-SC				
1	4.04	Glycerin	$C_3H_8O_3$	9.64
2	4.74	Glycine	$C_2H_5NO_2$	1.92
3	5.85	2,4-Dimethyl-2-oxazoline-4-methanol	$C_6H_{11}NO_2$	2.95
4	6.61	Cyclopropane-1,1-dicarboxylic acid	$C_5H_6O_4$	2.05
	6.82	Cyclopentanone	C_5H_8O	2.84
5	8.74	Furan, 2-methyl-	C_5H_6O	9.59
6	10.45	2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	4.85
7	11.62	1,4-Pentanediamine	$C_5H_{14}N_2$	4.37
8	13.40	2-Cyclopenten-1-one, 3-methyl-	C_6H_8O	4.91
9	15.24	Oxazole, 2-ethyl-4,5-dihydro-	C_5H_9NO	5.46
10	24.30	(Z), (Z)-2,5-Dimethyl-2,4-hexadienedioic acid	$C_8H_{10}O_4$	2.84
11	31.86	Ethyl citrate	$C_{12}H_{20}O_7$	2.53
			Total	**53.95**
TIR-600-SC				
1	4.16	Glycerin	$C_3H_8O_3$	3.46
2	5.14	Pyridine	C_5H_5N	2.29
3	5.39	Ethanone, 1-cyclopropyl-	C_5H_8O	2.25
4	6.37	2-Pentene, 4,4-dimethyl-, (E)-	C_7H_{14}	4.47
5	6.58	1,2-Cyclohexanedione	$C_6H_8O_2$	1.28
6	8.33	Styrene	C_8H_8	15.57
7	9.34	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	8.72
8	10.45	4-Cyclohexene-1,2-diol	$C_6H_{10}O_2$	5.28
9	10.95	∞-Methylstyrene	C_9H_{10}	4.05
10	11.67	Pyridine, 2,4,6-trimethyl-	$C_8H_{11}N$	4.13
11	16.25	2-Propen-1-amine, N, N-bis(1-methylethyl)-	$C_9H_{19}N$	11.85

Peak ID	Retention Time (min.)	Structure name	Formula	% of Total
			Total	**63.36**
TIR-700-SC				
1	5.11	Pyridine	C_5H_5N	1.52
2	6.37	Ethyl trans-2-pentenoate	$C_7H_{12}O_2$	7.50
3	8.32	Styrene	C_8H_8	2.21
4	9.43	Decaborane (14)	$B_{10}H_{14}$	22.65
5	10.95	Benzene, 2-propenyl-	C_9H_{10}	0.90
6	11.67	Pyridine, 2,4,6-trimethyl-	$C_8H_{11}N$	3.10
7	13.35	Benzene, 1-propynyl-	C_9H_8	1.72
8	15.49	Phenol, 4-methylamino, ethyl(ether)	$C_9H_{13}NO$	1.86
9	15.65	Ethanone, 2,2-dihydroxy-1-phenyl-	C_8H_8O3	1.38
10	16.29	2-Propen-1-amine, N, N-bis(1-methylethyl)-	$C_9H_{19}N$	20.91
11	17.33	4-Piperidinone, 2,2,6,6-tetramethyl-	$C_9H_{17}NO$	6.05
12	18.05	Azulene	$C_{10}H_8$	3.36
13	18.88	Trans-3-methylpenta-1,3-diene-5-ol, acetate	$C_8H_{12}O_2$	1.92
14	24.89	Pyrazole[4,5-b] imidazole, 1-formyl-3-ethyl-6-á-d-ribofuranosyl-	$C_{12}H_{16}N_4O_5$	2.98
15	27.23	Pyrrolizin-1,7-dione-6-carboxylic acid, methyl(ester)	$C_9H_{11}NO_4$	0.88
			Total	**78.95**
TIR- Temperature Investigation Run; SC – Secondary condensate				

5.1.3 Effect of pyrolysis temperature on solid product characteristics

The solid products obtained from this work, expectedly contained a mixture of ash (inorganic material) and char. Ash content, elemental composition, and calorific value of the solid products obtained from fast pyrolysis of trommel fines are tabulated in Table 5.5. Table 5.2 above showed that the solid products were the highest yield of products obtained from pyrolysis temperature investigation, because of the high as content of the feedstock (Table 5.2). The degradation of the organic fraction of the feedstock via fast pyrolysis process would leave the ash in solid product. It was obvious that ash were the main components of the solids produced (Table 5.5). The ash content in the solid product or residue ranged for 62 - 87 wt.% (dry basis), with TIR-500 having the highest ash content of 86.3 wt.%. Low heating temperature caused an increase in char content yield (Table 5.5).

The elemental compositions and heating value of solid products are also listed in Table 5.5. The percentage of carbon was higher at low temperature and decreased with increasing temperature until reaching a maximum then further increase in temperature led to slight increase. The heating values of the solid products corresponded to the carbon contents. The HHV were in the range of 4 - 8 MJ kg $^{-1}$ dry ash free basis until reaching a maximum then further increase led to decrease. The low calorific value of the solid product would not make it a viable source of process heat. However, it could not be directly disposed of in landfills without heavy penalty based on Loss on Ignition (LOI). So, the solid products could be used for soil amendments or processed into briquettes however, this would require pre-treatment to remove the inorganics (heavy metals, glass, etc.) in the solid products as the accumulation of inorganics (heavy metals, glass, etc.) in the solid product and their mobility to the soil may hinder this application (Wang et al., 2005b; Jiang, 2006; Lehmann et al., 2006; Yi, 2007).

Table 5.5: Ash content, elemental composition and heating value of solid products (char pot) produced from TIR fast pyrolysis of trommel fines.

SOLID PRODUCTS	**TIR-400**	**TIR-500**	**TIR-600**	**TIR-700**
Average Reaction Temperature (°C)	**420**	**525**	**640**	**737**
Ash content (wt.%) [a]	62.8 ± 0.64	86.3 ± 0.52	77.6 ± 0.24	75.4 ± 0.46
Char (wt.%) [a]	37.2 ± 0.64	13.7 ± 0.52	22.4 ± 0.24	24.6 ± 0.46
Elemental Analysis (wt.%)				
Nitrogen	0.50	0.33	0.56	0.42
Carbon	21.3	9.0	18.5	13.4
Hydrogen	1.23	0.57	0.64	0.45
Sulphur	0.33	0.23	0.71	0.54
Oxygen [b]	13.9	3.51	1.97	9.78
Bomb Calorimeter (MJ kg^{-1}) [a]	8.55 ± 0.23	4.12 ± 0.71	6.17 ± 0.44	4.63 ± 0.52
HHV dry (MJ kg^{-1}) [a, c]	6.95	3.13	6.51	3.82
LHV dry (MJ kg^{-1}) [a, d]	0.50	0.03	0.23	0.06
TIR- Temperature Investigation Run; [a] dry basis; [b] calculated by difference; [c] Eq. 3.10; [d] Eq. 3.11				

5.1.4 Effect of pyrolysis temperature on process conversion efficiency

The process conversion efficiency was calculated using the calorific values of the products produced from fast pyrolysis of trommel fines as previously described in section 3.10. Figure 5.7 below shows the effect of temperature on the fast pyrolysis process conversion efficiency of dry physically pre-treated trommel fines samples. The fast pyrolysis process conversion efficiency range between 29 – 43% increasing with increasing pyrolysis temperature from 475 °C to 550 °C and then decreasing at higher temperatures. In fast pyrolysis, the organic product is generally regarded as the main product while solid products and permanent gases are valuable by-products, so with respect to that, the highest organic yield was observed at TIR-500 (refer to section 5.1) and the process conversion efficiency at optimum processing condition is about 43% (dry basis) with a temperature range of 500 - 550 °C (Figure 5.6). An operator processing this type of waste would be able to recover 43% of the energy content of the feedstock fed into the fast pyrolysis reactor thus reducing the amount of waste sent to landfill.

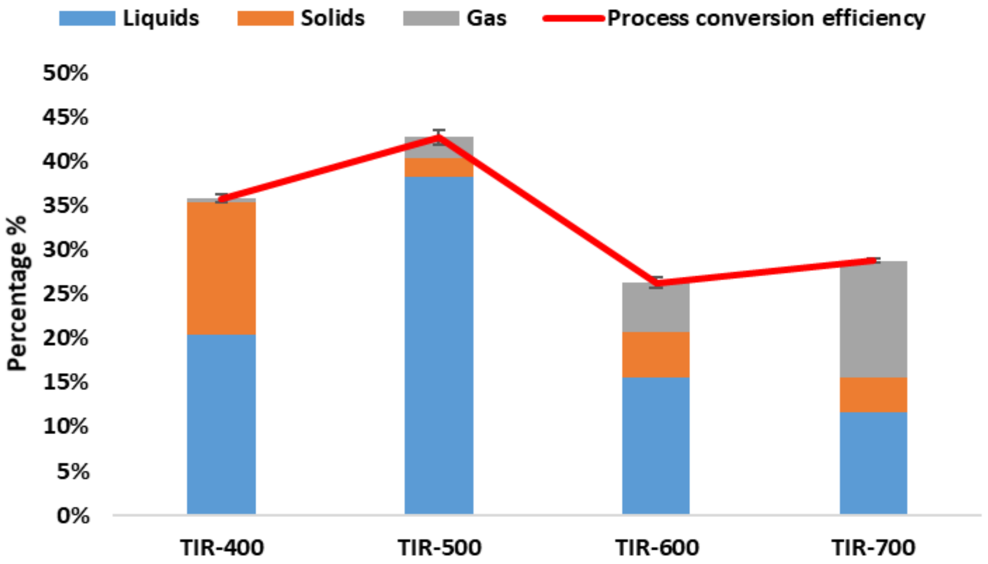

Figure 5.7: Fast pyrolysis process conversion efficiency from TIR investigation

5.1.5 Temperature investigation (TIR) conclusion

The influence of reactor temperature on the fast pyrolysis products yield of PT trommel fines has been experimentally investigated. In the current study the yield of liquid, solid and gases produced from temperature investigation of fast pyrolysis of trommel fines are slightly lower than the 50-75 wt.% reported in the literatures for woody material (Mohan et. al 2006). However, the yield was lower due to the high ash content of the trommel fines feedstock used. The optimal reaction temperature to produce the highest liquid yield was around 500 - 550 °C (33.1 wt.% dry basis) with a primary condensate organic yield of 13.0 wt.% dry basis and secondary condensate organic yield of 7.00 wt.% (dry basis). The fast pyrolysis reaction temperatures have a dominant effect on the pyrolysis product yield. In general, the yield of liquid organics increased with increasing pyrolysis temperature from 475 °C to 550 °C and then decreases at higher temperatures. The solid residues gave the highest yield of products obtained from fast pyrolysis of trommel fines because of the high as content of the feedstock (36.23 wt.% dry basis). Increase in temperature led to a slight decrease in solid product yield and higher gas yields due to secondary cracking taking place at higher temperatures. The process efficiency increased with increasing pyrolysis temperature from 475 °C to 550 °C and then decreasing at higher temperatures. The highest process efficiency was obtained at TIR-500 (43% dry basis).

5.2 Effect of feedstock moisture content

The effect of moisture content on the fast pyrolysis of trommel fines was investigated using three different levels; 2.69 wt% (bone dry), 5 wt% and 10 wt%. Table 5.6 shows the process parameters, product yields, product distributions and mass balance closure results obtained from the fast pyrolysis of PT trommel fines at different moisture contents. The primary aim of these sets of experiments was to investigate the impact of moisture content on the yields of fast pyrolysis products at optimum reaction temperature. The product yields were determined on a dry basis, considering the moisture content of the feedstock. Therefore, the water yields presented is the water generated by the fast pyrolysis reaction excluding the water input in the feed. Each experiment was conducted three times. TIR-500 (refer to section 5.1.1) results from the temperature investigation experiments are presented in this study as MCR-01 because the trommel fines feedstock used in those experiments were bone dry (>3% wt.% moisture content). Again, in this study the mass balances were within a 5% range of each other, so the highest mass balance closure obtained are reported and the rest are presented as standard deviations (Kalgo, 2011, Scott,2014).

The overall mass balance closure for all investigated trommel fines moisture content where between 88 – 98 wt.% dry basis. The mass balance closures decreased with increasing water content with MCR-01 with 2.69 wt. % moisture content having the highest closure and MCR-10 with 9.29 wt.% moisture content with the lowest closure. The loss was mostly related to the unidentified and undetectable permanent gases (refer to section 5.1), but not neglecting the small amount of trommel fines samples and the losses in taking some representative tar derived liquid samples for water and solids contents analyses. It is therefore suggested for future work that the gases should be sampled for GC/MS analysis to identify the extra peaks. However, two sets of data on gas yields are shown in Figure 5.8; one was based the actual yields and the other, calculated by difference, to indicate the analytical errors on the gases from the available GC.

Table 5.6: Mass balance summary for moisture content (MCR) experiments using dry physical pre-treated trommel fines (PT)

Parameter	**MCR-01**	**MCR-05**	**MCR-10**
Set Temperature (°C)	500	500	500
Average Reaction Temperature (°C)	525	534	519
Feed Moisture (wt.%)	**2.69 ± 0.06**	**5.54 ± 0.26**	**9.29 ± 0.17**
Run duration (minutes)	60	60	60
Average Feed rate (g h^{-1})	158.9 ± 13.8	186.8 ± 10.4	191.1 ± 7.85
Total Liquid/Tar (wt.%) [a b]	**32.6 ± 0.56**	**29.0 ± 1.20**	**22.9 ± 1.73**
PC Organics	12.5 ± 0.40	6.37 ± 0.50	4.20 ± 0.24
SC Organics	7.07 ± 0.72	11.9 ± 0.90	11.0 ± 1.63
Reaction water	13.0 ± 0.56	10.8 ± 0.20	7.66 ± 0.34
Solid Residue (wt.%) [a c]	**52.1 ± 1.23**	**51.5 ± 1.09**	**52.8 ± 2.22**
Gas (wt.%) [a]	**12.9 ± 0.02**	**12.1 ± 0.66**	**12.3 ± 0.28**
Hydrogen	0.00	0.00	0.00
Carbon monoxide	0.08	0.03	0.07
Methane	0.52	0.21	0.36
Carbon dioxide	8.82	5.31	7.02
Ethylene	0.25	0.27	0.13
Ethane	0.24	0.18	0.18
Propylene	2.45	5.61	4.16
Propane	0.41	0.30	0.24
n-Butane	0.16	0.17	0.11
Closure (wt.%) [a]	**97.6 ± 0.69**	**92.6 ± 0.55**	**88.0 ± 0.77**

MCR – Moisture Content Run; [a] dry basis; [b] ash free; [c] including oil solid content; PC – Primary condensate; SC – Secondary condensate

The total liquid yields produced from fast pyrolysis of trommel fines at different moisture content decreased with increasing moisture content (Figure 5.8) and the highest liquid yield was observed at MCR-01 (32.6 wt.% dry basis) with a primary condensate organic yield of 12.5 wt.% (dry ass free basis) and secondary condensate organic yield of 7.07 wt.% (dry ash free basis). The current study also shows that the primary condensate organic yield decreased with increasing moisture content and the secondary condensate organic yield increased slightly. When compared to literature on pyrolysis of RDF, MSW and its components, the organic yield obtained is smaller (Czernik and Bridgwater, 2004; Mohan et. al 2006; Velghe et al., 2011; Zhou et al., 2013; Chen et al.,2014; Ding et al., 2016). In addition, the reaction water yields were found to decrease with increasing moisture content, indicating that high water content may promote reforming reactions, leading to the reduction in reaction water and increase in gas yields.

The solid residues gave the highest yield of products obtained from fast pyrolysis of trommel fines at different moisture content. Approximately 50 wt.% dry basis of the pyrolysed trommel fines were solid products. This finding is consistent with the feedstock high ash content (36.23 wt. % dry basis) and this high ash content resulted to a high solid yield. Further research is required to reduce the yield of solids produced after fast pyrolysis. This is a topic for future work. When considering the effect of trommel fines moisture content on product yields, increasing the trommel fines moisture content had no effect on solid product yield.

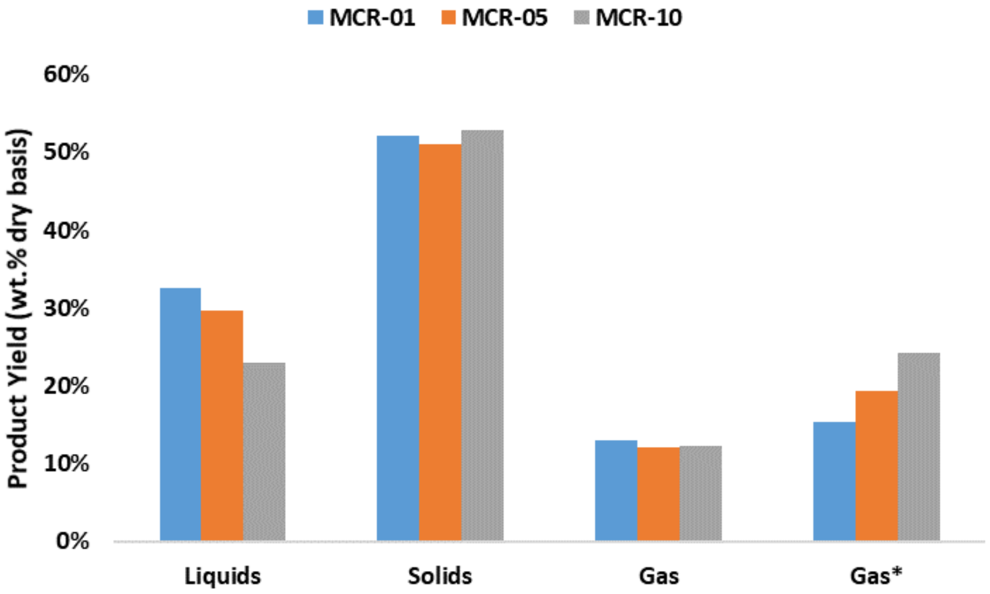

Figure 5.8: Yield of products obtained from of MCR experiments

Gas* - Gas calculated by difference

The gas yield increased slightly with increasing moisture content hence the decrease in mass balance closure as moisture content increases. The increase in gas yields were caused by the lighter fraction of the fast pyrolysis liquid vapour being converted into gas. According to Table 5.6, the gas products contain mainly of carbon dioxide and propylene with small quantities of C_1–C_4 hydrocarbon gases. Figure 5.9 present the gas compositions in volume %. It can be noticed from the graphs that increase in trommel fines moisture content had no effect on the gases identified except on CO_2 and propylene. It can be noticed from the graphs that Hydrogen and CO mass yields and proportions appeared small within the moisture content range studied.

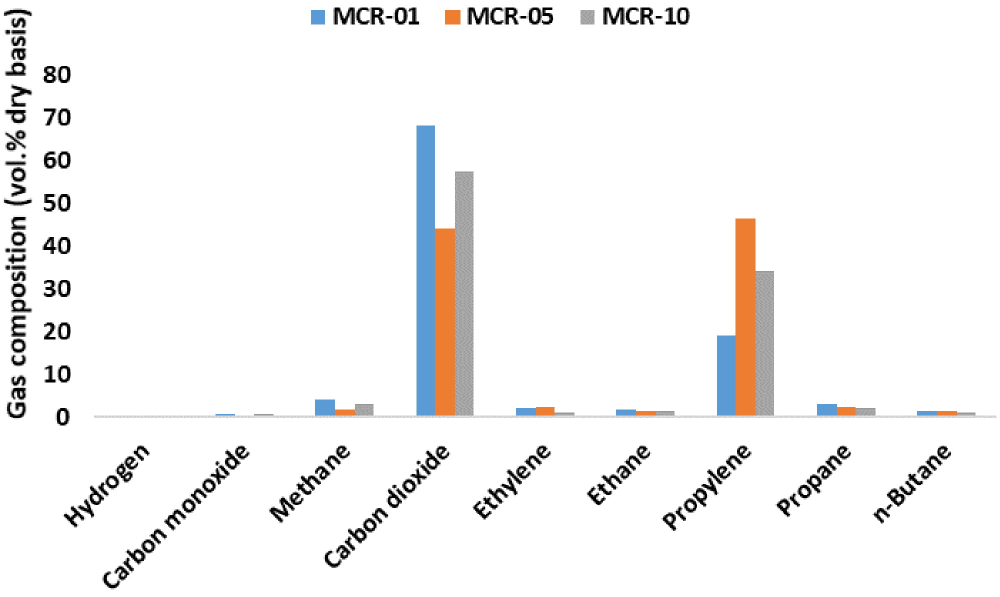

Figure 5.9: Composition of gaseous products obtained from MCR experiments

5.2.1 Effect on feedstock moisture content on liquid product characteristics

The water in the liquid products originated from the original moisture in the feedstock and dehydration reactions occurring during the pyrolysis process (Balat, 2008). It has been reported in many studies that the water content in biomass fast pyrolysis liquid products varies over a wide range of 15 – 35 wt.%, depending on the feedstock and process conditions (Elliott 1994; Bridgwater 2004). In this work the results of the analysis of water content in the liquid products seen in Table 5.7 showed that the total water contents of trommel fines liquid products (primary and secondary condensate) from the MCR investigations were in the range of 66 – 74 wt.%, which is rather high when compared to literature (Elliott 1994; Bridgwater 2004), decreasing slightly with increasing feed moisture content due to the production of lighter fractions of the fast pyrolysis vapours at higher moisture content. Figure 5.10 shows the photographs of the primary and secondary condensates produced from fast pyrolysis of PT trommel fines with different moisture content.

Table 5.7 shows that the solid content in the trommel fines liquid products increased with increasing moisture content. They fluctuated in the range of 3 – 29 wt.% (dry basis) which is a higher range than of those of wood bio-oils (Czernik and Bridgwater 2004). Solids in the liquid products are composed of char fines entrained out of the cyclone and the secondary char formed by secondary reactions of pyrolysis vapours such as repolymerisation and recondensation. In addition, they also contained inorganic materials (sand and glass fines) from the ash. These solid fines can escape the cyclone due to their very small particles (less than about 10 μm in diameter) and the gas stream velocity in the cyclone, is not high enough to separate these small solid particles.

The elemental compositions of both the primary and secondary condensate liquids at different moisture content are listed in Table 5.7. The percentages of carbon for both primary and secondary condensate decreased with increasing moisture content. With regards to nitrogen contents, increase in moisture content leads to a slight increase in nitrogen content for both the primary and secondary condensate and are higher than typical wood bio-oil. The higher nitrogen content may be due to the high nitrogen content in the original trommel fines feedstock. The presence of nitrogen compounds can be a drawback when burning the liquids because of the high potential for NOx emissions.

The heating values of the primary and secondary condensate liquids are also shown in Table 5.7. It was found that the heating values decrease with increasing for both the primary and secondary condensate with MCR-01 liquids having the highest values for both the primary and secondary condensate 32.4 MJ kg $^{-1}$ and 17.4 MJ kg $^{-1}$ (dry basis) respectively. The HHV of the primary condensate was found to be slightly higher when compared to literature Diebold, 2000; Czernik and Bridgwater 2004; Putun et al. 2004; Lee et al. 2005 Oasmaa & Meier, 2005; Oasmaa et al., 2005 and has potential for energy recovery.

Table 5.7: Water content, solids contents, elemental composition and heating value of liquid products produced from MCR fast pyrolysis of trommel fines.

LIQUID/TAR PRODUCTS	**MCR-01**	**MCR-05**	**MCR-10**
Feed Moisture (wt.%)	**2.69**	**5.54**	**9.29**
Primary Condensate (wt.%) [a]			
Water content	5.8 ± 0.56	8.81 ± 0.82	9.73 ± 0.68
Solid content	3.58 ± 0.85	10.8 ± 2.67	29.0 ± 0.86
Elemental Analysis (wt.%) [a]			
Nitrogen	2.91	3.97	3.59
Carbon	72.9	68.4	67.5
Hydrogen	8.75	7.90	7.77
Sulphur	0.10	0.19	0.17
Oxygen [b]	15.3	19.6	21.0
Bomb Calorimeter (MJ kg^{-1}) [a]	32.4 ± 0.09	27.8 ± 1.58	22.2 ± 0.09
HHV dry (MJ kg^{-1}) [a c]	31.2	27.1	26.9
LHV dry (MJ kg^{-1}) [a d]	22.5	17.4	17.0
Secondary Condensate (wt.%) [a]			
Water content	67.9 ± 2.78	57. 4 ± 2.48	62.0 ± 3.37
Elemental Analysis (wt.%) [a]			
Nitrogen	6.36	6.52	7.51
Carbon	54.7	52.0	51.6
Hydrogen	6.63	6.60	6.42
Sulphur	1.47	1.05	1.05
Oxygen [b]	30.9	33.8	33.4
HHV dry (MJ kg^{-1}) [a c]	17.4	16.0	14.7
LHV dry (MJ kg^{-1}) [a d]	8.89	7.98	7.02

MCR – Moisture Content Run; [a] dry basis; [b] calculated by difference; [c] Eq. 3.11; [d] Eq. 3.12

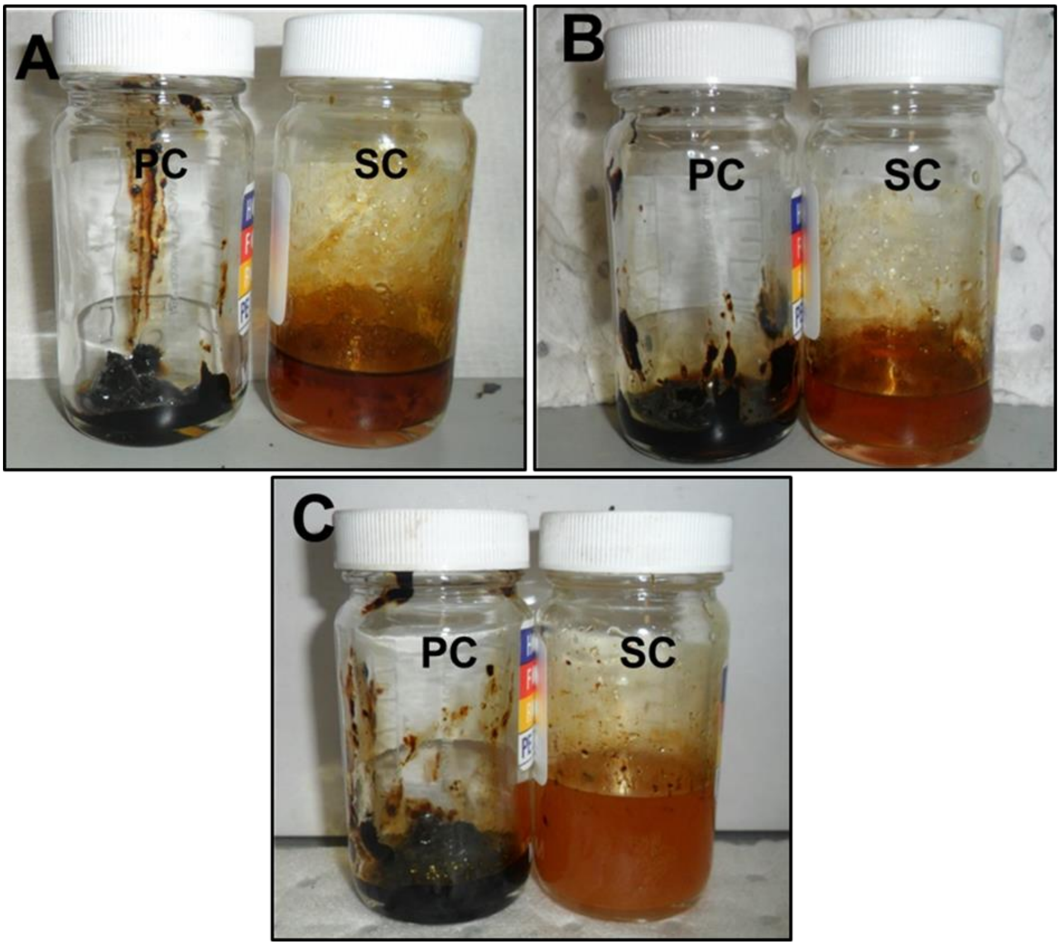

Figure 5.10: Liquid/tar products from MCR experiments

A - MCR-01(- bone dry < 3 wt.%); B - MCR-05 (5 wt.%); C - MCR-10 (10 wt.%); PC - Primary Condensate; SC - Secondary Condensate

5.2.2 Effect on feedstock moisture content on organic liquid product

The chromatograms of the primary and secondary condensate liquids from feedstock moisture content investigation are shown below in Figure 5.11 and 5.12 respectively. The major organic compounds along with their retention time, structure name, and molecular formula for the primary and secondary condensate are shown in Table 5.8 and 5.9 respectively. The main components were furans, aromatic hydrocarbons and phenols with a carbon number range of 3 – 24. GC-MS analysis of the primary condensate from fast pyrolysis of trommel fines shows the presence of phenolic compounds such as Phenols, methoxy phenols and dimethoxy phenols derived from the pyrolysis of the lignin constituent of the feedstocks (Table 5.8). Increase in moisture content increases the intensity of the phenol groups in the primary condensate (Figure 5.11). The intensity of the peaks in the secondary condensate (Figure 5.12) seemed to also increase with increasing moisture content. Essentially, the increase in moisture content led to further cracking of the compounds to produce lighter fractions. The secondary condensate liquid fraction collected from the dry ice condensers showed the presence of nitrogen containing organic compounds (Table 5.9). These compounds are in the form of pyridines and their derivatives. This finding is in line with the result of the elemental analysis of the secondary condensate liquid which shows an increase in nitrogen content with increasing moisture content (Table 5.7).

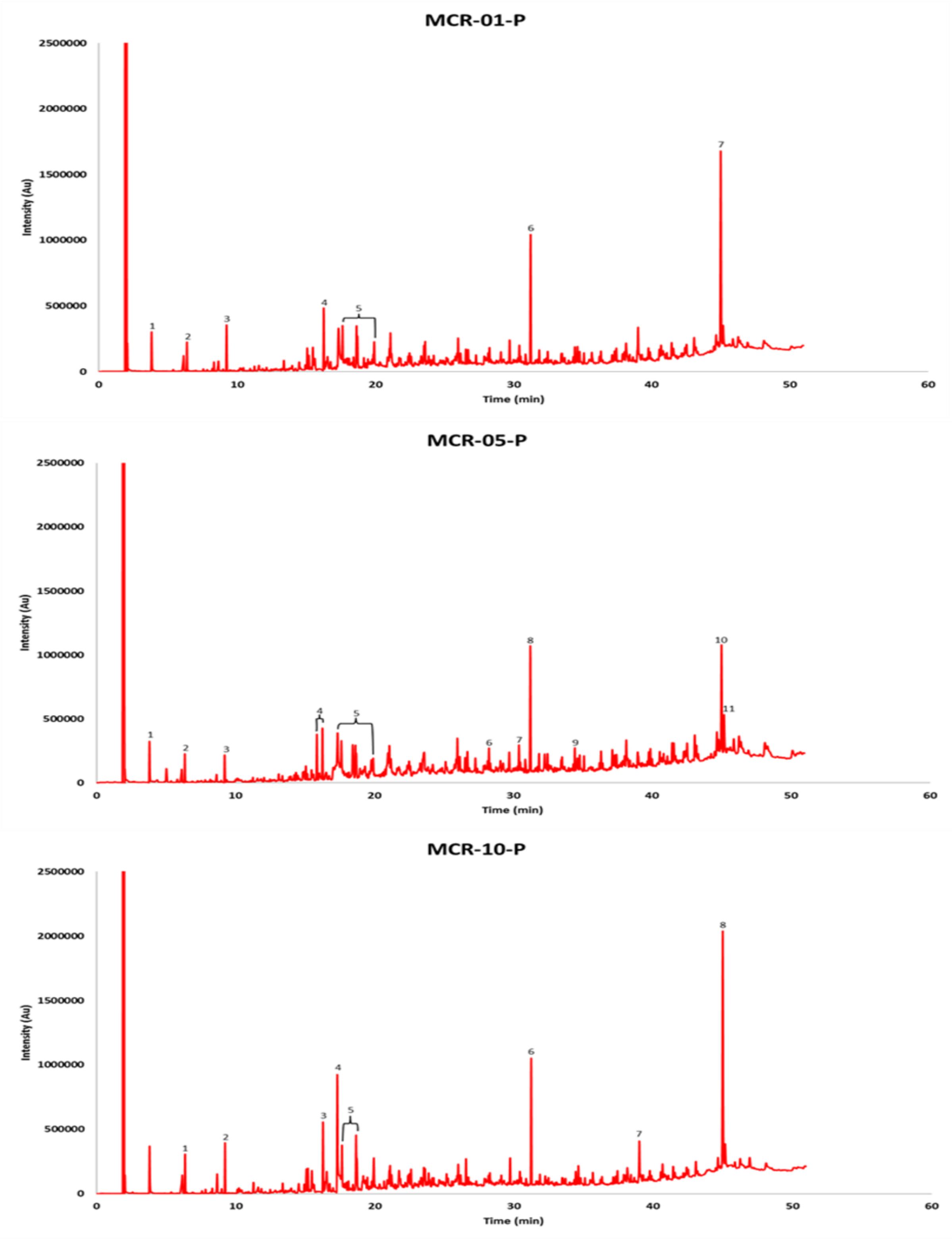

Figure 5.11: GC–MS spectrum of the primary condensate liquids from MCR experiments.

MCR-01-P (2.69 wt. % moisture content); MCR-05-P (5.54 wt. % moisture content); MCR-10-P (9.29 wt. % moisture content); PC – Primary condensate

Table 5.8: Main components of the primary condensate organic liquids MCR experiments identified by GC–MS.

Peak ID	Retention Time (min.)	Structure name	Formula	Peak Area % of Total
		MCR-01-PC		
1	3.81	Glycerin	$C_3H_8O_3$	3.23
2	6.37	3-Penten-2-one, 4-methyl-	$C_6H_{10}O$	2.28
3	9.24	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	3.69
4	16.27	Phenol	C_6H_6O	5.11
5	17.63	Phenol, 2-methyl-	C_7H_8O	2.89
	18.64	Phenol, 4-methyl-	C_7H_8O	3.96
	18.71	Phenol, 3-methyl-	C_7H_8O	2.74
	19.92	Phenol, 3,4-dimethyl-	$C_8H_{10}O$	1.32
6	31.24	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl) bis-	$C_{16}H_{16}$	11.13
7	45.00	Benzene, 1,1'-(1-butenylidene) bis-	$C_{16}H_{16}$	20.06
			Total	**56.42**
		MCR-05-PC		
1	3.82	Glycerin	$C_3H_8O_3$	2.97
2	6.37	3-Hexen-2-one	$C_6H_{10}O$	1.90
3	9.24	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	1.90
4	15.87	Phenol	C_6H_6O	3.47
	16.27	Phenol	C_6H_6O	3.94
5	17.37	Phenol, 3-methyl-	C_7H_8O	4.03
	17.63	Phenol, 3-methyl-	C_7H_8O	2.46
	18.45	Phenol, 4-methyl-	C_7H_8O	2.89
	18.65	Phenol, 4-methyl-	C_7H_8O	2.65
	18.71	Phenol, 4-methyl-	C_7H_8O	1.77
	19.92	Phenol, 3,5-dimethyl-	$C_8H_{10}O$	1.59
6	28.26	9-Hexadecenoic acid	$C_{16}H_{30}O_2$	1.51
7	30.42	1-Docosanol	$C_{22}H_{46}O$	1.77
8	31.24	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl) bis-	$C_{16}H_{16}$	9.74
9	34.44	Oleic Acid	$C_{18}H_{34}O_2$	1.64
10	45.00	Benzene, 1,1'-(1-butenylidene) bis-	$C_{16}H_{16}$	8.92
11	45.18	Phenol, 4,4'-(1-methylethylidene) bis-	$C_{15}H_{16}O_2$	3.73
			Total	**56.85**
		MCR-10-PC		
1	3.82	Glycerin	$C_3H_8O_3$	3.67
2	6.37	3-Penten-2-one, 4-methyl-	$C_6H_{10}O$	2.79
3	9.24	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	3.58
4	16.28	Phenol	C_6H_6O	5.25
5	17.31	2,2,6,6-Tetramethyl-4-piperidone	$C_9H_{17}NO$	9.86

Peak ID	**Retention Time (min.)**	**Structure name**	**Formula**	**Peak Area % of Total**
6	17.64	Phenol, 4-methyl-	C_7H_8O	2.93
	18.66	Phenol, 4-methyl-	C_7H_8O	4.61
	18.72	Phenol, 4-methyl-	C_7H_8O	2.45
7	31.24	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl) bis-	$C_{16}H_{16}$	9.43
8	39.01	Ethyl Oleate	$C_{20}H_{38}O_2$	3.15
9	45.00	Benzene, 1,1'-(1-butenylidene) bis-	$C_{16}H_{16}$	21.92
			Total	**69.64**
MCR-01-P (2.69 wt. % moisture content); MCR-05-P (5.54 wt. % moisture content); MCR-10-P (9.29 wt. % moisture content); PC– Primary condensate				

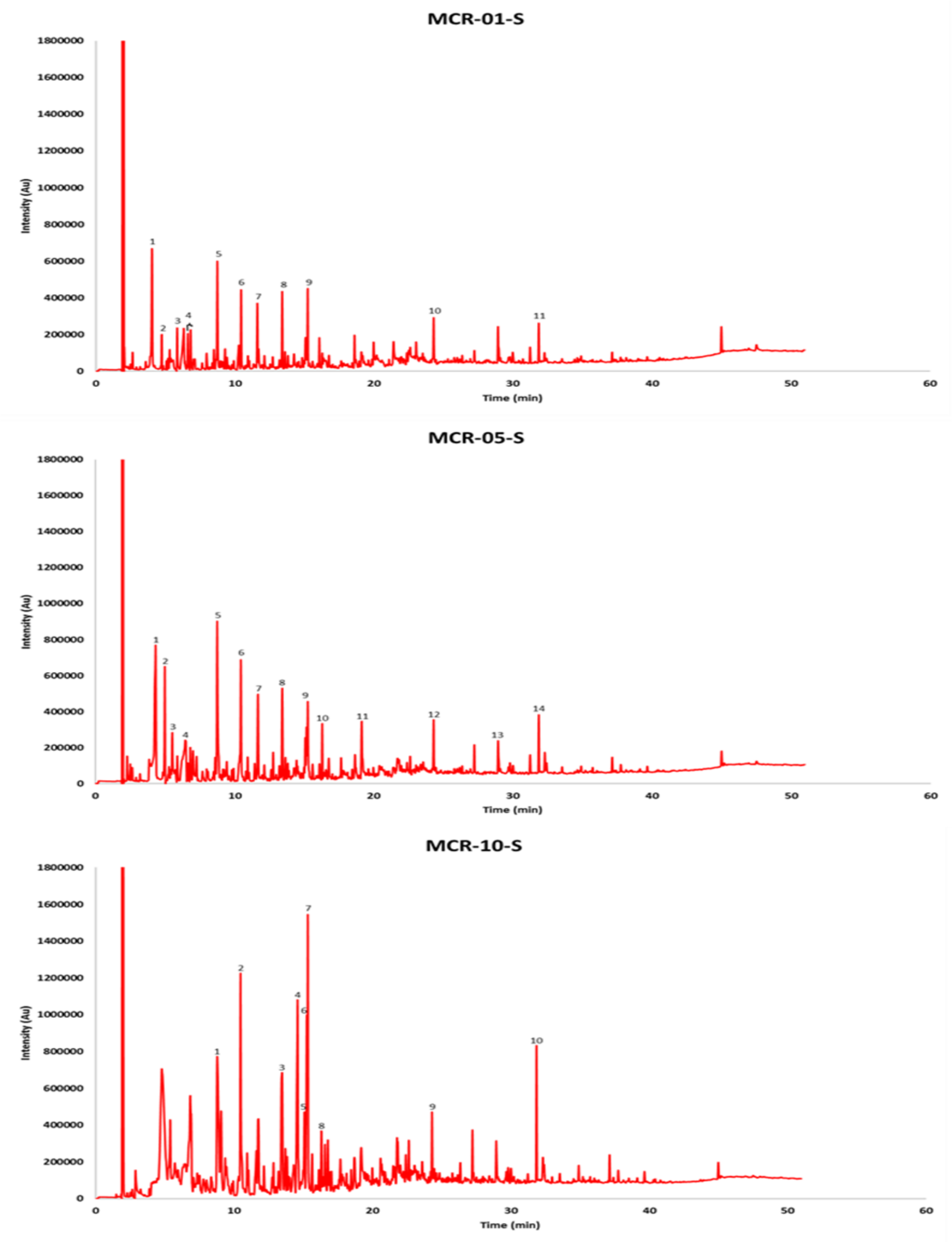

Figure 5.12: GC–MS spectrum of the secondary condensate liquids from MCR fast pyrolysis of trommel fines.

MCR-01-S (2.69 wt. % moisture content); MCR-05-S (5.54 wt. % moisture content); MCR-10-S (9.29 wt. % moisture content); SC – Secondary condensate

Table 5.9: Main components of the secondary condensate organic liquids from MCR experiments identified by GC–MS.

Peak ID	Retention Time (min.)	Structure name	Formula	Peak Area % of Total
		MCR-01-SC		
1	4.04	Glycerin	$C_3H_8O_3$	9.64
2	4.74	Glycine	$C_2H_5NO_2$	1.92
3	5.85	2,4-Dimethyl-2-oxazoline-4-methanol	$C_6H_{11}NO_2$	2.95
4	6.61	Cyclopropane-1,1-dicarboxylic acid	$C_5H_6O_4$	2.05
	6.82	Cyclopentanone	C_5H_8O	2.84
5	8.74	2-Cyclopenten-1-one	C_5H_6O	9.59
6	10.45	2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	4.85
7	11.62	1,4-Pentanediamine	$C_5H_{14}N_2$	4.37
8	13.40	2-Cyclopenten-1-one, 3-methyl-	C_6H_8O	4.91
9	15.24	Oxazole, 2-ethyl-4,5-dihydro-	$C_5H_9N_O$	5.46
10	24.30	(Z), (Z)-2,5-Dimethyl-2,4-hexadienedioic acid	$C_8H_{10}O_4$	2.84
11	31.86	Ethyl citrate	$C_{12}H_{20}O_7$	2.53
			Total	**53.95**
		MCR-05-SC		
1	4.32	Glycerin	$C_3H_8O_3$	10.41
2	4.99	Methane, trimethoxy-	$C_4H_{10}O_3$	5.15
3	5.52	Pyridine	C_5H_5N	2.05
4	6.81	Cyclopentanone	C_5H_8O	1.30
5	8.75	2-Cyclopenten-1-one	C_5H_6O	10.86
6	10.45	2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	3.81
7	11.68	1,4-Pentanediamine	$C_5H_{14}N_2$	5.46
8	13.42	2-Cyclopenten-1-one, 3-methyl-	C_6H_8O	5.41
9	15.26	4-Methyl-5H-furan-2-one	$C_5H_6O_2$	4.83
10	16.29	Phenol	C_6H_6O	2.35
11	19.13	1H-Imidazole, 4-methyl-	$C_4H_6N_2$	3.30
12	24.30	(Z), (Z)-2,5-Dimethyl-2,4-hexadienedioic acid	$C_8H_{10}O_4$	2.22
13	28.93	7H-Purin-6-amine, 7-methyl-	$C_6H_7N_5$	1.88
14	31.86	Ethyl citrate	$C_{12}H_{20}O_7$	2.48
			Total	**61.49**
		MCR-10-SC		
1	8.79	2-Cyclopenten-1-one	C_5H_6O	7.22
2	10.47	2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	5.67
3	13.47	2-Cyclopenten-1-one, 3-methyl-	C_6H_8O	5.40
4	14.59	2,4-Dimethyl-2-oxazoline-4-methanol	$C_6H_{11}NO_2$	7.30
5	15.08	2-Cyclopenten-1-one, 2,3-dimethyl-	$C_7H_{10}O$	1.42
6	15.26	1,2-Cyclopentanedione, 3-methyl-	$C_6H_8O_2$	4.21

Peak ID	Retention Time (min.)	Structure name	Formula	Peak Area % of Total
7	15.33	d-Galactano-1,4-lactone, 5,6-O-(ethylboranediyl)-2,3-di-O-trifluoroacetyl-	$C_{12}H_{11}BF_6O_8$	6.74
8	16.31	Phenol	C_6H_6O	1.32
9	24.30	(Z), (Z)-2,5-Dimethyl-2,4-hexadienedioic acid	$C_8H_{10}O_4$	1.44
10	31.86	Ethyl citrate	$C_{12}H_{20}O_7$	2.53
			Total	**43.24**
MCR-01-S (2.69 wt. % moisture content); MCR-05-S (5.54 wt. % moisture content); MCR-10-S (9.29 wt. % moisture content); SC – Secondary condensate				

5.2.3 Effect on feedstock moisture content on solid product characteristics

Ash content, elemental composition, and calorific values of the solid products obtained from feedstock moisture content investigation of fast pyrolysis of trommel fines are tabulated in Table 5.10. Table 5.6 above showed that the solid products were the highest yield of products obtained from fast pyrolysis of trommel fines and moisture content of the feedstock had no effect on the yield of solids produced. It was obvious that ash were the main components of the solids produced (Table 5.10). The ash content ranged for 82 - 87 wt.% (dry basis).

The elemental compositions and heating value of solid products are also listed in Table 5.10. The moisture content of the feedstock had no significant effect on the percentage of carbon. There was a slight increase with increasing moisture content. The heating values of the solid products were in the range of 4 – 5.54 MJ kg $^{-1}$ and was found to slightly increase with increasing moisture content until reaching a maximum then further increase led to decrease. The low calorific values of the solid residues might not make them viable as a source of process heat, but the requirement on LOI of solid materials destined for landfill, would require them to be burnt.

Table 5.10: Ash content, elemental composition and heating value of solid products (char pot) produced from MCR fast pyrolysis of trommel fines.

SOLID PRODUCTS	**MCR-01**	**MCR-05**	**MCR-10**
Feed Moisture (wt.%)	**2.69**	**5.54**	**9.29**
Ash content (wt.%) [a]	86.34 ± 0.52	85.45 ± 0.56	82.56 ± 0.24
Char (wt.%) [a]	13.66 ± 0.52	14.55 ± 0.56	17.44 ± 0.24
Elemental Analysis (wt.%) [a]			
Nitrogen	0.33	0.35	0.57
Carbon	9.02	9.66	11.80
Hydrogen	0.57	0.71	0.99
Sulphur	0.23	0.26	0.46
Oxygen [b]	3.51	3.57	3.62
Bomb Calorimeter (MJ kg^{-1}) [a]	4.12 ± 0.71	5.54 ± 0.74	4.17 ± 0.14
HHV dry (MJ kg^{-1}) [a c]	3.13	3.50	4.37
LHV dry (MJ kg^{-1}) [a d]	0.04	0.07	0.17
MCR – Moisture Content Run; [a] dry basis; [b] calculated by difference; [c] Eq. 3.11; [d] Eq. 3.12			

5.2.4 Effect of feedstock moisture content on process conversion efficiency

As previously describe in section 5.1.4, the process conversion efficiency was determined to study the effect of feedstock moisture content. Figure 5.13 below shows the effect of feedstock moisture content on the fast pyrolysis process conversion efficiency of dry physically pre-treated trommel fines samples. The fast pyrolysis process conversion efficiency range between 24 – 43%, decreasing with increasing feedstock moisture content. With respect to the organic product generally regarded as the main product in fast pyrolysis, the decrease in process conversion efficiency with increasing feedstock moisture content can be attributed to the organic liquids yields obtained from the moisture content investigation (refer to section 5.2) which decreased with increasing feedstock moisture content.

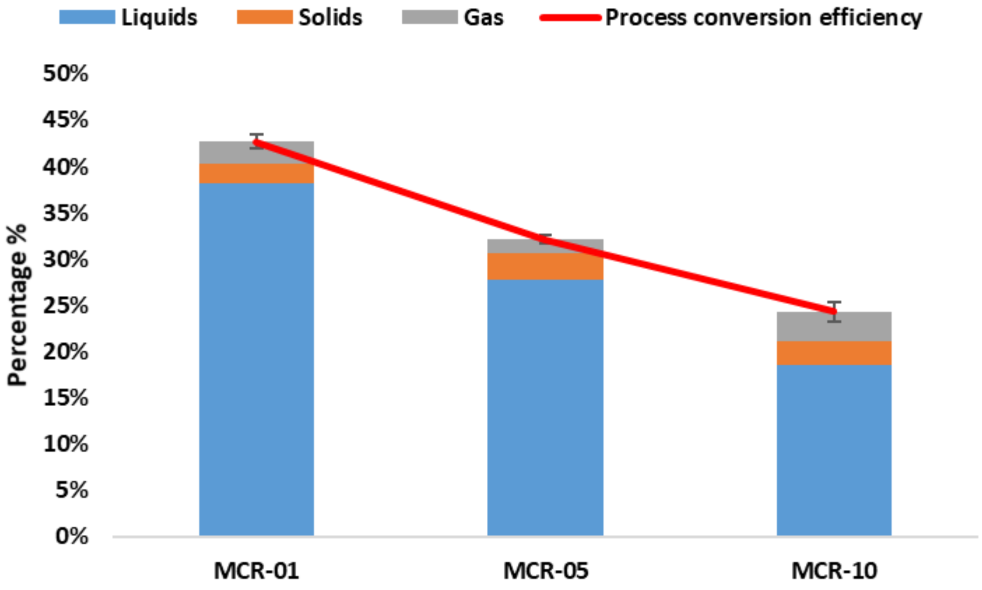

Figure 5.13: Fast pyrolysis process conversion efficiency from moisture content (MCR) investigation

5.2.5 Moisture content investigation (MCR) conclusion

The impact of feed moisture content on the yield of liquid, solid and gases produced from fast pyrolysis of PT trommel fines has been experimentally investigated. The organic liquid yields decreased with increasing moisture content and the highest organic liquid yield was observed at MCR-01 (20.1 wt.% dry basis). When considering the effect of trommel fines moisture content on product yields, increasing the trommel fines moisture content had no effect on solid product yields. The gas yield increased slightly with increasing moisture content. The increase in gas yields could have been caused by the lighter fraction of the fast pyrolysis vapour being converted into gas. The process efficiency decreased with increasing feedstock moisture content. The highest process efficiency was obtained at <3 feedstock moisture content (MCR-01 - 43% dry basis).

5.3 Effect of feedstock pre-treatment method

Table 5.11 shows the process parameters, product yields, product distributions and mass balance closure results obtained from the fast pyrolysis of pre-treated trommel fines (PT, AW and AWS). The samples contained similar moisture contents of approximately 3 wt%. The primary aim of these sets of experiments was to investigate the impact of pre-treatment methods products at optimum reaction temperature. The product yields were determined on a dry basis, therefore, the water yields presented was the water generated by the fast pyrolysis reaction excluding the water input in the feed. Each experiment was conducted three times.

TIR-500 (refer to section 5.1.1) results from the temperature investigation experiments are presented in this study as PT because the trommel fines feedstock used in those experiments were processed at optimum conditions. In addition, the mass balances were within a 5% range, so the highest mass balance closure obtained are reported and the rest are presented as standard deviations (Kalgo, 2011; Scott; 2014).

The average reaction temperatures from the pre-treatment method investigation experiments were slightly different from each other however were all between 500 – 530 °C (Table 5.11). The slight differences in temperature would not significantly affect the results. According to literature, for pyrolysis, temperature differences become significant on the process only when it was as large as ± 50 °C (Velghe et al. 2011; Zhou et al. 2013; Chen et al., 2014; Ding et al. 2016). The overall mass balance closure for the pre-treated trommel fines feedstock where between 93 – 98 wt.% dry basis.

Table 5.11: Mass balance summary for pre-treatment method experiments

Run No.	**PT**	**AW**	**AWS**
Set Temperature (°C)	500	500	500
Average Reaction Temperature (°C)	525	516	514
Feed Moisture (wt.%)	2.69 ± 0.06	3.22 ± 0.50	3.63 ± 0.32
Ash Content (wt.%)	36.2 ± 1.86	23.1 ± 0.46	22.8 ± 0.69
Run duration (minutes)	60	60	60
Average Feed rate (g h^{-1})	158.9	109.94	107.74
Liquid/Tar (wt.%) [a, b]	**32.6 ± 0.56**	**44.8 ± 0.90**	**43.5 ± 1.06**
PC Organics	12.5 ± 0.40	8.81 ± 0.44	9.02 ± 0.07
SC Organics	7.07 ± 0.72	27.6 ± 0.40	25.8 ± 0.39
Reaction water	13.0 ± 0.56	8.30 ± 0.85	8.69 ± 0.60
Solid Residue (wt.%) [a]	**52.1 ± 1.23**	**31.7 ± 0.34**	**33.5 ± 0.09**
Gas (wt.%) [a]	**12.9 ± 0.02**	**16.7 ± 0.56**	**15.8 ± 0.36**
Hydrogen	0.00	0.00	0.00
Carbon monoxide	0.08	0.03	0.04
Methane	0.52	0.18	0.20
Carbon dioxide	8.82	4.55	4.69
Ethylene	0.25	0.16	0.22
Ethane	0.24	0.10	0.12
Propylene	2.45	11.4	10.1
Propane	0.41	0.23	0.33
n-Butane	0.16	0.08	0.11
Closure (wt.%)	**97.6 ± 0.69**	**93.1 ± 0.81**	**92.8 ± 0.61**

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon); [a] dry basis; [b] ash free; [c] including oil solid content; PC – Primary condensate; SC – Secondary condensate

The total liquid yields produced from fast pyrolysis pre-treated trommel fines samples (PT, AW and AWS) increased after agitated washing of the trommel fines samples (Figure 5.14) and the highest liquid yield was obtained with the AW trommel fines sample (44.8 wt.% dry basis) with a primary condensate organic yield of 8.81 wt.% (daf) and secondary condensate organic yield of 27.6 wt.% (daf) From the results obatined the addition of a surfactant (Decon Neutracon) to the pre-treatment procedure, did not affect the total liquid yield. The current study also shows that the primary condensate organic yield decreased after washing while the secondary condensate organic yield increased after washing. The PT liquid yield obtained were lower when compared to literature on pyrolysis of RDF, MSW and its components, while the AW and AWS liquid yield are similar to literature data for pyrolysis of RDF, MSW and its components (Diebold, and Czernik, 1997; Oasmaa, and Kuoppala, 2003; Czernik and Bridgwater, 2004; Fratini et al., 2006; Mohan et. al 2006; Velghe et al., 2011; Khan et al., 2016).

The liquid yields obtained from the fast pyrolysis of AW and AWS were the highest yields of products obtained from their fast pyrolysis process. In addition, the reaction water yields were found to decrease after washing. (Table 5.11).

The solid yield is the highest yield of products obtained from PT fast pyrolysis. Approximately 52 wt.% dry basis of the pyrolysed PT trommel fines were solid products, however the solid yield decreased with the washed samples (AW and AWS). This finding is consistent with the reduced ash content in AW (23.1 wt.% dry basis) and AWS (22.8 wt.% dry basis) when compared to PT (36.23 wt.% dry basis) because of washing. The reduced ash content resulted to a reduced solid yield.

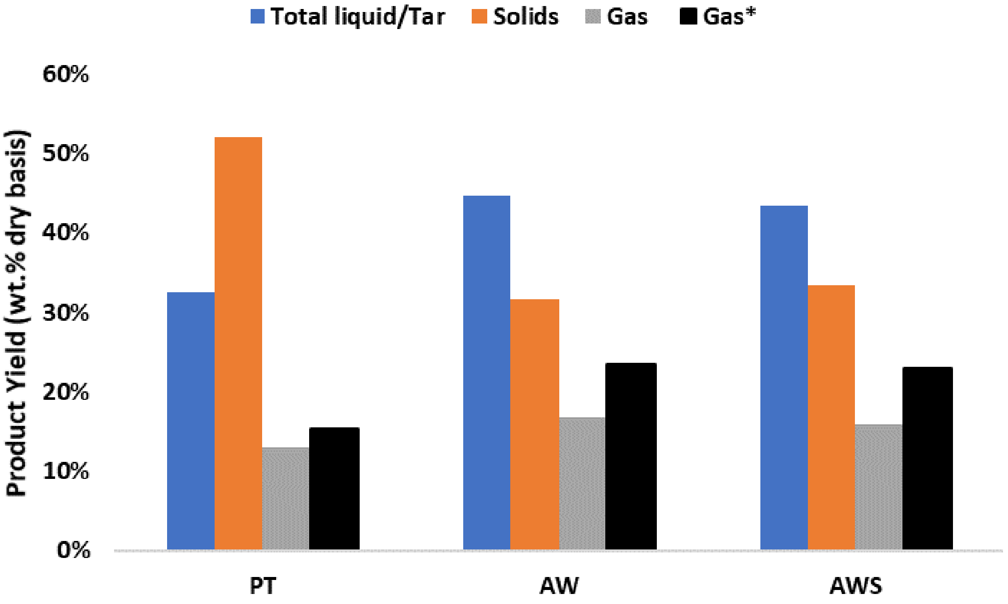

Figure 5.14: Yield of products obtained from feedstock pre-treatment method experiments

Gas* - Gas calculated by difference

The gas yield increased slightly after agitated washing and sedimentation hence the decrease in mass balance closure due to incomplete gas identification with the available GC (Table 5.11). The increase in gas yields can be attributed to the lighter fraction of the fast pyrolysis liquid vapour being converted into gas. According to Table 5.11, the gaseous products contain mainly of carbon dioxide and propylene with small quantities of C_1–C_4 hydrocarbon gases. Figure 6.15 below present the gas compositions in volume % and it can be noticed from the graphs that after the agitated washing process the methane and CO_2 volume decreased, the propylene volume increased but had no effect on the rest of the gases identified.

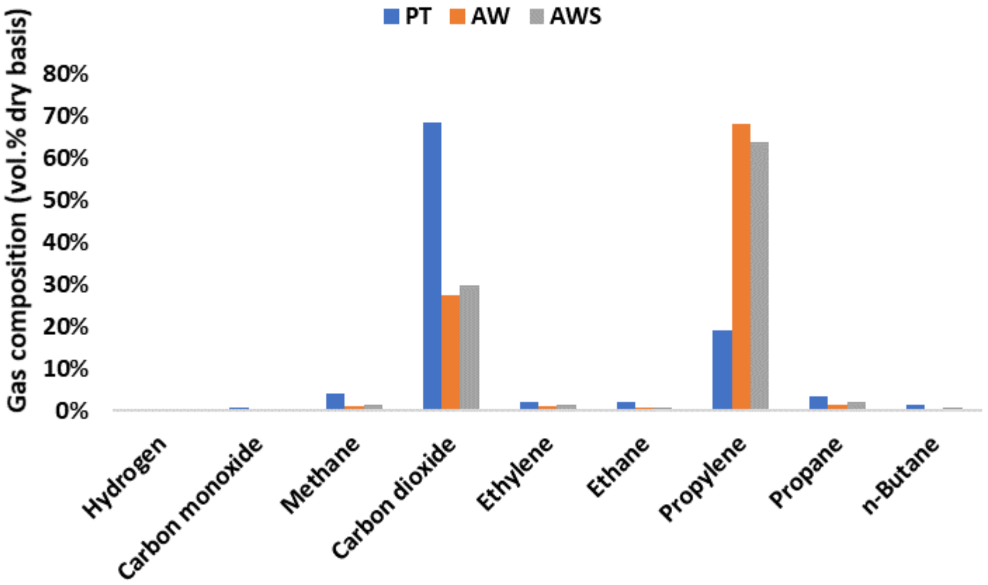

Figure 5.15: Composition of gaseous products obtained from feedstock pre-treatment method experiments

5.3.1 Effect of feedstock pre-treatment method on liquid product characteristics

The results of the analysis of water content in the liquid products obtained from dry and wet physical pre-treatment method investigations of are presented in Table 5.12. The total water contents of trommel fines liquid products (primary and secondary condensate) from the pre-treatment method investigation was in the range of 34 – 74 wt.%. The water content in the secondary condensate decreased with the wet physically pre-treated samples (AW and AWS). The AW and AWS secondary condensate water content (28.7 and 31.4 wt.% respectively) compared well with literature range of 15 – 35 wt.% (Elliott 1994; Bridgwater 2004). The decrease in water content can be attributed to reduction in secondary cracking of the fast pyrolysis vapours as the result of the reduced ash content in the wet physically pre-treated samples (AW and AWS). This resulted in the production of lighter organic fractions of the fast pyrolysis vapours being produced with the wet physically pre-treated samples (AW and AWS) hence the increase in organic yields in the secondary condensate (Table 5.11). The solids contents entrained in the liquid products produced from dry and wet physical pre-treatment method investigations (Table 5.12) show that the solid content decreased slightly with the wet physically pre-treated samples (AW and AWS). Figure 5.16 shows the photographs of the primary and secondary condensates produced from fast pyrolysis of PT trommel fines with different water content.

The elemental compositions and heating values of both the primary and secondary condensate liquids produced from dry and wet physical pre-treatment method investigations are listed in Table 5.12. The percentages of nitrogen, carbon and sulphur for both primary and secondary condensate decreased with the wet physically pre-treated samples (AW and AWS) while the hydrogen increased. With regards to nitrogen contents, the wet physically pre-treated methods (AW and AWS) proved to be effective in reducing the presence of nitrogen compounds in the liquids, which could have been a drawback when burning the liquids because of the high potential for NOx emissions.

It was found that the heating values of the primary and secondary condensate liquids remained fairly the same for all three samples (PT, AW and AWS) as seen in Table 5.12. The heating values of the primary condensate were 32.4 MJ kg $^{-1}$ (PT), 32.5 MJ kg $^{-1}$ (AW) and 33.8 MJ kg $^{-1}$ (AWS). However, there was observable differences in the heating values of the secondary condensates, as follows; 17.4 MJ kg $^{-1}$ (PT), 25.7 MJ kg $^{-1}$ (AW) and 26.4 MJ kg $^{-1}$ (AWS) samples, respectively. The heating values of the primary condensate obtained from dry and wet physical pre-treatment method investigations was found to be slightly higher when compare to literature on pyrolysis of biomass, while the heating values of the secondary condensate liquids compared well with literature on pyrolysis of RDF, MSW and its components (Diebold, 2000; Czernik and Bridgwater 2004; Putun et al. 2004; Lee et al. 2005 Oasmaa & Meier, 2005; Oasmaa et al., 2005; Velghe et al. 2011; Zhou et al. 2013; Chen et al., 2014; Ding et al. 2016) and has potential for energy recovery.

Table 5.12: Water content, solids contents, elemental composition and heating value of liquid products produced from pre-treatment method investigations

LIQUID/TAR PRODUCTS	**PT**	**AW**	**AWS**
Primary Condensate (wt.%) [a]			
Water content	5.8 ± 0.56	5.39 ± 0.60	6.52 ± 0.74
Solid content	3.58 ± 0.85	2.34 ± 0.74	2.68 ± 0.62
Elemental Analysis (wt.%) [a]			
N	2.91	1.20	1.24
C	72.9	64.0	66.5
H	8.75	11.2	10.7
S	0.10	0.12	0.13
O [b]	15.3	23.52	21.50
Bomb Calorimeter (MJ kg^{-1}) [a]	32.4 ± 0.09	32.5 ± 0.23	33.8 ± 0.41
HHV dry (MJ kg^{-1}) [a c]	31.2	31.8	32.3
LHV dry (MJ kg^{-1}) [a d]	22.5	29.4	28.4
Secondary Condensate (wt.%) [a]			
Water content	67.9 ± 2.78	28.7 ± 0.72	31.41 ± 0.36
Elemental Analysis (wt.%)			
N	6.36	0.21	0.20
C	54.7	48.5	47.1
H	6.63	11.2	10.8
S	1.47	0.42	0.55
O [b]	30.9	39.7	41.4
HHV dry (MJ kg^{-1}) [a c]	17.4	25.8	26.4
LHV dry (MJ kg^{-1}) [a d]	8.89	23.3	23.1

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon); [a] dry basis; [b] calculated by difference; [c] Eq. 3.11; [d] Eq. 3.12

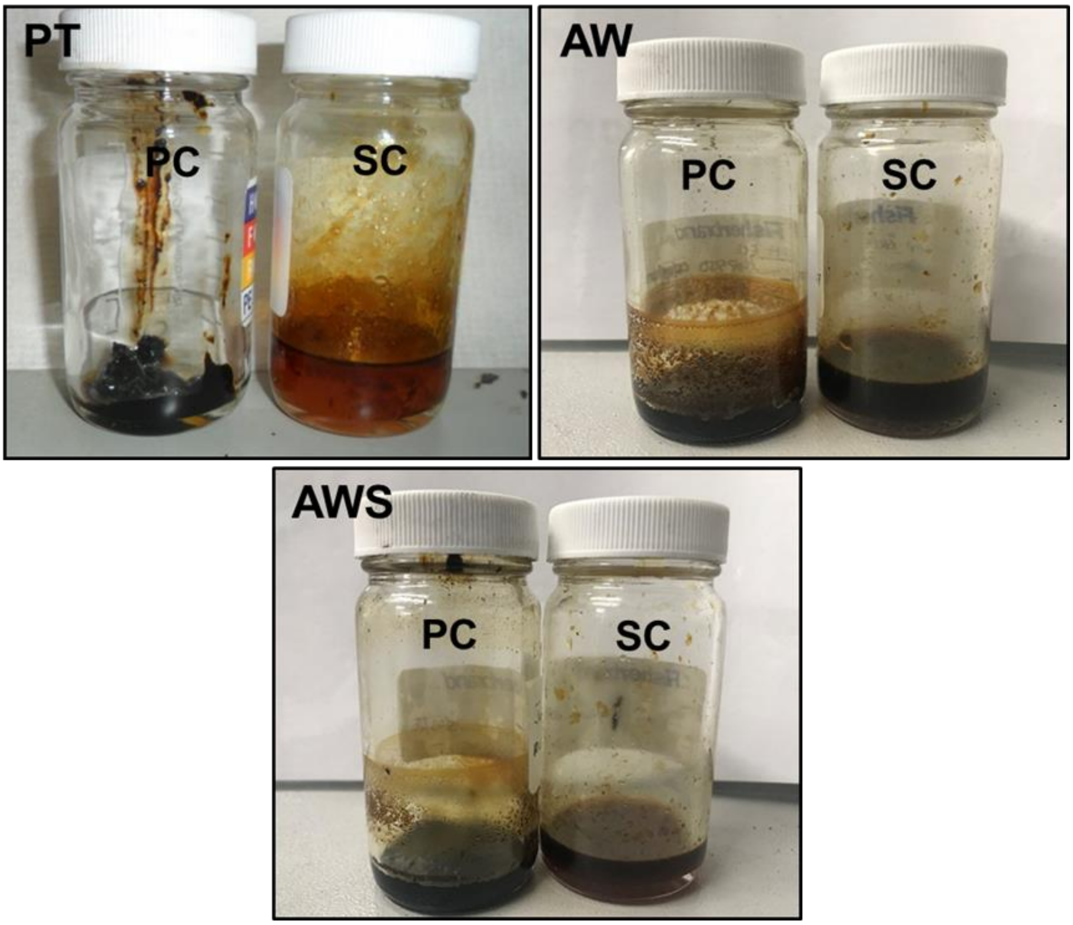

Figure 5.16: Liquid/tar products from fast pyrolysis of dry and wet physically pre-treated trommel fines samples

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon); PC - Primary Condensate; SC - Secondary Condensate

5.3.2 Effect of feedstock pre-treatment method on organic liquid products

The chromatograms of the organic portions of the primary and secondary condensate liquids from feedstock pre-treatment method investigation are shown below in Figure 5.17 and 5.18 respectively. The major organic compounds along with their retention time, structure name, and molecular formula for the primary and secondary condensate are shown in Table 5.13 and 5.14 respectively. The molecular chains of complex compounds in the trommel fines have been broken, generating compounds with a carbon number range of 3 – 16 and the main components are, furans, and phenols.

The GC-MS analysis of the primary condensate from the dry physically pre-treated sample (PT) shows the presence of phenolic compounds such as phenols, methoxyphenols and dimethoxy phenols derived from the pyrolysis of the lignin constituent of the feedstocks. While the wet physical treated samples (AW and AWS) contained mostly benzene compounds (Table

5.13). The use of the surfactant (Decon Neutracon) led to a pre-treated trommel fines that produced more benzene groups in the primary condensate (Figure 5.17).

The GC-MS analysis of the secondary condensate from the dry physically pre-treated sample (PT) shows the presence of nitrogen containing organic compounds (Table 5.14). These compounds are in the form of pyridines and their derivatives. However, the presence of these nitrogen-containing organic compounds decreased while the furan compounds increased with the wet physically pre-treated sample (AW and AWS in Figure 5.18). The decrease in nitrogen containing organic compounds is in line with the result of the elemental analysis of the secondary condensate liquid which shows a decrease in nitrogen content with the wet physically pre-treated trommel fines feedstock (AW and AWS as seen in Table 5.12).

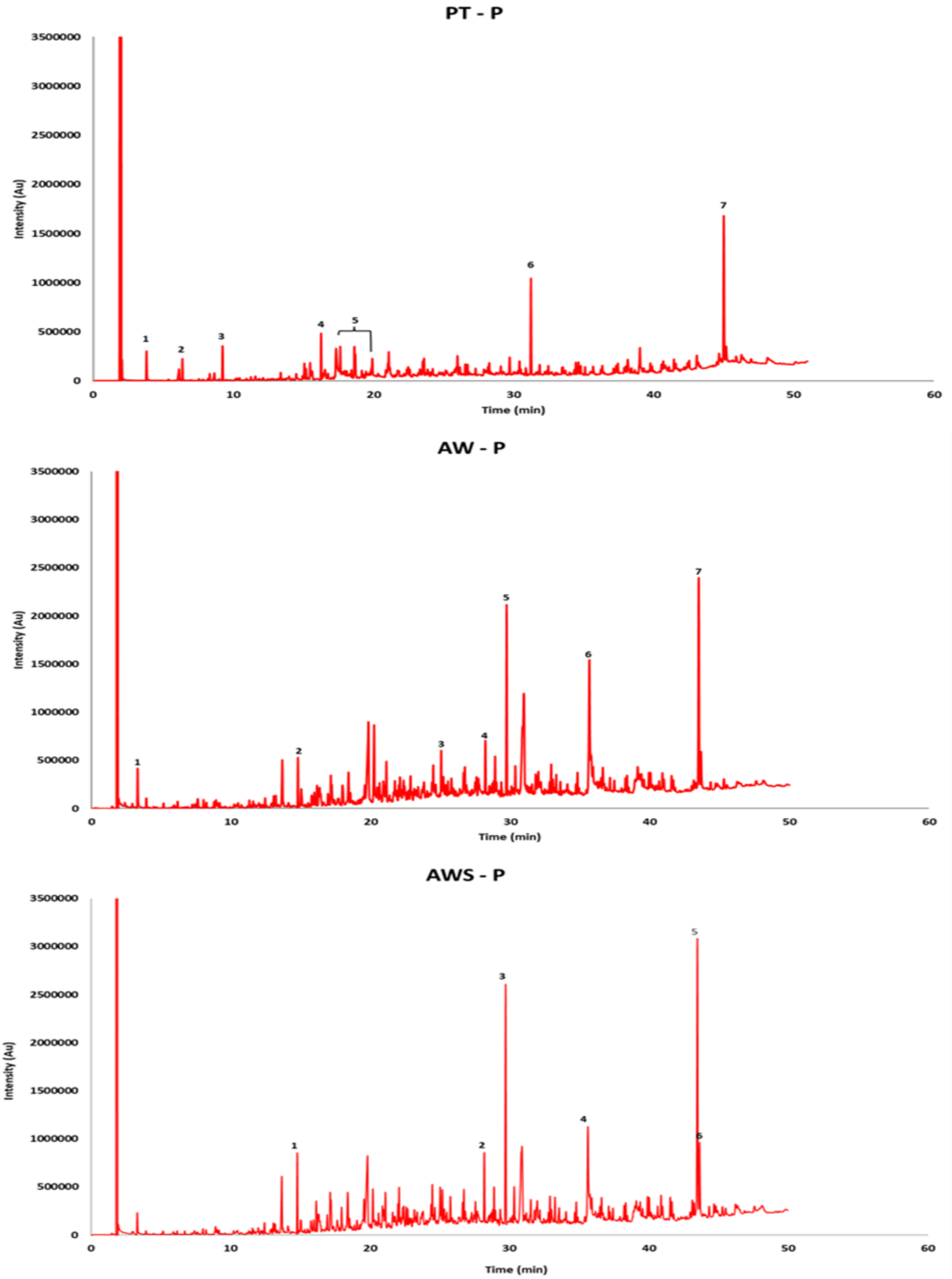

Figure 5.17: GC–MS spectrum of the primary condensate liquids from feedstock pre-treatment method experiments.

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon); PC – Primary condensate

Table 5.13: Main components of the primary condensate liquids from feedstock pre-treatment method experiments identified by GC–MS.

Peak ID	Retention Time (min.)	Structure name	Formula	Peak Area % of Total
PT-PC				
1	3.81	Glycerin	$C_3H_8O_3$	3.23
2	6.37	3-Penten-2-one, 4-methyl-	$C_6H_{10}O$	2.28
3	9.24	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	3.69
4	16.27	Phenol	C_6H_6O	5.11
5	17.63	Phenol, 2-methyl-	C_7H_8O	2.89
	18.64	Phenol, 4-methyl-	C_7H_8O	3.96
	18.71	Phenol, 3-methyl-	C_7H_8O	2.74
	19.92	Phenol, 3,4-dimethyl-	$C_8H_{10}O$	1.32
6	31.24	Benzene, 1,1'-(1-butenylidene) bis-	$C_{16}H_{16}$	11.13
7	45.00	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl) bis-	$C_{16}H_{16}$	20.06
			Total	**56.42**
AW-PC				
1	3.327	Glycerin	$C_3H_8O_3$	2.79
2	14.802	Phenol	C_6H_6O	3.17
3	25.055	Phenol, 2-methoxy-4-(1-propenyl)-	$C_{10}H_{12}O_2$	2.70
4	28.213	Benzene, 1,1'-(1,3-propanediyl) bis-	$C_{15}H_{16}$	3.75
5	29.739	Benzene, 1,1'-(1-butenylidene) bis-	$C_{16}H_{16}$	14.02
6	35.658	Hexadecanoic acid	$C_{16}H_{32}O_2$	11.94
7	43.487	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl) bis-	$C_{16}H_{16}$	17.72
			Total	**56.09**
AWS-PC				
1	14.805	Phenol	C_6H_6O	5.88
2	28.216	Benzene, 1,1'-(1,3-propanediyl) bis-	$C_{15}H_{16}$	5.36
3	29.745	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl) bis-	$C_{16}H_{16}$	19.83
4	35.643	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	8.60
5	43.494	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl) bis-	$C_{16}H_{16}$	25.74
6	43.655	Phenol, 4,4'-(1-methylethylidene) bis-	$C_{15}H_{16}O_2$	6.79
			Total	**72.19**
PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon); PC – Primary condensate				

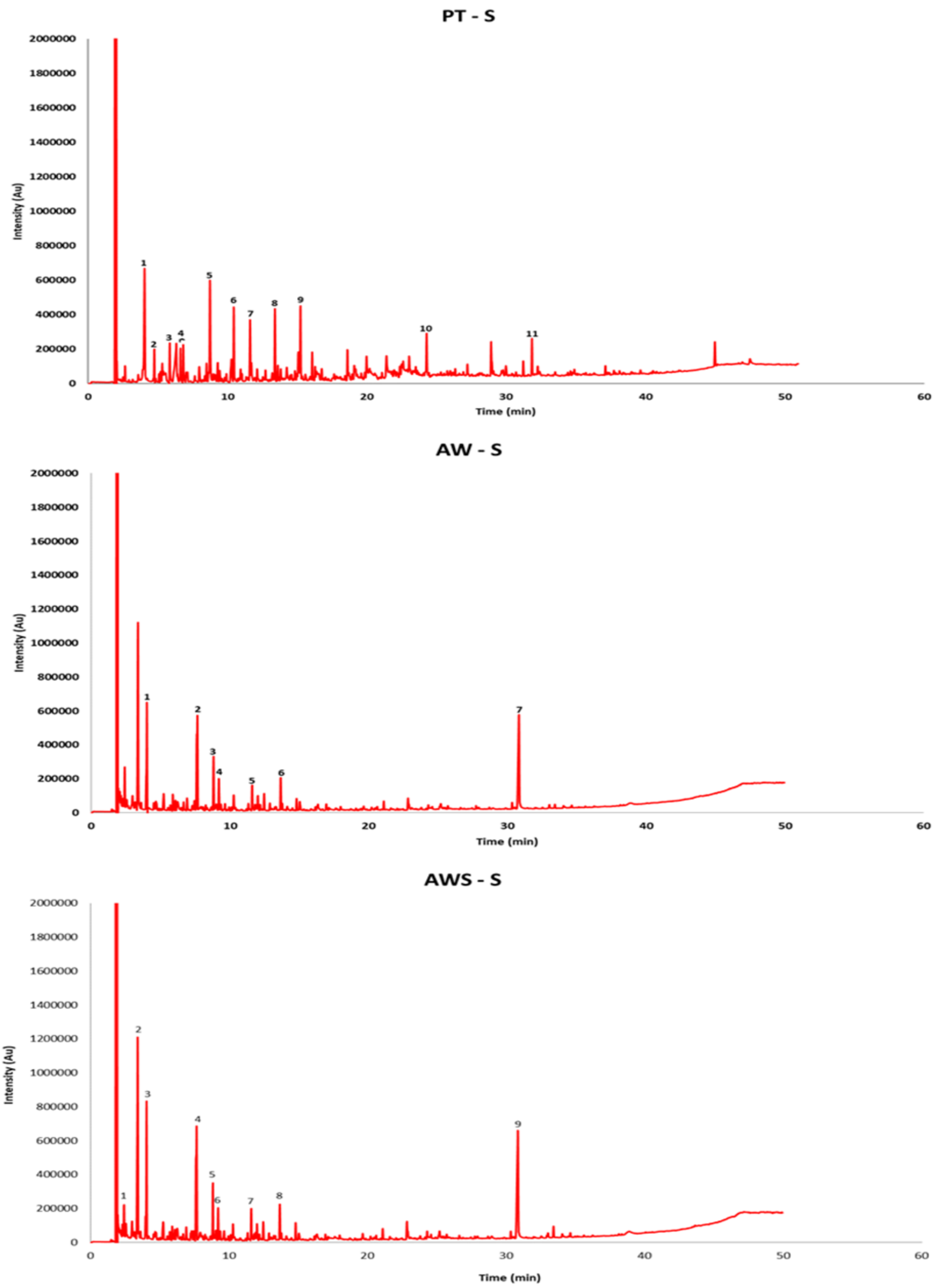

Figure 5.18: GC–MS spectrum of the secondary condensate liquids from feedstock pre-treatment method experiments.

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon); SC – Secondary condensate

Table 5.14: Main components of the secondary condensate liquids from feedstock pre-treatment method experiments identified by GC–MS.

Peak ID	Retention Time (min.)	Structure name	Formula	Peak Area % of Total
PT-SC				
1	4.04	Glycerin	$C_3H_8O_3$	9.64
2	4.74	Glycine	$C_2H_5NO_2$	1.92
3	5.85	2,4-Dimethyl-2-oxazoline-4-methanol	$C_6H_{11}NO_2$	2.95
4	6.61	Cyclopropane-1,1-dicarboxylic acid	$C_5H_6O_4$	2.05
	6.82	Cyclopentanone	C_5H_8O	2.84
5	8.74	Furan, 2-methyl-	C_5H_6O	9.59
6	10.45	2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	4.85
7	11.62	1,4-Pentanediamine	$C_5H_{14}N_2$	4.37
8	13.40	2-Cyclopenten-1-one, 3-methyl-	C_6H_8O	4.91
9	15.24	Oxazole, 2-ethyl-4,5-dihydro-	C_5H_9NO	5.46
10	24.30	(Z), (Z)-2,5-Dimethyl-2,4-hexadienedioic acid	$C_8H_{10}O_4$	2.84
11	31.86	Ethyl citrate	$C_{12}H_{20}O_7$	2.53
			Total	**53.95**
AW-S				
1	4.011	2-Butanone, 4,4-dimethoxy-	$C_6H_{12}O_3$	14.22
2	7.606	Furan, 3-methyl-	C_5H_6O	6.62
	7.652	Furfural	$C_5H_4O_2$	10.50
3	8.817	1,3-Dioxolane, 2,2,4-trimethyl-	$C_6H_{12}O_2$	5.74
4	9.2	2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	3.68
5	11.597	2-Furancarboxaldehyde, 5-methyl-	$C_6H_6O_2$	2.67
6	13.655	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	3.76
7	30.832	1,6-Anhydro-D-glucopyranose (levoglucosan)	$C_6H_{10}O_5$	19.67
			Total	**46.00**
AWS-S				
1	2.413	Pentanone	$C_5H_{10}O$	2.52
2	3.399	Acetic acid, 1-methylethyl ester	$C_5H_{10}O_2$	19.86
3	4.043	1,2-Propanediol, 2-acetate	$C_5H_{10}O_3$	11.81
4	7.658	Furfural	$C_5H_4O_2$	15.08
5	8.832	1,3-Dioxolane, 2,2,4-trimethyl-	$C_6H_{12}O_2$	4.48
6	9.207	Furan, 2,5-dimethyl-	C_6H_8O	2.89
7	11.602	2-Furancarboxaldehyde, 5-methyl-	$C_6H_6O_2$	2.29
8	13.665	1,2-Cyclopentanedione, 3-methyl-	$C_6H_8O_2$	2.83
9	30.858	1,6-Anhydro-D-glucopyranose (levoglucosan)	$C_6H_{10}O_5$	18.14
			Total	**79.91**

Peak ID	Retention Time (min.)	Structure name	Formula	Peak Area % of Total
PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon); SC – Secondary condensate				

5.3.3 Effect of feedstock pre-treatment method on solid product characteristics

Ash content, elemental composition, and calorific value of the solid products obtained from dry and wet physical pre-treatment method investigations of are tabulated in Table 5.15. Table 5.11 above showed that the solid products decreased with the wet physically pre-treated samples (AW and AWS). Ash were the main components of the solids produced (Table 5.15), however, the ash content decreased while the char content in the solid products increased with the AW and AWS. For instance, results from Table 5.15 show that for AW and AWS the ash contents decreased by 26.2 wt% and 21.2 wt%, respectively compared to PT. On the contrary, the char contents from these two wet pre-treated sample, increased more than 2-fold compared to PT. The increased char proportions in the solid residues also significantly increased the HHV of the residues by more than 300% compared to PT.

The elemental compositions and heating value of solid products from feedstock pre-treatment method investigations show that the nitrogen, carbon, hydrogen and sulphur contents increased with the wet physically pre-treated samples (AW and AWS). The increase in carbon content was in line with the increase in char content in the samples (AW and AWS) which resulted to increase heating values (Table 5.15).

Table 5.15: Ash content, elemental composition and heating value of solid products (char pot) produced from pre-treatment method investigations.

SOLID PRODUCTS	**PT**	**AW**	**AWS**
Ash content (wt.%) [a]	86.4 ± 0.52	63.7 ± 0.63	68.1 ± 1.43
Char (wt.%) [a]	13.7 ± 0.52	36.3 ± 0.63	31.9 ± 1.43
Elemental Analysis (wt.%) [a]			
N	0.33	1.29	1.08
C	9.02	31.12	26.37
H	0.57	2.27	1.94
S	0.23	0.43	0.43
O [b]	3.51	1.20	2.07
Bomb Calorimeter (MJ kg^{-1}) [a]	4.12 ± 0.71	13.5 ± 1.27	11.7 ± 0.93
HHV dry (MJ kg^{-1}) [a, c]	3.13	12.1	10.2
LHV dry (MJ kg^{-1}) [a, d]	0.04	1.97	1.35

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon); [a] dry basis; [b] calculated by difference; [c] Eq. 3.11; [d] Eq. 3.12

5.3.4 Effect of pre-treatment method on process conversion efficiency

As previously describe in section 5.1.4, the process conversion efficiency was determined to study the effect of feedstock pre-treatment method. The process conversion efficiency obtained from dry and wet physical pre-treatment method investigations are shown in Figure 5.19. The process conversion efficiency ranged between 43 – 74% increasing with the wet physically pre-treated samples (AW and AWS). With respect to the organic product generally regarded as the main product in fast pyrolysis, the increase in process conversion efficiency observed with the wet physically pre-treated samples (AW and AWS) can be attributed to the organic liquids yields obtained from the pre-treatment method investigation (refer to section 5.2), which increased with the wet physically pre-treated samples (AW and AWS). The highest process conversion efficiency was obtained with the AW trommel fines sample (74%), followed by the AWS sample obtained by washing the PT with 1% Decon Neutracon at 70%. The increase in process conversion efficiency with the wet physically pre-treated trommel fines sample (AW and AWS) could be mainly due to the elimination of the inorganics after the sedimentation process.

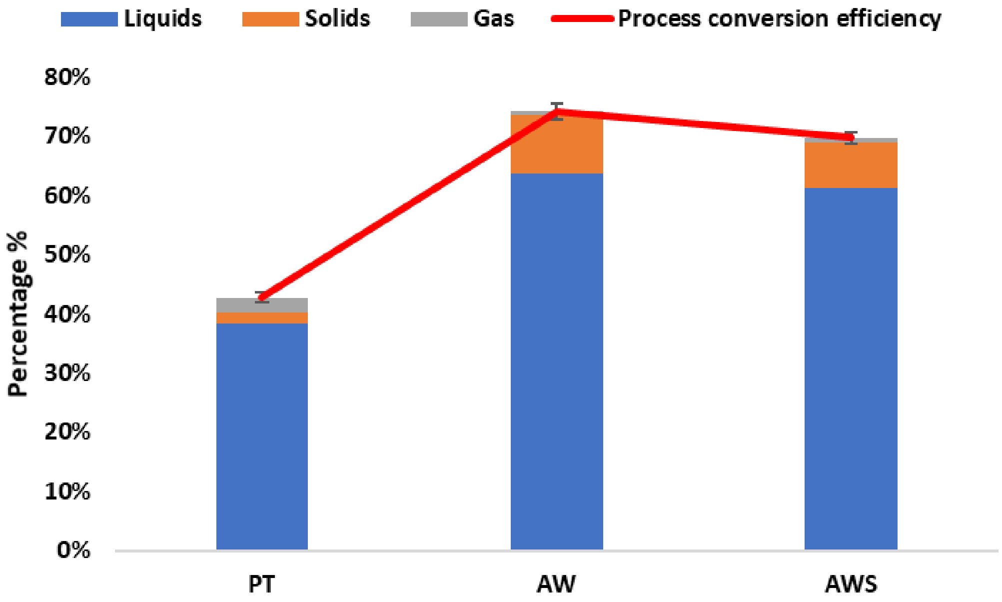

Figure 5.19: Fast pyrolysis process conversion efficiency from pre-treatment method investigation.

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)

5.3.5 Comparative studies (dry and wet physical pre-treatment) conclusion

The impact of dry and wet physically pre-treated methods on the yield of liquid, solid and gases produced from fast pyrolysis of pre-treated trommel fines has been experimentally investigated. The total liquid yields (organic and water) increased with the wet physically pre-treated samples (AW and AWS) and the highest liquid yield was with the AW trommel fines sample (44.8 wt.% dry basis) with an organic yield of 36.5 wt.% dry basis. The solid yields are the highest yield of products obtained from fast pyrolysis of PT trommel fines sample (52.1 wt.% dry basis) but decreased with the wet physically pre-treated trommel fines samples (AW; 31.7 wt.% dry basis; AWS; 33.5 wt.% dry basis). There is no clear evidence that the addition of a surfactant (Decon Neutracon) to the wet physical pre-treatment method influenced the yield of liquid and solid products, however an increase in gas yield was observed with the AWS sample. The process efficiency increased with the wet physically pre-treated sample (AW and AWS). The highest process conversion efficiency was obtained with the AW trommel fines sample (74%).

5.4 Mass balance on the ash contents of pre-treated trommel fines samples

Results from the trommel fines experiments carried out on the commissioned 300 g h^{-1} bubbling fluidised bed fast pyrolysis rig show a reduced yield of organic liquids especially for the PT trommel fines samples when compared to literature for MSW feedstocks produced under similar processing conditions (Mohan et. al 2006; Velghe et al., 2011; Zhou et al., 2013; Chen et al.,2014; Ding et al., 2016). This was the case for all the commissioning and subsequent experiments carried out where organic liquid yield comparisons were possible. To understand the reason for the low organic yields, reference is made to section 2.6.4 where the effects of char and inorganic components of the feedstock on organic liquid yield of fast pyrolysis are reviewed. The swift removal of char from reaction zones was identified as essential to prevent further cracking of organic vapours generated to maximise organic liquid yields.

The inorganic constituents (stones, glass, alkali earth metals etc.) present in the dry physically pre-treated trommel fines sample (PT) were retained in the reactor bed (Figure 5.20 PT) and char product. As the inorganic constituents present in PT trommel fines sample and chars formed during experiments on the commissioned unit were unable to be removed, the cracking of generated fast pyrolysis vapours continued unabated. This resulted in low organic liquid yields for all the parameters investigated. It is also believed that the inorganic constituents and the high amounts of char retained in the bed were responsible for the large amounts of reaction water generated compared to pyrolysis of RDF, MSW and its components (Mohan et. al 2006; Velghe et al., 2011; Zhou et al., 2013; Chen et al.,2014; Ding et al., 2016). Research has shown that extended pyrolysis vapour cracking result in higher gas yields and reaction water (Sitzmann, 2009).

However, the reduction of ash in the wet physically pre-treated samples (AW and AWS) led to a reduction of inorganic constituents (stones, glass, alkali earth metals etc.) in reactor bed and a decrease in solid residue obtained (Figure 5.20 AW; AWS) after fast pyrolysis process, which subsequently led to an increase in organic yield. Table 6.16 attempts to give a clearer picture of the peculiarity of the solid residue retention problems identified in the reactor. This should show the extent to which the char retained impacted reduced organic liquid yields. A comparison has been made on the distribution of solid residue produced from fast pyrolysis experiments of the three pre-treated trommel fine samples (PT, AW and AWS). The table shows the yields, location and distribution of solid residue recorded after experiments. Although up to 87% of the solid residue on the 300 g h^{-1} unit were recovered from the process char-pots (where they should be), about 3 – 12% of the solid residue was recovered from the reactor itself decreasing after the wet treatment procedures. As more pyrolysis vapours come in contact with the produced solids in the reactor bed, the extent of cracking experienced by the vapours is increased. It was concluded that as more solids are collected in the reactor, the vapour residence time will decrease due to a restriction to gas and vapour flow.

Figure 5.20: Reactor contents at the end of experiments after carbon burn off for dry and wet physically pre-treated trommel fine samples

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)

Table 5.16: Solid residue distribution for dry and wet physically pre-treated trommel fine samples

Feedstock type	**PT**	**AW**	**AWS**
Solid residue (SR) yield (wt%)	**52.1 ± 1.23**	**31.7 ± 0.34**	**33.5 ± 0.09**
Char pots (% SR)	87.1	95.9	94.5
Fluidised bed (% SR)	11.8	3.44	4.71
Liquid products (% SR)	0.95	0.71	0.79
PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)			

5.5 Overall mass balance closures

Results from all fast pyrolysis of dry and wet physically pre-treated trommel fines experiments showed that the highest mass balance closure obtained was 97.6 wt.% (dry basis) at around 500 - 550 °C and with feedstock moisture content of <3% using the PT trommel fines sample. However, the mass balance closures deceased with increased temperature and increased feedstock moisture content. It also decreased after the wet physically pre-treated trommel fines procedures. While the mass balances may be acceptable depending on the intended use of the data, closures higher than 95% are preferred. The low mass balance closures were because of the construction of the feed system and the unidentified gas peaks already discussed above (refer to section 5.1).

As it can be seen in Figure 5.21 below, the fast screw inlet into the reactor retained some amount of feedstock. This was the case unless all the feedstock in the hopper was fed or the feed level in the hopper dropped below the feeding screw. After most experiments, feedstock particles that had fused together because of heating effects from the reactor to the reactor inlet remained in the pipe work that joined the reactor to the feed system. The mass retained in that space was usually between 1-5 g of feedstock depending on the feedstock type. For example, the retained mass increased with the wet physically pre-treated trommel fines samples (AW and AWS) and these particles were difficult to retrieve. Practically, retrieval was only possible after the feed hopper had been emptied and the reactor had cooled down. The reactor contents were then emptied before the feeding screw was operated to push the feedstock particles in the space into the reactor for recovery or hovered out. The feedstock particles in that space between reactor and feed system were found to have undergone thermal decomposition. The extent of thermal decomposition increased with the particles closest to the reactor. Since the mass of particles retained in that space were yet to reach the reactor, they could not be considered to have undergone complete pyrolysis. Similarly, because the particles had started undergoing thermal decomposition, they could not be classified as unreacted feedstock.

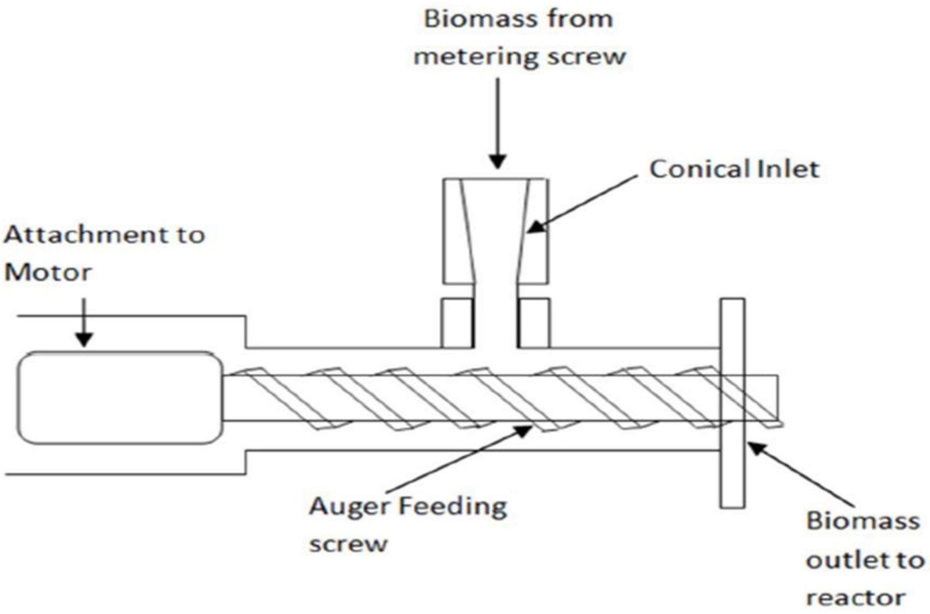

Figure 5.21: Fast screw inlet to reactor (not to scale)

For the reasons highlighted, all the feedstock particles retained in the space between the feed system and the reactor were classified as process losses. The only conclusion that could be reached with certainty regarding the particles left in the space between the feed system and the reactor was that they had been completely dehydrated. The extent of organic decomposition could not be ascertained with certainty. The fact that the particles had been dehydrated had little bearing on the mass balance closures since results are reported on a dry basis. Another reason for the low mass balance closures can be attributed to the short duration of the experiments carried out. Due to time constraints, each experiment was only conducted for a duration of 1 hour. It was theorised that the hold up in the condensing unit will increase over the duration of the run until it reached a constant value. To reduce the errors in the mass balance calculations caused by the hold up, it is recommended that future experiments be carried out for extended durations of time.

5.6 Summary

This chapter has explored the processing of dry and wet physically pre-treated trommel fines samples to produce valuable products using the commissioned 300 g h^{-1} fast pyrolysis units. Over 62 fast pyrolysis experiments were conducted throughout the course of this research. Some 15 experiments were prior and post modification commissioning experiments for the commissioned 300 g h^{-1} fast pyrolysis units. About 23 experiments were terminated or deemed inconclusive due to feedstock and reactor problems previously discussed in chapter 3.

A total of 24 successful pyrolysis experiments were selected and have been reported in this chapter. Some 18 of the experiments were based on pyrolysis temperature and feedstock moisture content investigation. Mass balances were calculated and compared with experimental results of similar feedstocks from literature. The results showed that although liquid products could be generated with the trommel fines feedstock, the liquid and organic yields were significantly less than reported values in literature as a result of the high ash content in the feedstock. A further 6 successful experiments were carried out to investigate the impact of ash reduction on product yields and distributions during which mass balances were calculated and the impact of ash reduction on solid and water contents were investigated. The results showed that liquid products (organic and water) increased the wet physically pre-treated trommel fines samples (AW and AWS) as a result of the decrease in ash content.

During the experiments carried out using the commissioned 300 g h^{-1} fast pyrolysis units, operational problems were discovered that included bridging in the feed system (refer to section 3.6.1), hydrodynamic limitations and poor mass balance closures. The causes of all the major problems were identified and their impacts on the process reviewed extensively. The true operational limits of the downstream equipment are yet to be determined because of the limitations imposed by poor feeding and reactor operation. At the end of this phase of the research, it was concluded that there was room for improvement to the commissioned 300 g h^{-1} fast pyrolysis system for difficult, high-ash content samples such as trommel fines. Alternative feed and reactor systems could be necessary to optimise the process.

6 Process design considerations for trommel fines fast pyrolysis

Having identified some engineering problems associated with the processing of trommel fines in an existing bubbling fluidised bed reactor, some alternative design and/or modifications have been proposed in this chapter. A redesign of the feeding system of the commissioned fluidised bed reactor to make it more suitable for the transport of trommel fines feedstock into the reactor is proposed. In addition, some proposed modifications of parts of the reactor to optimise its use for fast pyrolysis of feedstocks with high ash contents such as trommel fines and a suitable alternative fast pyrolysis reactor, has been suggested.

6.1 Proposed alternative feeding system for trommel fines fast pyrolysis process

One of the objectives of this study was to optimise the operation of the commissioned fluidised bed unit to process trommel fines. However, the feeding system has been identified as one of the culprits for the poor operation of the entire fluidised bed system. The feeding system used in this study is a multiple screw feeding system which consist of a Ktron KT-20 dual screw gravimetric feeding system with an air-tight hopper and variable speed motor for feeding attached to a fast speed feed screw used to feed the feedstock into the reactor (refer to section 3.5). The bridging problem explained in section 3.6.1 was because of the poor design of the fast speed feed screw inlet and the pre-pyrolysis problem explained in section 5.5 has been linked to the deficient design of the fast speed feed screw process section. This makes an alternative feeding system into the reactor a necessity.

6.1.1 Consideration of feeding systems

Different types of solid feeding systems are currently in use for fluidised bed to transfer the feedstock from storage to the processing stage. The most common feed systems for solid transport in use are rotary valve systems, pneumatic feed systems, piston feed systems, pump feed systems and screw feed systems. Rotary valve systems are limited to large scale and industrial systems and are rarely used for small scale applications because they are expensive (Wilén et al., 1993; Cuenca et al., 1995; Wilson, 1998; Bortolamasi et al., 2001; Cummer et al., 2002). Pneumatic feeders are used in small and lab scale operations (150 g h^{-1} unit), however their major drawback is the complex design, extra equipment like blowers and stirrers while an added need for a transport gas increases the operating costs associated with such units (Molerus. 1996; Joppic et al., 1997; Molerus et al., 1999; Hassan et al., 2000; Badger, 2002).

Piston feeders are more advanced and are used in systems pressurized up to 15 MPa but the design and operation of piston feeders is more complicated than for other feeding systems. Reliability and durability are major concerns since piston feeders are often associated with high pressure processes. Wear, gas leakage and feeding fluctuations are the main problems encountered during piston feeder operation (Simpson, 1998; Cummer et al., 2002; SME, 2002). Pumps feeders are also sometimes used to transport solids, combined with pneumatic feeders but are mainly suitable for the transportation and feeding of slurries (Schmieder et al., 1999; Schmieder et al., 2000; Antal et al., 2004; Matsumura et al., 2005).

Screw feed systems however, are the most commonly used for feedstock delivery in fluidised bed systems. Their ease of use and adaptability to the volumetric control of material flow from bins and hoppers make them popular. They can be enclosed and hence lock vapours and gases (Burkhardt et al., 1967; Wilson et al., 1991; Wilson, 1998; Bell et al., 2003). A list of screw feeders and their characteristics is shown in the Table 6.1 below. These different types of feeding systems, reviewed by Levelton (1986), are appropriate for solid feedstock feed systems because they can also be used at low pressures and for feed sizes <6 mm.

Table 6.1: Types of screw feeder Configurations (Levelton, 1986, Kalgo 2011)

Screw Feeder Type	**Comments**
Constant Cross Section	Common Design, Proven for many materials
Variable Cross Section	Frequently used for pressure applications
Choked Screws	Complicated design. Delivers plugs of solids. Needs further development
Plug Screws	Screw jamming for variable materials
Multiple Screws	Proven design. Common for larger units

A proper feedstock feeder design is essential to the performance of any pyrolysis process. The key essential elements of a feedstock feeding system (Marinelli et al., 1992; Kalgo, 2011) are

- A storage unit that can exhibit the right flow pattern for the required material. This may be in form of a hopper, silo or bin. In this study this was achieved using a Ktron KT-20 gravimetric feeding system which consists of an air-tight hopper with a nitrogen purge with a dual screw gravimetric feeding system with variable speed motor for feeding.
- A conveying system that will allow unhindered delivery of the material to the reactor unit while accurately metering the required amount of feed. In this study a fast screw was used but due to the characteristic of the trommel fines feedstock, the fast screw was not effective in delivering the feedstock into the pyrolysis unit hence the necessity for an alternative feeding system to convey the feedstock into the pyrolysis reactor.

Other important requirements that an efficient feeder system should be able to deliver for a fast pyrolysis process include

- Uniform distribution of feedstock into the reactor unit. In the case of the fluidised bed unit used in this study, this is achieved easily as the reactor is no larger than 65 mm in diameter (see chapter 3). This size allows for easy distribution of the feedstock across the entire cross-sectional area of the unit.
- A leak proof system that will ensure that the pyrolysis gases and vapours do not leak. It should be able to prevent back flow of any gases into the feed system or escaping to the surroundings.
- Accurate metering and transport of the feedstock to the fluidised bed reactor.

6.1.1.1 Feedstock consideration

In selecting a feed system suitable for trommel fines, the initial step is will be to consider and analyse the type of material that will be fed through the feed system. This analysis should consider the physical characteristics of the material focusing on bulk density, particle size, particle shape and moisture content (Michaël, 2007; Kalgo, 2011). These factors play a role in the precise metering and transport of the feedstock. As the feed system proposed will handle various types of feedstock including grasses, woods and agricultural residue, the physical characteristics of a range of materials must be taken into consideration. Table 6.2 below assesses the trommel fines feedstock components that may be fed through the feed system and their characteristics.

Table 6.2: Properties of trommel fines components considered for feeding (Levelton, 1982, Michaël, 2007; Kalgo, 2011)

Material	**Bulk Density (kg m^{-3})**	**Typical size (d_p in mm)**	**Flowability**	**Other properties**
Paper and cardboard	250 - 1500	$d_p < 1$	Free flowing	Hygroscopic, packs under pressure
Yard trimming and wood	100 - 800	$d_p < 1$	Free flowing	Light, packs under pressure
Food		$d_p < 1$	Sluggish	Hygroscopic
Plastics	500 - 4000	$d_p < 1$	Very sluggish	Light, packs under pressure
Glass	2000 - 8000	$d_p < 1$	Free flowing	Packs under pressure
Metals	1000 - 20000	$d_p < 1$	Free flowing	May agglomerate
Textile	100 - 600	$d_p < 1$	Sluggish	Hygroscopic, packs under pressure
Rubber	1000 - 1500	$d_p < 1$	Very sluggish	Light, may agglomerate

6.1.2 Proposed feed system configuration

Based on existing fast pyrolysis units in literature and experience from using the 300 g h^{-1} bubbling fluidised bed fast pyrolysis rig, one of the most promising alternatives identified and thought to be applicable within the context of this research in delivering the trommel fines feedstock into the pyrolysis reactor is the varying pitch plug screw feeder. In coming up with an alternative feedstock feeder into the reactor, the Ktron KT-20 dual screw gravimetric feeding system with an air-tight hopper could be coupled with the varying pitch plug screw feeder making it a single unit. This decision would eliminate the need for a new hopper, transport and metering components of the system thus reducing the cost. For added flexibility and ease of use, the Ktron KT-20 dual screw will adjust accurately the feedstock feed rate and the varying pitch plug screw which will operate at higher speeds will facilitate rapid and unhindered transportation of the feedstock in to the reactor. Figure 6.1 below is a schematics diagram of the proposed varying pitch plug screw feeder modified from a similar system reported in literature (Cummer et al., 2002; Kraft et al., 2006).

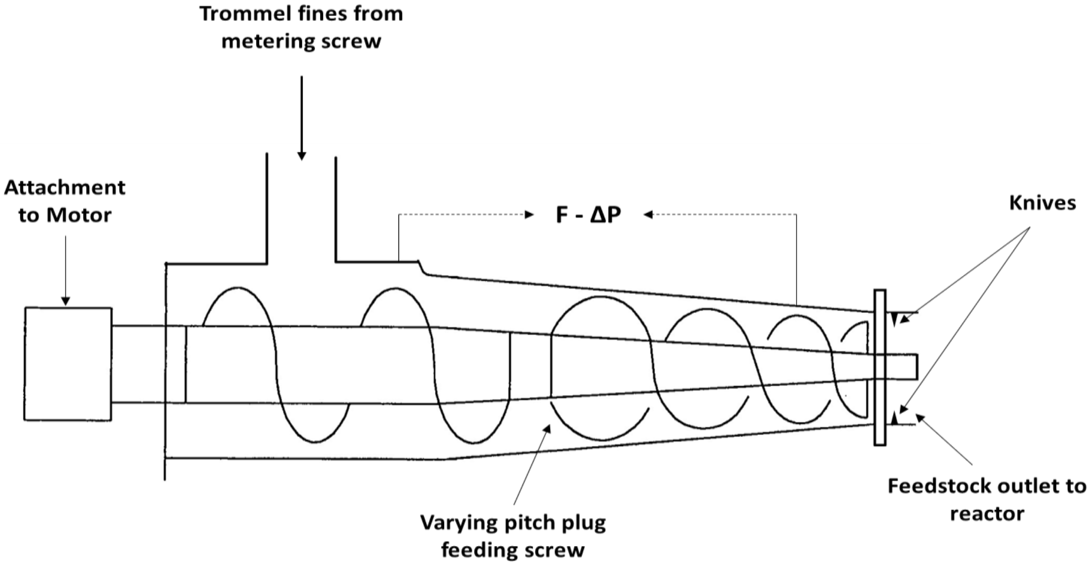

Figure 6.1: Schematic diagram of proposed varying pitch plug screw feeder (Adopted from: Cummer et al., 2002; Kraft et al., 2006).

The varying pitch plug screw feeder is intended to compress the feedstock into a compact plug, which forms a barrier preventing back flow of gases and bed materials. The plug compression is usually aided by tapering the feed channel or gradually reducing the pitch of the screw as it nears the reactor and knives can be introduced on the end section of the opening as an extrudate-breaker (see Figure 6.1). According to Bates, (2003) the screw should end before the casing so that the material is pushed forward within a confined channel, however, he did not advocate making the delivery pipe converge to increase the seal pressure, even though this is common in the biomass industries. Pressurization of the feed hopper is also advisable.

The change in pressure (ΔP) before and after the reducing section of the varying pitch plug screw should be monitored to ensure plug is maintained. If necessary, the varying plug screw feeder should be water cooled at the feed point to minimise pre-pyrolysis and large lumps formation due to melting and infusion of some feed components e.g. lignin. A backpressure adjuster (hydraulically adjustable throttle) can be employed to regulate both the strength of the plug and its pressure seal against backpressure and owing to the conical shape of the backpressure adjuster, which also breaks extrudates. Literature studies have shown that this kind of screw feeder or a modified version has been deployed in the pulp and biomass industry in Sweden and Canada (Wilén et al., 1993; Cummer et al., 2002).

The frictional effects of the feedstock on the varying pitch plug screw, together with the configuration of the screw itself and material properties, determine the efficiency. Higher filling fraction and less slip in the screw feeder lead to higher efficiency. However, their ineffectiveness arises due to various properties of the feedstock (e.g. compressibility, permeability, cohesion and adhesion), and may be further exacerbated by operating conditions (e.g. filling fraction in screw pockets and vibration of the screw).

Attention must be given to the varying reducing-pitch screw design, as well as its connection to the hopper to make the compression and sealing more reliable (Burkhardt, 1967; Wilson et al., 1991; Wilson, 1998; Bell et al., 2003). Literature studies have shown that the variable pitch screws appeared to have little advantage in achieving uniform flow along the full length of the opening for various feedstock fuels (such as hog fuel and wood chips) (Bundalli et al., 1986; Nelson, 1996). Based on literature, communications with the mechanical engineering department at Aston University and material cost estimates, the cost associated with fabricating the proposed alternative feeding screw is dependent on material type and the contractor. However, the breakdown for the estimated cost (parts and labour) can be seen in Table 6.3.

Table 6.3: Alternative feeding screw cost breakdown

Varying pitch plug screw	**Cost**
Parts	£850 - £1200
Labour	£150 - £300
Total Cost	**£1000 - £1500**

6.2 Proposed modification to fluidised bed reactor

Observations during the commissioning stage of the 300 g h^{-1} fluidised bed reactor and processing of the trommel fines feedstock showed that a number of optimal conditions for reactor operation were not met. Experimental reaction times were operationally limited to 1 hour, which further reinforced the conclusion that the reactor could not be operated as a continuous process at the intended optimum conditions. This has necessitated the need to propose for modifications to be made to the fluidised bed unit to allow for a wider range of operating conditions and higher throughput than the current unit.

6.2.1 Justification for fluidised bed reactor modifications

The following discussions present justifications for the proposed modification of the fluidised bed reactor.

6.2.1.1 Hydrodynamic limitations of current fluidised bed reactor

The hot commissioning phase and parameter investigations showed that the existing 300 g h^{-1} bubbling fluidised bed reactor could not operate at the required throughput because of geometric limitations. A bubbling fluidised bed fast pyrolysis process should be able to achieve selective entrainment of particles and it is required that the hydrodynamic parameters of the bed should be able to entrain char and unreacted feedstock particles but allow the fluidising medium (sand) to collapse back to the bed. These operational limits are a function of reactor geometry, mainly the transport disengaging height (TDH), gas flowrate and the expanded bed height.

The optimum gas flowrate for the existing 300 g h^{-1} bubbling fluidised bed reactor particularly for fast pyrolysis is between 10 - 15 L min^{-1} of nitrogen purge into the reactor and 10 L min^{-1} into the feed hooper. The static bed height with 150 g of sand in the reactor stood at 9 cm and this did not allow for a nitrogen purge into the reactor > 8 L min^{-1}. The hot commissioning phase also showed that the reactor geometry (H: 355 mm and D: 40 mm) allowed minimal space for bed expansion at the optimal operational conditions. This led to excessive entrainment of the fluidising sand which serves as the heat transfer medium to the feedstock particles. As entrainment of sand occurred, the extent of heat transfer to the feedstock particles is significantly reduced. This leads to reduced yields and a reduction in char pot capacity since the fluidising medium (sand) ends up in the char pot. Similarly, operating at lower gas flowrate (< 8 L min^{-1}) limits the ability of the system to eject higher density materials like the glass, stones, etc. found in the trommel fines feedstocks. The retention of ash in bed material would lead to increased bed weight, poor fluidization and pressure build up. Hence the parametric experiments conducted in this study were limit to 1 hour processing time.

6.2.1.2 Operational limit of downstream equipment

Another reason to modify the existing fluidised bed reactor stemmed from the need to determine the operational limits of the downstream equipment. The condensing unit were designed to carry vapour loads from the processing of 300 g h^{-1} of feedstock. The commissioning phase and parametric experiments could not be said to have determined their operational limits since the existing reactor was never operated at its designed capacity.

6.2.1.3 Improvements to mass balances and process yields

One reoccurring characteristic of experiments carried out during the commissioning phase was the range of mass balance closures (85 – 97%). The lower mass balance closures were attributed to the feeding problems (bridging as described in section 3.6.1) and hydrodynamic limitations (entrainment of char) of the commissioned unit as described in section 6.2.1.1 above. Another reason for the low mass balance closures was the short duration of the experiments carried out. It was theorised that the hold up in the condensing unit would increase over the duration of the run until it reached a constant value (Peacocke, 2008). Thus, to reduce the errors in the mass balance calculations caused by the hold up, it is of the recommendation that experiments are carried out at extended durations of time.

6.2.2 Proposed modified fluidised bed reactor configuration

Literature studies have shown that during pyrolysis, the inorganics (e.g. glass) end up in the reactor bed and or char pot. They can contribute to secondary cracking in the pyrolysis vapours which results in increased reaction water yields and decreased organic yields in bio-oil. (Philpot, 1970; Sekiguchi, and Shafizadeh, 1984; Czernik, Johnson, and Black, 1994; Agblevor, and Besler, 1996; Diebold, and Czernik, 1997; Miskolczi, Ateş, and Borsodi, 2013). Similar conclusion can be drawn from fast pyrolysis of trommel fines using the 300 gh^{-1} fluidised bed reactor. Operating at a low gas flowrate (< 8 L min^{-1}) limited the ability of the system to eject bigger particle and higher density materials like the glass, stones etc. found in the trommel fines feedstocks resulting to increased reactor bed weight and pressure build up as previously explained in section 6.2.1.1. Hence the reactor could not be operated as a continuous process at the intended optimum conditions. Certain modifications need to be made to the existing 300 g h^{-1} fluidised bed reactor in order for it to be able to process trommel fines on a continuous process. Based on experience from using the 300 g h^{-1} bubbling fluidised bed fast pyrolysis rig, the possible modifications that can be made to the existing rig can be seen in Figure 6.2 modified from similar pyrolysis system reported in literature (Ates et al., 2013; Miskolczi et al., 2013).

A vertical tube opening of around one fifth of the diameter (40 mm) of the existing 300 g h^{-1} bubbling fluidised bed reactor with a knife gate valve should be introduced just above the distributor plate (Figure 6.2). This would allow for entrainment of higher density materials like the glass, stones etc. found in the trommel fines feedstocks from the reactor bed when there is pressure and bed build up allowing for a continuous process. However, the fluidising sand which serves as the heat transfer medium to the feedstock particles could also be entrained via the vertical opening which would reduce heat transfer to the feedstock particles. But the entrainment of the fluidising sand can be compensated by increasing the temperature of the nitrogen going into the reactor.

Pressure probes should be fitted at the bottom and middle sections of the reactor respectively to measure the pressure difference (ΔP) across the reactor zone. The reactor pressure difference should be interlocked with the knife gate valve on the vertical tube opening to open and close as the pressure varies with solids and pressure build up in the reactor (Ates et al., 2013; Miskolczi et al., 2013). A pneumatic hammer should be introduced to dislodge the stagnant material in the vertical tube opening. A secondary cyclone should be introduced in series with the existing one to aid the rapid and complete char separation to reduce the solid content in the downstream parts of the process (Philpot, 1970; Sekiguchi, and Shafizadeh, 1984; Czernik, Johnson, and Black, 1994; Agblevor, and Besler, 1996; Diebold, and Czernik, 1997; Miskolczi, Ateş, and Borsodi, 2013).

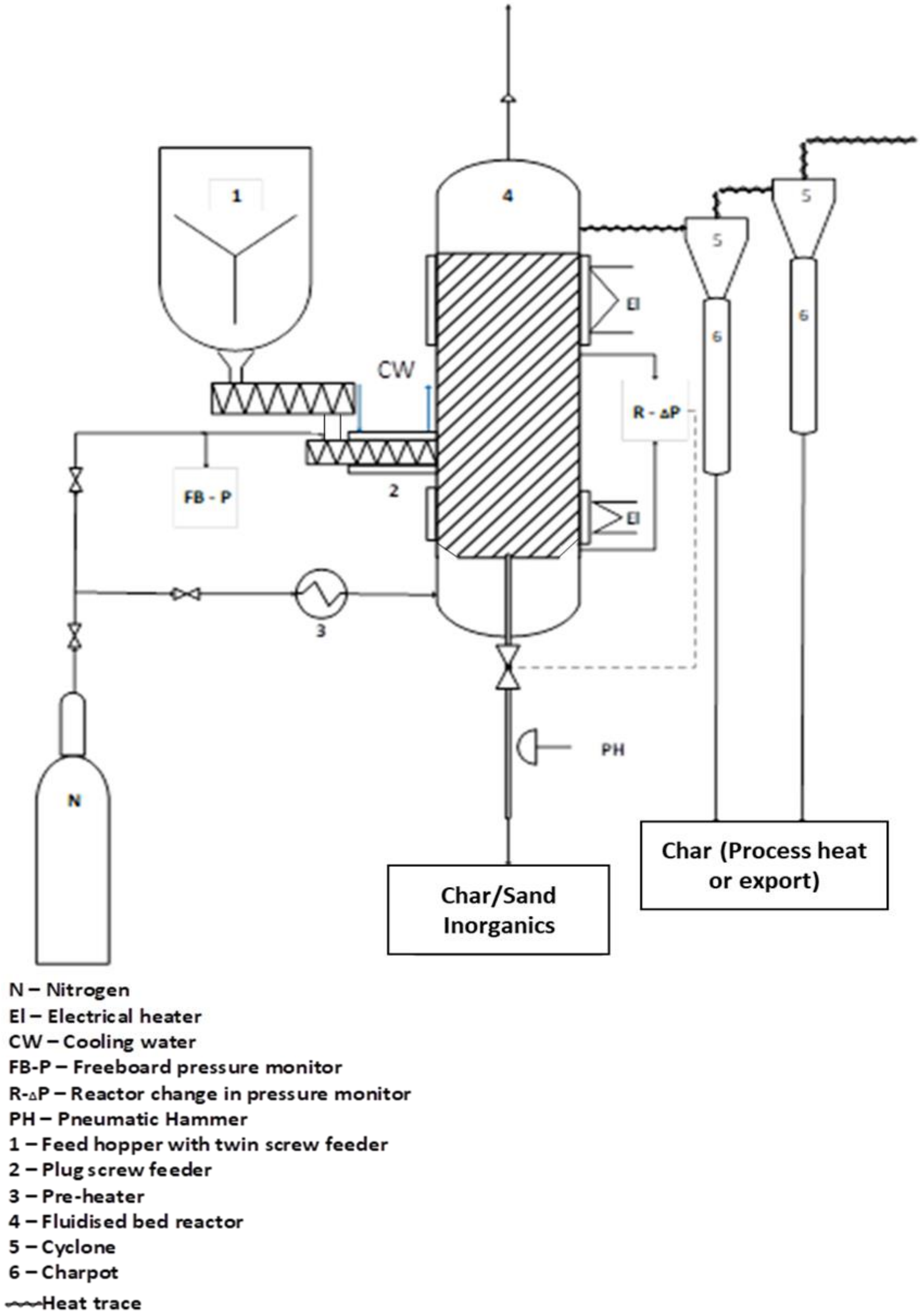

Figure 6.2: Schematic diagram of proposed modifications to the existing 300 g h $^{-1}$ bubbling fluidised bed reactor

Based on literature, communications with the mechanical engineering department at Aston University and material cost estimates, the cost associated with modifying the existing 300 g h^{-1} bubbling fluidised bed reactor is also dependant on material type and the contractor assigned to do the medications. However, the breakdown for the estimated cost (parts and labour) can be seen in Table 6.4.

Table 6.4: Existing reactor modification cost breakdown

Existing reactor modification	**Cost**
Parts	£400 - £750
Labour	£100 - £250
Total Cost	**£500 - £1000**

6.3 Proposed alternative reactor for trommel fines fast pyrolysis

Apart from using a bubbling fluidised bed reactor, it will be interesting to observe the fast pyrolysis of dry and wet physically pre-treated trommel fines using a different fast pyrolysis reactor. Amongst the most common fast pyrolysis reactors (rotating cone, ablative, conical spouted bed and circulating fluidised bed) previously mentioned in section 2.5 of thesis, that have been developed to optimize the yields of liquid products, an ablative reactor is substantially different in concept when compared to the other types of fast pyrolysis reactors (rotating cone, conical spouted bed and circulating fluidised bed). In all the other types of fast pyrolysis reactors including bubbling fluidised bed reactors (reactor used in this study), the rate of reaction is limited by the rate of heat transfer through the feedstock particles, hence small particles are required to avoid the retention of aerosols inside the particles and to achieve high heat transfer rates (Bridgwater et al. 2000; Scott et al. 1999; Bridgwater 2003; Mohan et al. 2006; Shen et al., 2009; Bridgwater, 2011; Westerhof et al., 2012).

However, in ablative fast pyrolysis reactor (Figure 6.3) the heat is transferred from the hot reactor wall to “melt” the feedstock that is in contact with it under pressure leaving an oily film that then evaporates to a product very similar to that derived from fluidised bed systems. The rate of reaction is proportional to the force exerted on the feedstock in contact with the reactor wall and the available heat transfer surface. (Bridgewater, 2011, 2012; Garcia-Nunez et al., 2017). Large particle size range feedstocks can be used for this type of reactor thus making it suitable for pyrolysing pre-treated trommel fines feedstock. In this study, the proximate analysis of the dry physically pre-treated trommel fines feedstock (PT; refer to chapter 4) showed that the volatile content increased while the ash content decreased with increasing dry physically pre-treated feedstock (PT) particle size.

Figure 6.3: Ablative fast pyrolysis reactor (Source: Bridgwater, 2011)

An ablative fast pyrolysis reactor is compact, it can be used to process large amount of the pre-treated trommel fines feedstock and do not require carrier gases or recirculation (Graham, 1984, 1994; Bridgewater, 2011, 2012; Garcia-Nunez et al., 2017), so the processing equipment is smaller, and the reaction system is thus more intensive. The absence of fluidising gas increases the partial pressure of the condensable vapours leading to more efficient collection and smaller equipment. (Graham, 1984, 1994; Bridgewater, 2011; Garcia-Nunez et al., 2017). One important aspect of ablative heat transfer is that when the feedstock contacts the hot reactor wall, ablation occurs and subsequently exposes new fresh feedstock to the hot surface. In theory, this allows for no limitations on particle size. The main advantages of ablative reactors are (Meier et al., 2007; Bridgewater, 2011; Garcia-Nunez et al., 2017):

- no need for feedstock milling and sieving efforts,
- compact design because of ideal heat transfer with high heating rates at relatively small contact surfaces
- energy and cost efficiency because no heating and cooling of the fluidised bed is required,
- the ability to use condensation units with small volume, requiring less space and lower cost (Meier et al., 2007)

However, the main disadvantages of ablatives fast pyrolysis reactors are that they require a heated surface area control system and operate with moving parts at high temperatures, which increases their complexity and induces inevitable wear and tear on the moving components. The presence of stones, aggregates and glass in the trommel fines feedstock can significantly enhance the mechanical hardware problems, such as abrasive wear and tear of the ablative fast pyrolysis reactor interiors. However, by coating the ablative reactor interiors with chemical, abrasion and corrosion resistant industrial protective coatings (e.g. Xylan, Epoxy PPS/Ryton, PVDF/Dykor ECTFE/Halar or ETFE/Tefzel) the rate of wear and tear of the reactor interiors can be reduced but such approach will increase the reactor cost (Bridgwater et al., 1999; Bridgewater, 2011; Garcia-Nunez et al., 2017).

Literature studies have shown that the ablative fast pyrolysis reactors can be built up to a capacity of 2 ton h^{-1} (minimum processing capacity for PT trommel fines, refer to chapter 7) for a single unit (Venderbosch et al., 2010; Bridgewater, 2012). The biomass-to-oil (BTO) process which was developed by PYTEC (Hamburg, Germany) is based on the ablative pyrolysis principle where wood with dimensions of 60 mm × 40 mm × 5 mm is put into direct contact with a rotating hot metal surface that melts the wood and produces oil that is combusted in a CHP unit running on a 300 MW_e diesel engine (Faix et al., 2010; Garcia-Nunez et al., 2017)

6.4 Summary

The true operational limits of the downstream equipment are yet to be determined because of the limitations imposed by poor feeding and reactor operation. At the end of this phase of the research, it was concluded that there is room for improvement to the commissioned fluidised bed system. Alternative feeding system and reactor unit modifications or an alternative reactor are necessary to optimise the process and have been reported in this chapter.

7 Economic evaluation of trommel fines fast pyrolysis

This chapter reports the method and results of the economic evaluation studies undertaken on the trommel fines fast pyrolysis process.

7.1 Introduction

In the UK, the application of pyrolysis and gasification technologies for MSW treatment is in relatively early stages of commercial operation in the UK, compared to the more established plants that have been built and are in operation in North America, Europe and Japan (Defra, 2007; 2013). The main driving factor behind the development of these technologies in the UK are increasing landfill costs (as a result of the Landfill Tax) and the implementation of the Landfill Directive as previously discussed in Chapter 1. Table 7.1 provides examples of pyrolysis and gasification plants in the UK, for treating MSW and other types of waste. Evidence points to the fact that these technologies are more often used at a scale of over 30,000 tonnes per annum, hence, the aim of this study is to contribute to the understanding of the economic implications of implementing small-scale thermal treatment plant in small communities to process trommel fines, which originate from MSW facilities.

Table 7.1: Example pyrolysis and gasification plants for power generation in the UK (Source; Defra 2013)

Manufacturer	Primary Technology	Location	In use	Capacity (tpa)	Feed stock	Power Generation
Energos	Grate Gasification	Isle of Wight	Since 2009	30,000	RDF	1.8MWe
First Power / 1st London Power	Rotary Kiln Pyrolysis	Huntingdon, Cambridgeshire	Since 2010	30,000	Mixed waste wood	3MWe
Planet Advantage	Grate Gasification	Dumfries	Since 2009	60,000	MSW / RDF	6.2MWe

This chapter evaluates the integration of the trommel fines fast pyrolysis process and energy production systems with consideration of technical and economic aspects. The originality of this study is presenting a performance model for the PT trommel fines fast pyrolysis process which is developed based on the results from previous experimental work and the model is constructed on an Excel spreadsheet and each section is represented by a table (Patel, 2011). The model initially presents the base case scenario which includes the calculated PT trommel fines fast pyrolysis process conversion efficiency (refer to section 3.10), its potential energy production and the revenue it can generate through the sale of electricity and heat for different system scales compared to the cost of landfilling the waste. Afterwards, the revenue from energy sale for different scales are then utilised in an economic evaluation for calculating the total repayment period, which is the number of years required to repay the investment.

A sensitivity analysis is performed to examine the impact of feedstock ash reduction on the revenue from energy sale and total repayment period. The present work represents the first time that the trommel fines fast pyrolysis process hypothetically linked for a CHP facility has been evaluated for economic performance. The work identifies the major opportunities for performance improvements and highlights the effects of system scale and the economics of feedstock choice. This chapter presents the performance model formulation, the limits of the model scope and details of assumptions made related to the technical aspects of the modelled system. The results of the economic evaluation of the pre-treated trommel fines fast pyrolysis process and energy production system analysis are presented and discussed in this chapter.

7.2 Methodology

7.2.1 Overall structure

This economic evaluation model uses the calculated process conversion efficiencies from processing pre-treated trommel fines feedstock to produce electricity and heat. It is assumed that the pre-treated trommel fines feedstock is processed in a fast pyrolysis reactor to produce pyrolysis liquid, gas and char product. The liquid and gas fractions are then combusted in a CHP engine for energy production. The starting point of the model is the entry of the prepared trommel fines feedstock into the fast pyrolysis reactor feeding system. The end points of the model are: (1) the output of the electricity and heat from the engine CHP system and (2) the output of char to the collecting char vessel. The downstream use of the char and energy products are not included in the scope of the model developed. Figure 7.1 reflects the calculations used in the economic evaluation model.

The model is constructed on an Excel spreadsheet. Firstly, the process conversion efficiencies of the pre-treated trommel fines samples are calculated from the results of product analysis from real experiments (refer to section 3.11). Secondly, these process conversion efficiencies are incorporated in the energy production table which includes total calorific value, total capacities, CHP efficiency factor, total available energy, units produced, selling price per unit of heat and electricity and revenue per year. These values include electricity and heat calculations, but the resulting values are used, in a separate section to calculate annual energy revenue, gate fee revenue and total energy revenue. These values are then fed into the capital cost calculation tab and are crucial in determining economic feasibility. In more detail, this output of this tab reflects the total available energy which is result of the multiplication between the efficiency factors and the available energy. Revenue from energy sale is the result of the selling price multiplied by units produced. Thirdly, the revenue from energy sale is fed into the capital cost calculations tab. This tab establishes a link between the process conversion efficiencies and total repayment period.

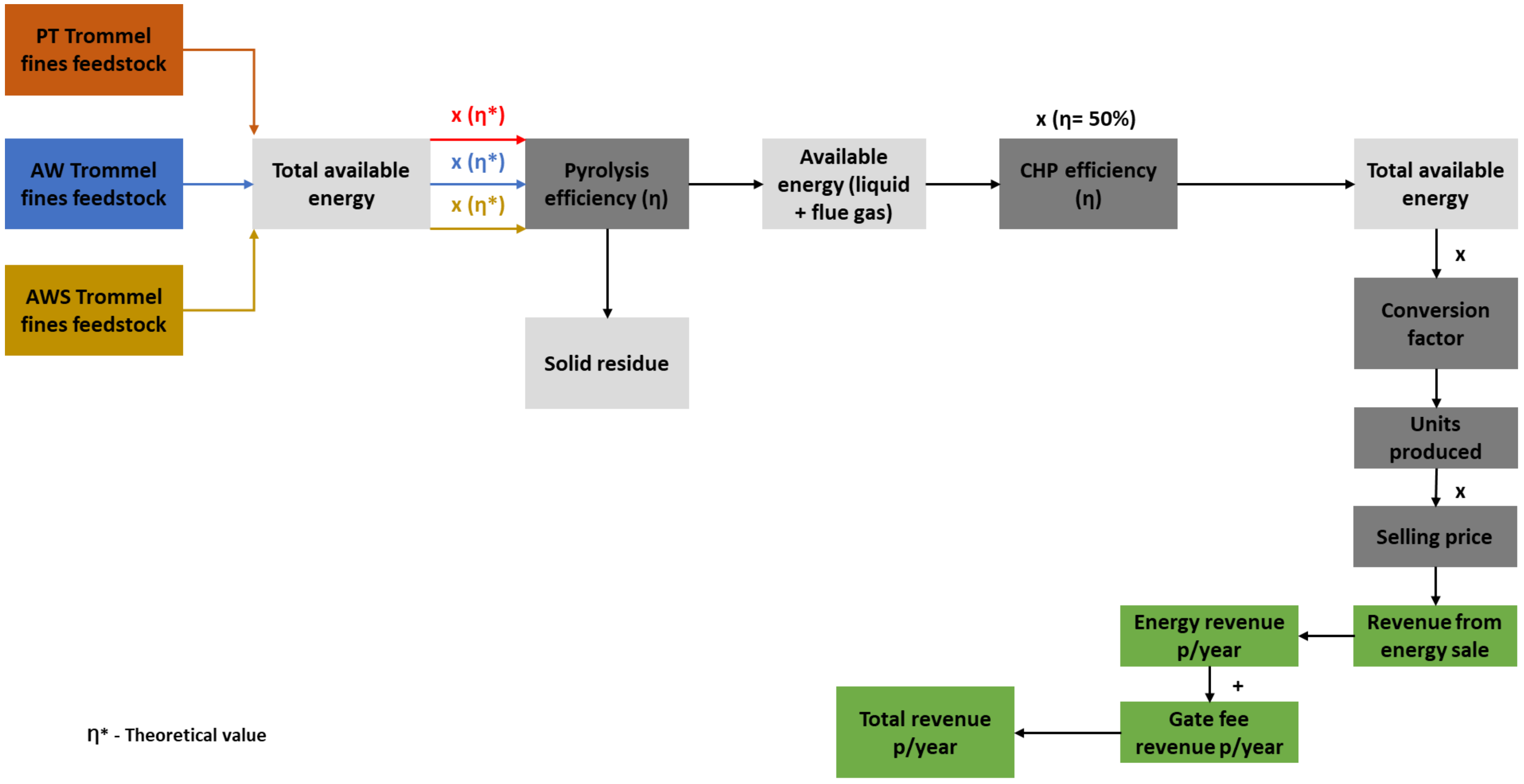

Figure 7.1: Structure of economic evaluation model indicating the tabs created and used in Microsoft Excel

7.2.2 General assumptions

The base year for this study is 2014 as this was the year this research commenced. All data have been updated using an inflation rate of 3% to present costs in British Pound Sterling (Bridgwater et al., 2002). The assumed annual plant operating time is 8000 h (Sinnott, 2005) and the total project life is taken to be 20 years. In this model, a theoretical situation was evaluated in which the PT trommel fines fast pyrolysis process is incorporated in an existing MRF-type operation where EfW is being added as an enhancement to the current capability. Thus, implying an assumption of zero feedstock transportation cost to the energy production facility since waste collection and delivery would be provided by the customer.

The PT trommel fines fast pyrolysis systems are evaluated at four different capacities: 200, 600, 1000 and 2000 kg h^{-1}. The fast pyrolysis system would require fabrication by contractors and when considering scale-up, account must be taken of the upper limit of reactor capacity for a single unit. For the reactor used in this study, this limit exists because the current design of the reactor is externally heated at the reactor skin and the heat demand for pyrolysis is proportional to the reactor volume. When the reactor exceeds a certain scale, the reactor may be unable to transfer sufficient internal heat for the pyrolysis reaction. Therefore, 2000 kg h^{-1} has been assumed for the upper limit of a single fast pyrolysis reactor. For fast pyrolysis system exceeding this capacity, multiple reactor units are used (Yang et al. 2017).

For the products from the PT trommel fines fast pyrolysis system, it is assumed that all the pyrolysis oil and gas produced in the pyrolysis system are used to generate electrical power and heat, which will be sold through the grid and heating networks. The costs of setting up a network through which the electricity and heat could be distributed have not been considered because it is assumed that the end customer would be in the same area where energy production is taking place. To clarify it is assumed in the economic evaluation model that the EfW facility would be integrated in the MRF and that the end customer, typically, a manufacturing process would consume the energy on a permanent basis (Catarina, 2014).

7.2.3 Energy production

The energy production reflects the energy that can be generated as electricity or heat from the PT trommel fines fast pyrolysis process. The energy production is used to calculate the revenue per year through a series of fixed factors. This translates the energy produced into an economic context providing a figure for revenue per year which will then be used to calculate the feasibility of the scenarios analysed. This revenue per year was calculated in three steps (Catarina, 2014):

$$\text{Available energy (E)} = \text{Total calorific value x Total tonnes [J]}$$ **(Eq. 7.1)**

$$\text{Net available energy} = (\text{E x efficiency}) \text{ x coversion factor [J]}$$ **(Eq. 7.2)**

$$\text{Revenue per year} = \text{Net available energy} \times \text{selling price per unit J [£ per year]}$$

(Eq. 7.3)

The conversion efficiency of the pyrolysis process was calculated using the equation described in section 3.10 while the efficiency of the CHP was assumed to be 50% (Carbontrust.com, 2018) of all energy produced for each calculation (electricity and heat). In this study, the electricity selling price (to the distribution grid) is taken as £0.055/kW h. The selling price for heat is taken to be 0.0349/kW h (DECC, 2015). The total revenue per year is the sum of the revenue resulting from the sale of electricity and heat and the revenue resulting from gate fee charges. The PT trommel fines landfill cost was assumed to be £86 per tonne while the gate fee cost was assumed to be £73 per tonne (Defra 2017).

7.2.4 Capital investment

The capital investment is calculated as a total plant cost (TPC), which includes both direct costs (installed equipment) and indirect costs (engineering, design, supervision, management, commissioning, contractor's fees, interest accrued during construction, contingency) plus interest rate (Bridgwater et al., 2002). Interest rates vary with the type of loan available and the risk involved in the project. The baseline equipment costs of the fast pyrolysis system components used in this work are derived either from the cost estimates for the equipment available at the Aston University demonstration plant (i.e. the 1 kg/h fast pyrolysis reactor) or from the cost estimates provided by commercial suppliers or manufacturers (Yang, 2014; Anonymous, 2015). Traditionally, EfW projects attract high risk, which is then reflected onto interest rates, because it is still considered an untested technology which is very sensitive to fluctuations in chemical and physical properties of feedstock. Furthermore, there is a lack of pilot facilities that could assist with technical performance data. Therefore, based on literature on work considering the similar economic studies and the risk on capital investment an interest rate of 20% has been used in this study (Tijmensen, 2002; Rogers, 2009; Dimitriou, 2013; IEA/NEA, 2015).

In this study, the TPC is chosen to be 1.69 times the direct plant cost (DPC) to include increments for engineering design and management overheads costs a contingency element, commissioning costs, contractor's fees and interest during construction. The direct plant cost (DPC) is the production of the equipment cost (EC) of the major components in the fast pyrolysis process, delivered to the plant gate and a number of multiplication factors to include increments for instrumentation, piping, erection and ducting, associated electrical equipment, structures and buildings, civil works and laggings. In this study the DPC is chosen to be 3.5 times the equipment cost (EC) (Bridgwater et al., 2002; Rogers et al., 2012).

Furthermore, the capital repayment produces a calculation of the Net Present Value (NPV) of the project. This is the sum of the present values of the annual net cash flows over the lifetime of the project (Eq. 7.4). This value is used to establish the relationship between the process conversion efficiency and number of years necessary to repay the capital investment. These values will be varied in the scenario analysis and the results of this are presented in section 8.3. The validity of this model can only be confirmed by comparison with actual cost data for installed plants, but there are few operational fast pyrolysis plants in the in the world which can be used as reference plants for model validation (Bridgwater et al., 2002, Catarina, 2014; Yang et al., 2017).

$$\mathrm{NPV} = \sum_{0}^{\mathrm{n}} \frac{\mathrm{NCF}}{(1+\mathrm{r})^{\mathrm{n}}} \qquad \textbf{(Eq. 7.4)}$$

Where: NPV – Net present value; NCF – Net cash flow; r – interest rate; n – number of years

7.2.5 Operating costs

The operating costs are split into maintenance costs, utility costs and labour costs. These are the ongoing costs incurred from plant operation and are represented as annual costs (Bridgwater et al., 2002, Catarina, 2014; Yang et al., 2017). These values will be varied in the scenario analysis and the results are presented in section 8.3.

7.2.5.1 Maintenance and overheads

The annual maintenance costs and overheads costs (including insurance, rent, taxes etc.) are calculated as a percentage of TPC per annum. This study uses 2.5% of TPC for plant maintenance and 2.0% of TPC for plant overheads costs in line with previous comparable work (Bridgwater et al., 2002, Catarina, 2014; Yang et al., 2017).

7.2.5.2 Utility cost

The utility cost includes electricity and cooling water usage for the fast pyrolysis and CHP system. In this work, the electricity consumed by the process is imported from the grid, to ensure stable operation of the plant. According to Bridgwater et al. (2002), electricity consumption for a fast pyrolysis and engine plant is estimated to be 36.8 kW h per tonne of wood feedstock. Adopting this data to the present work is reasonable because both processes involve similar arrangement and the fast pyrolysis reactors process provides heating to the same range of temperature. The average electricity price for non-domestic consumers was assumed to be £0.1001 per kW h (2014 rate) (DECC, 2015).

The water utility cost includes the cost of water usage (a fixed amount plus metre reading) and surcharges for sewerage and effluent treatment. In this study, the water consumption is estimated to be 17 m^3 per tonne of feedstock (Bridgwater et al., 2002) for the dry physically pre-treated trommel fines (PT) fast pyrolysis process, 27 m^3 for the wet physically pre-treated trommel fines (AW and AWS) fast pyrolysis process and, an approximate water cost of £2.80 m^{-3} is used here. This is an averaged value combining the costs of water utility and process waste water disposal (Anglian, 2014; Yang et al., 2017). A surfactant cost is added to the AWS trommel fines fast pyrolysis and in this study the surfactant consumption is estimated to be 0.1 m^3 per tonne of feedstock an approximate surfactant cost of £60 per tonne.

7.2.5.3 Labour cost

There is no established model for staffing levels on fast pyrolysis process. In this study, the staffing level was adopted from Yang et al., (2017) due to the similarities in system capacities. A day team and a shift team staffing requirements are considered. The day team includes the plant manager and technician, and the number of staff required depends on the load of management work and any maintenance and support contracts that are in place. The shift team members include the plant operators and their supervisor, and the number of staff required depends on the number of equipment items that need to be operated (Yang et al., 20017). The annual labour cost is assumed to be £46680 per employee based on the average wage for employees in the electricity industry (Rogers et al., 2012; Bovill, 2014; ONS, 2015). Table 7.2 below shows the estimated labour requirement for the process.

Table 7.2: Staffing level for trommel fines fast pyrolysis energy system (Adopted from Yang et al., 2017)

Capacity (kg h^{-1})	Day team		Shift team		Total (head)
	Manager	Technician	Supervisor	Operator	
200	1	0.5	1	2	10.5
600	1	1	1	3	14
1000	1	1.5	1	3	14.5
2000	1	2	1	4	15.5

7.3 Results and discussion

The results of these situations were discussed based on their technical and economic effects on capital cost repayment period and used to determine the minimum processing capacity of the system. This factor was used to measure the feasibility of the PT trommel fines fast pyrolysis system. The sensitivity analysis compares the dry and wet physically pre-treated trommel fines (PT, AW and AWS) fast pyrolysis process at optimum processing capacity and examine the impact of ash reduction on the revenue from energy sale, operating cost and total capital cost repayment period. A plant life of 20 years was selected as the point at which the facility was most likely to breakdown. Therefore, a scenario that would result in a repayment period longer than 20 years would be deemed unfeasible. The conclusions of this exercise would establish the risks involved in trommel fines fast pyrolysis process investments.

7.3.1 Energy revenue, capital and operating costs for physically pre-treated trommel fines (PT) fast pyrolysis energy system

Table 7.3 presents the integrated PT trommel fines fast pyrolysis process and energy production systems characteristics and the results of the calculated energy production potential and annual total revenue (combined electricity and heat output) at different waste processing capacities (200, 600, 1000, 2000 kg h^{-1}). The calculated costs of landfilling the PT trommel fines are also presented in Table 8.3, while the capital and operating cost associated with running the facility at different processing capacities are presented in Table 7.4. These data are utilised as the baseline information for the economic analysis.

Table 7.3: PT trommel fines energy production, total revenue and landfill costs at different capacities

	CAPACITY (kg h^{-1})			
Item	**200**	**600**	**1000**	**2000**
Total PT per year (Tonnes)	**1600**	**4800**	**8000**	**16000**
PT CV MJ kg^{-1}	13.80	13.80	13.80	13.80
PT FP process conversion efficiency (η)	43%	43%	43%	43%
CHP efficiency	50%	50%	50%	50%
Conversion factor (to joules)	278	278	278	278
Electricity selling price (£/unit)	0.055	0.055	0.055	0.055
Heat selling price (£/unit)	0.0349	0.0349	0.0349	0.0349
Gate fee (£/tonne)	£73	£73	£73	£73
Landfill disposal (£/tonne)	£86	£86	£86	£86
Available energy (MJ)	22080	66240	110400	220800
Total Available energy (MJ)	4747	14242	23736	47472
Units produced	1319722	3959165	6598608	13197216
Income from heat (£)	£46,058	£138,175	£230,291	£460,583
Income from electricity (£)	£72,585	£217,754	£362,923	£725,847
Energy revenue (£)	£118,643	£355,929	£593,215	£1,186,430
Gate fee revenue (£)	£116,800	£350,400	£584,000	£1,168,000
Total revenue (£)	**£235,443**	**£706,329**	**£1,177,215**	**£2,354,430**
PT Land fill cost per year (£)	**£137,600**	**£412,800**	**£688,000**	**£1,376,000**
PT – Physically pre-treated trommel fines; FP – Fast pyrolysis				

Table 7. 4: PT trommel fines capital and operating cost at different processing capacities

	CAPACITY (kg h^{-1})			
Item	**200**	**600**	**1000**	**2000**
Total plant cost (TPC)	**£266,175**	**£798,525**	**£1,330,875**	**£2,661,750**
Direct plant cost (DPC)	£157,500	£472,500	£787,500	£1,575,000
Operating cost (£/year)	**£584,171**	**£935,614**	**£1,147,018**	**£1,663,858**
Maintenance (£/year)	£6,654	£19,963	£33,272	£66,544
Overheads (£/year)	£5,324	£15,971	£26,618	£53,235
Utility (£/year)	£82,054	£246,162	£410,269	£820,539
Labour cost (£/year)	£490,139	£653,519	£676,859	£723,540

Figure 7.2 below shows that the total energy revenue potential (combine electricity and heat output) per year is greater than the cost of landfilling PT trommel fines per year at all the different waste processing capacities evaluated (200, 600, 1000, 2000 kg h^{-1}). This is an indication that thermal recovery of energy from heterogeneous and complex waste materials

such as trommel fines can potentially reduce the amount of landfill tax an operator pays per year.

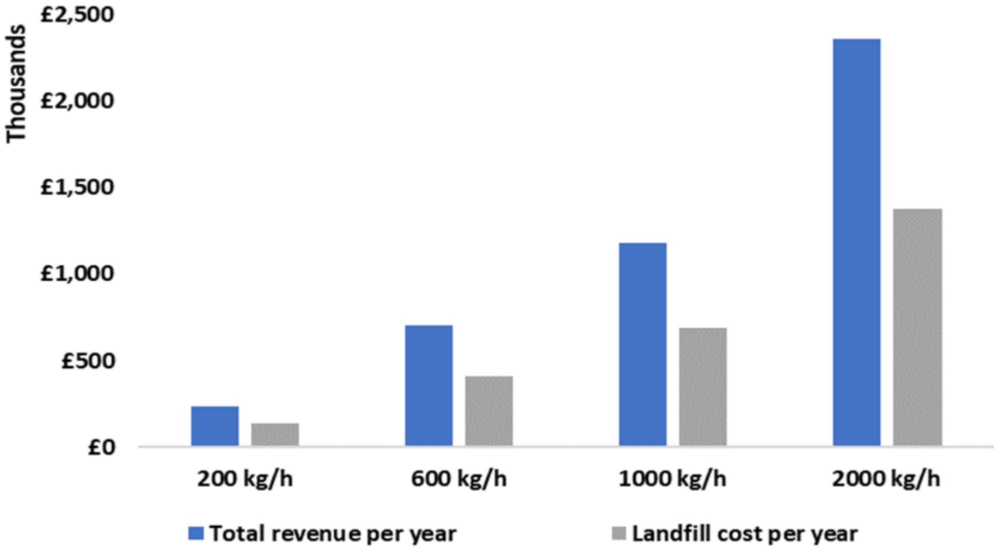

Figure 7.2: Comparison of total revenue from fast pyrolysis per year and land fill cost per year for PT trommel fines at different capacities

However, the operating cost per year associated with running the facility at the different capacities evaluated is greater than the total energy revenue per year at 200 and 600 kg h^{-1} processing capacity as can be seen in Figure 7.3. The total revenue per year only becomes greater than the operating cost per year for processes greater than 1000 kg h^{-1}. The high operating cost associated with the PT trommel fine fast pyrolysis system can be attributed to the high utility and labour cost which make up most of the operating cost (Figure 7.4). For the 200 and 600 kg h^{-1} PT trommel fine fast pyrolysis systems, high labour cost (Table 7.3) is to be expected as there is likely to be a minimum labour requirement to operate the systems that may result in poor productivity in small systems. However, in small scale systems it is very probable that the total labour required could be reduced by sharing labour between the steps and between adjacent facilities (Bridgwater et al., 2002; Catarina, 2014; Yang et al., 2017).

There is also likely to be savings as system capacity increases. Nevertheless, for this study, the current labour requirements are left at their original values because labour costs are likely to be higher in early demonstration plants while the labour costs in established plant are likely to be lower (Bridgwater et al., 2002; Catarina, 2014; Yang et al., 2017). For 200 kg h^{-1} and 600 kg h^{-1} PT trommel fine fast pyrolysis systems, the utility and labour cost combined alone are greater than the total revenue per year generated. This is an early indication that the PT trommel fine fast pyrolysis plants might not be feasible at systems less than 1000 kg h^{-1}.

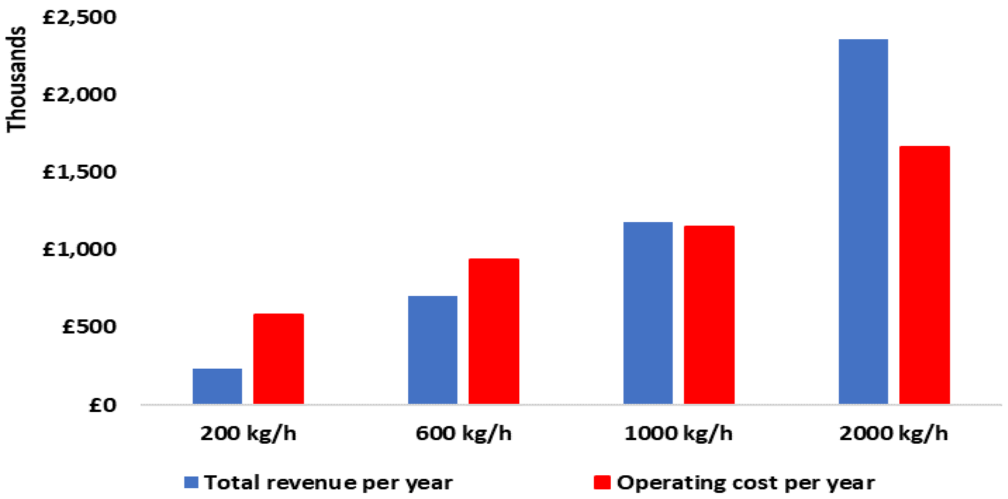

Figure 7.3: Comparison of total revenue per year to operating cost per year for PT trommel fines fast pyrolysis energy production system at different capacities

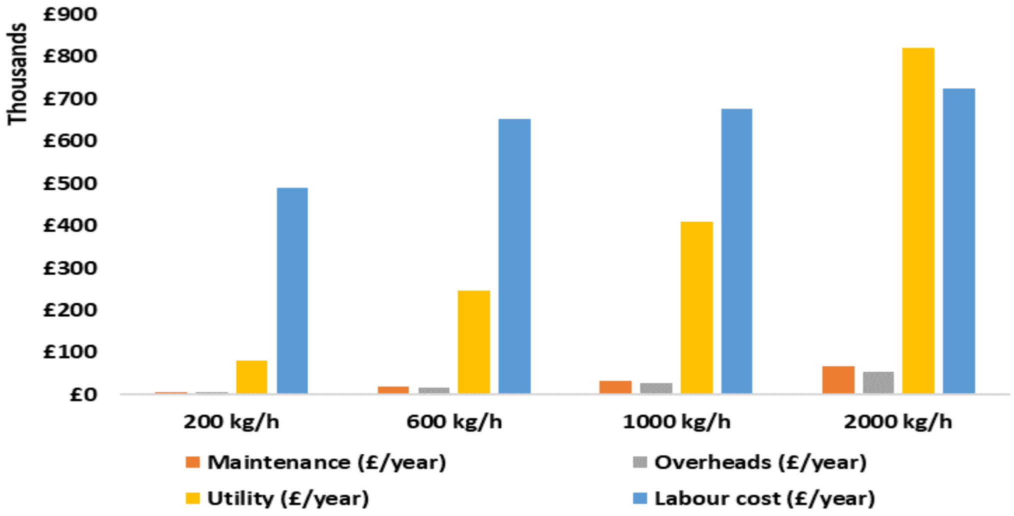

Figure 7.4: Breakdown of operating cost for PT trommel fines fast pyrolysis energy production system at different capacities

7.3.1.1 Economic evaluation for physically pre-treated trommel fines (PT) fast pyrolysis process

The capital investment cost, operating costs and total revenue per year for the PT trommel fines fast pyrolysis plant at different waste processing capacities (refer to section 7.3.1) were used to calculate the net present value (NPV) at 20% capital investment interest rate, which is the sum of the present values of the annual net cash flows over the 20 years lifetime of the project. This is the result of the total revenue per year excluding the total repayment per year. If the resulting NPV is zero, the project is equivalent to putting the capital investment in a bank paying an annual interest rate of 20% and if the NPV is positive, the project is better than the bank option. However, if the NPV is negative, the project is worse than the bank option and is not feasible. The NPV were then applied to the repayment period calculation which reveals that the PT trommel fine fast pyrolysis systems only become economically feasible from 2000 kg h^{-1} as shown in Figure 7.5 below with a total capital investment payback period of 8.6 years at 20% interest rate. The non-feasibility of the PT trommel fine fast pyrolysis systems scale below 2000 kg h^{-1} can be attributed to the high operating cost associated with running the facility previously discussed in section 7.3.1, which is higher or similar to the total revenue per year generated (Figure 7.3).

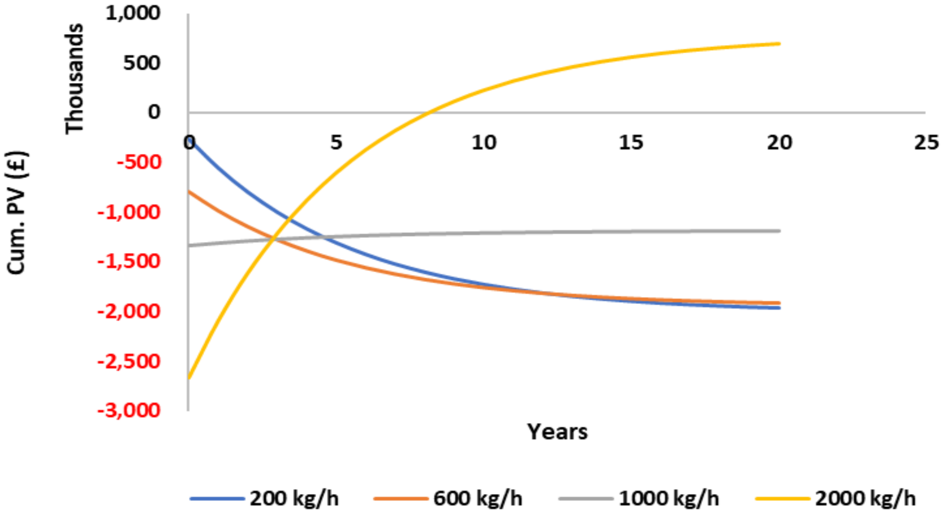

Figure 7.5: Comparison of cumulative present value (Cum. PV) for PT trommel fine fast pyrolysis energy system at different capacities

Cum. PV – Cumulative present value

7.3.2 Effect of feedstock pre-treatment method on energy revenue and operating costs

Table 7.5 below reports the integrated dry and wet physically pre-treated trommel fines (PT, AW and AWS) fast pyrolysis process and energy production system characteristics and the results of the calculated potential energy production and total revenue per year (combined electricity and heat output) at 2000 kg h^{-1} processing capacity. The calculated cost of landfilling the dry and wet physically pre-treated trommel fines (PT, AW and AWS) are also presented in Table 7.5, while the operating cost associated with running the facility for each pre-treatment process are presented in Table 7.6. These data along with the 2000 kg h^{-1} capital investment data previously presented in Table 7.4 are utilised as the baseline information for the economic analysis.

Table 7.5: Dry and wet physically pre-treated trommel fines energy production, total revenue and landfill costs

SAMPLE	**PT**	**AW**	**AWS**
Capacity (kg h^{-1})	**2000**	**2000**	**2000**
Total PT per year (Tonnes)	**16000**	**16000**	**16000**
Feedstock CV MJkg^{-1}	13.80	15.70	16.10
FP process conversion efficiency (η)	43%	74%	70%
CHP efficiency	50%	50%	50%
Conversion factor (to joules)	278	278	278
Electricity selling price (£/unit)	0.055	0.055	0.055
Heat selling price (£/unit)	0.0349	0.0349	0.0349
Gate fee (£/tonne)	£73	£73	£73
Landfill disposal (£/tonne)	£86	£86	£86
Available energy (MJ)	220800	251200	257600
Total Available energy (MJ)	47472	92944	90160
Units produced	13197216	25838432	25064480
Income from heat (£)	£460,583	£901,761	£874,750
Income from electricity (£)	£725,847	£1,421,114	£1,378,546
Energy revenue (£)	£1,186,430	£2,322,875	£2,253,297
Gate fee revenue (£)	£1,168,000	£1,168,000	£1,168,000
Total revenue (£)	**£2,354,430**	**£3,490,875**	**£3,421,297**
PT Land fill cost per year (£)	**£1,376,000**	**£1,376,000**	**£1,376,000**
PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)			

Table 7.6: Dry and wet physically pre-treated trommel fines 2000 kg h^{-1} fast pyrolysis energy system operating costs

SAMPLE	PT	AW	AWS
Operating cost (£/year)	**£1,663,858**	**£2,111,858**	**£2,207,858**
Maintenance (£/year)	£66,544	£66,544	£66,544
Overheads (£/year)	£53,235	£53,235	£53,235
Utility (£/year)	**£820,539**	**£1,268,539**	**£1,364,539**
Electricity consumption (£/year)	*£58,939*	*£58,939*	*£58,939*
Water usage (£/year)	*£761,600*	*£1,209,600*	*£1,209,600*
Surfactant (£/year)			*£96,000*
Labour cost (£/year)	£723,540	£723,540	£723,540

Figure 7.6 below shows that the total energy revenue potential (combine electricity and heat output) per year for all the pre-treated trommel fines samples is greater than the cost of landfilling trommel fines per year at 2000 kg h^{-1} processing capacity. As can be seen from Figure 8.5 the potential total energy revenue per year increased with the wet physically pre-treated trommel fines samples (AW and AWS). The increase in total energy revenue per year with the wet physically pre-treated trommel fines samples (AW and AWS) can be attributed to the increased fast pyrolysis process conversion efficiency (Table 7.5) obtained (refer to section 5.3). The highest process conversion efficiency was obtained with the AW trommel fines sample (74%), followed by the AWS sample obtained by washing the PT with 1% Decon Neutracon at 70% (Table 7.5). Hence the highest total revenue per year was obtained with the AW trommel fines sample (Figure 7.6).

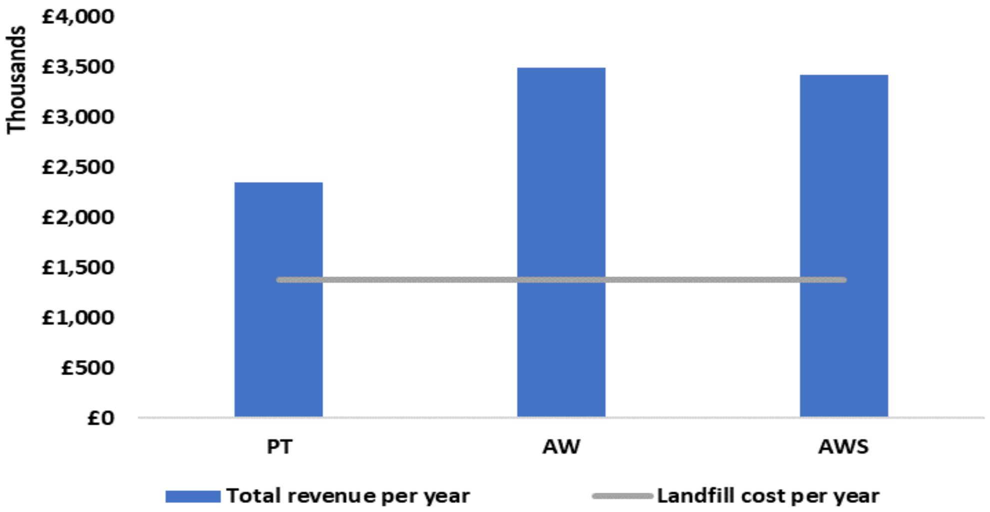

Figure 7.6: Comparison between of total revenue per year 2000 kg h^{-1} fast pyrolysis system (dry and wet pre-treated trommel fines) and annual landfill costs

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)

The operating cost per year associated with running the 2000 kg h^{-1} fast pyrolysis system facility for dry and wet physically pre-treated trommel fines was found to be lower than the total energy revenue per year for both dry and wet physically pre-treated trommel fines sample (PT, AW, AWS) as can be seen in Figure 7.7. However, the operating cost increases with the wet physically pre-treated trommel fines sample with AWS trommel fines sample having the highest operating cost (Table 7.6). The increasing operating cost associated with the wet physically pre-treated trommel fine (AW and AWS) fast pyrolysis energy systems relates to the increasing utility cost which increased with the wet physically pre-treated trommel fine fast pyrolysis energy systems (AW and AWS) as seen in Figure 7.8 because of additional water consumption cost required for the wet physically pre-treated trommel fine (AW and AWS) fast pyrolysis energy systems (Table 7.6). The addition of the surfactant consumption cost resulted in the AWS trommel fine fast pyrolysis energy system having the highest operating cost. The increased utility cost associated with running the wet physically pre-treated trommel fines (AW and AWS) fast pyrolysis systems is to be expected, however the utility cost could be reduced. In this study, the economic evaluation model assumed that the pre-treated trommel fines feedstock is processed in a fast pyrolysis reactor to produce pyrolysis liquid, gas and char product and the liquid and gas fraction are then combusted in a CHP engine (typically diesel engines) for energy production. Combusting the pyrolysis vapours directly to produce energy in a gas engine CHP as supposed to condensing the pyrolysis vapours to produced liquids prior to combustion to generate energy would reduce the amount of water consumed during the process thus reducing the utility cost associated with the process.

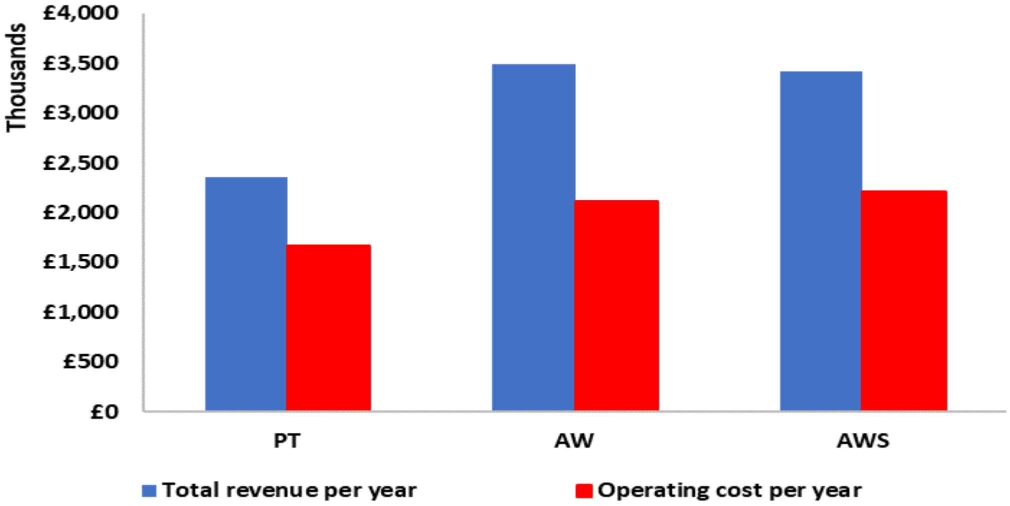

Figure 7.7: Comparison of total revenue per year to operating cost per year for dry and wet physically pre-treated trommel fines 2000 kg h^{-1} fast pyrolysis energy system

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)

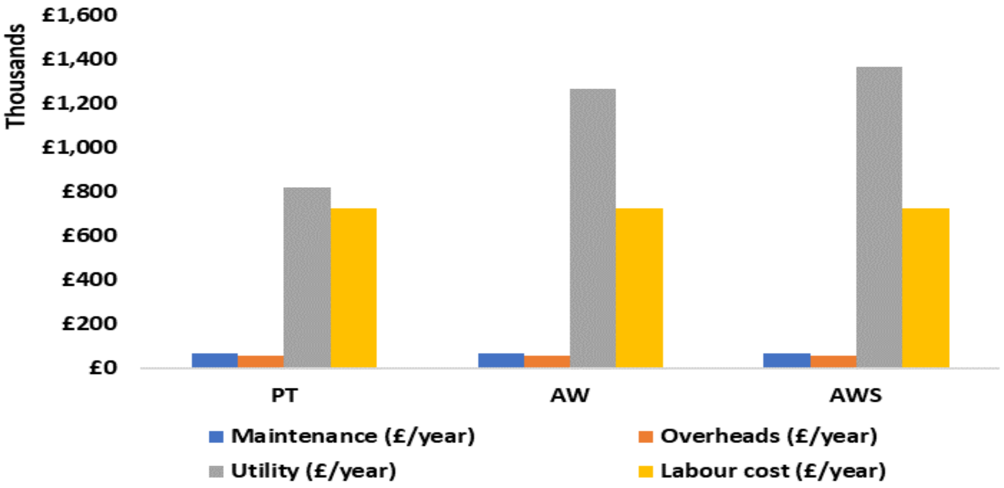

Figure 7.8: Breakdown of operating cost for dry and wet physically pre-treated trommel fines 2000 kg h^{-1} fast pyrolysis system

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)

7.3.2.1 Effect of pre-treatment method on economic evaluation for pre-treated trommel fines fast pyrolysis process

As previously described in section 7.3.1.1, the net present values (NPV) at 20% capital investment interest rate were calculated for the dry and wet physically pre-treated trommel fines (PT, AW and AWS) fast pyrolysis systems using the capital investment cost, total revenue per year and operating costs for the dry and wet physically pre-treated trommel fines (PT, AW and AWS) fast pyrolysis systems at 2000 kg h^{-1} processing capacity over the 20 years lifetime of the project. It has already been established in section 7.3.1.1 that the dry physically pre-treated trommel fines (PT) fast pyrolysis system is feasible at 2000 kg h^{-1} processing capacity, however, the effect of ash reduction on pre-treated trommel fines fast pyrolysis process can be seen in Figure 7.9 below which shows that the NPV increased with the wet physically pre-treated trommel fines samples (AW and AWS) with AW trommel fines sample having the highest NPV over the 20 year life time of the project (Figure 7.9).

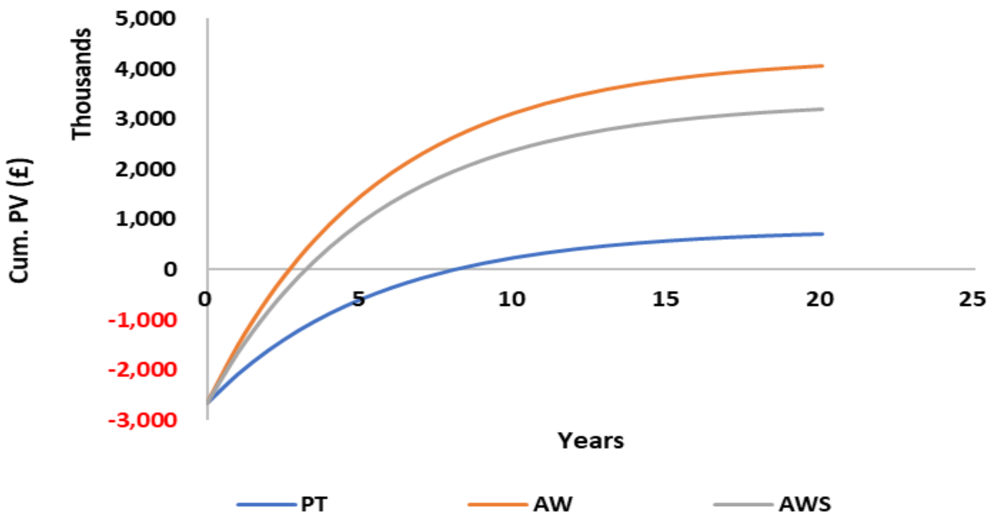

Figure 7.9: Comparison of cumulative present value (Cum. PV) for dry and wet physically pre-treated trommel fines 2000 kg h^{-1} fast pyrolysis system

Cum. PV – Cumulative present value; PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon).

The increase in NPV with the wet physically pre-treated trommel fines samples (AW and AWS) resulted in a reduced capital investment repayment period with AW having the earliest repayment period of 2.7 years (Figure 7.10). The reduced repayment period observed with the AW and AWS feedstock can be attributed to the increase in fast pyrolysis process conversion efficiencies (74% and 70% respectively) and increased calorific values of the feedstock (Table 7.4) which resulted to an increased total energy revenue per year (Table 7.4). This preliminary work suggests that the wet pre-treatment process is an effective process to help make the trommel fine feedstock suitable for fast pyrolysis and further improve the feasibility of the trommel fines fast pyrolysis process, thus making thermal recovery of energy possible from heterogeneous and complex waste materials such as trommel fines. However, this preliminary work also suggests that the addition of a surfactant (Decon Neutracon) to the washing process may not be necessary as the total capital repayment period slightly increased with the AWS trommel fines sample (3.4 years) when compared to the total capital repayment period of 2.7 years observed for the AW trommel fines sample (Figure 7.10). The addition of a surfactant to the washing process increases the operating cost associated with the AWS trommel fines fast pyrolysis process but does not affect the fast pyrolysis process conversion efficiency (Table 7.4).

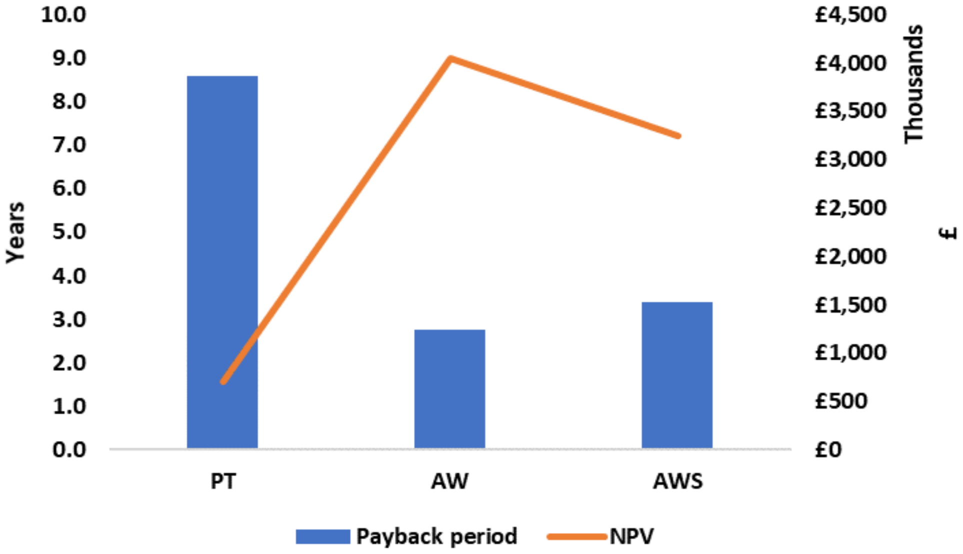

Figure 7.10: Comparison of calculated capital investment repayment period for dry and wet physically pre-treated trommel fines 2000 kg h^{-1} fast pyrolysis system

PT - Physical pre-treated Trommel Fines; AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)

7.3.3 Economic evaluation of AW and AWS trommel fines samples at lower processing capacities

In this study the AW and AWS trommel fines samples where only evaluated at PT trommel fines' minimum processing capacity (2000 Kg h^{-1}) for comparison purposes. However, due to the low capital investment payback period (< 4 years) associated with the processing of AW and AWS, it was decided to evaluate the economic performance of the AW and AWS trommel fines samples at lower processing capacities (< 2000 Kg h^{-1}). Perhaps, they could be and may present both technical and economic advantages at lower processing capacities.

The operating cost per year associated with running the AW and AWS facility at the low processing capacities (< 2000 kg h^{-1}) evaluated is greater than the total energy revenue per year at 200 and 600 kg h^{-1} processing capacities as can be seen in Figure 7.11. The total revenue per year only becomes greater than the operating cost per year for processes greater than 1000 kg h^{-1}. The high operating cost associated with the AW and AWS trommel fine fast pyrolysis system can be attributed to the high utility and labour cost which make up most of the operating cost as previously explained in section 7.3.1. This is an indication that the AW and AWS trommel fine fast pyrolysis plants is not be feasible at systems lower than 1000 kg

h^{-1}. On the basis of these results, only the 1000 capacity was further considered to determine the minimum processing capacity using NPV and payback period.

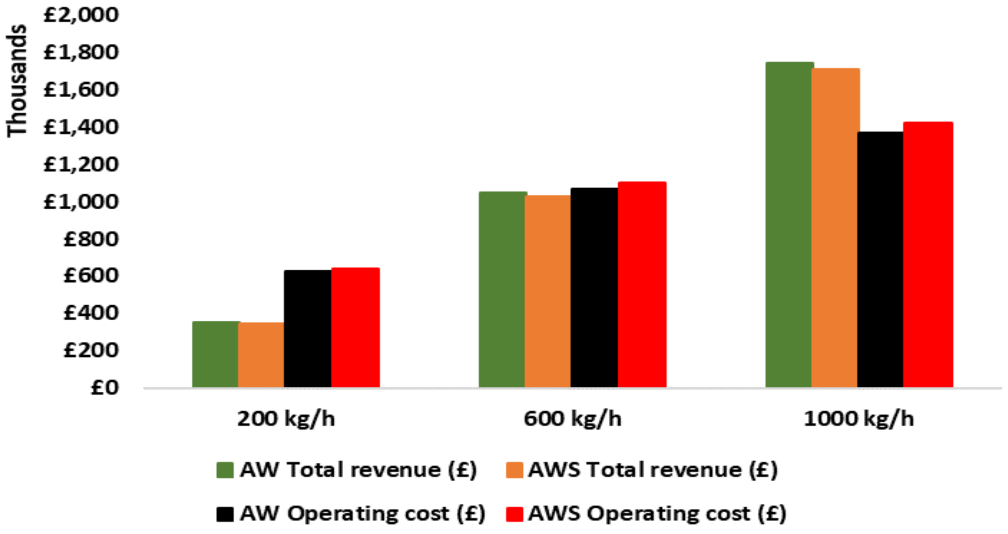

Figure 7.11: Comparison of total revenue per year to operating cost per year for AW and AWS trommel fines fast pyrolysis energy production systems at lower processing capacities.

AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon).

As previously describe in section 7.3.1.1, the net present values (NPV) at 20% capital investment interest rate were calculated for AW and AWS trommel fines fast pyrolysis systems at 1000 kg h^{-1} processing capacity over the 20 years lifetime of the project. The effect of wet physical pre-treatment method on trommel fines fast pyrolysis process can be seen in Figure 7.12 below which shows that the NPV decreased with the AWS trommel fines samples with AW trommel fines sample having the highest NPV over the 20 year life time of the project at 1000 kg h^{-1} processing capacity. (Figure 7.12).

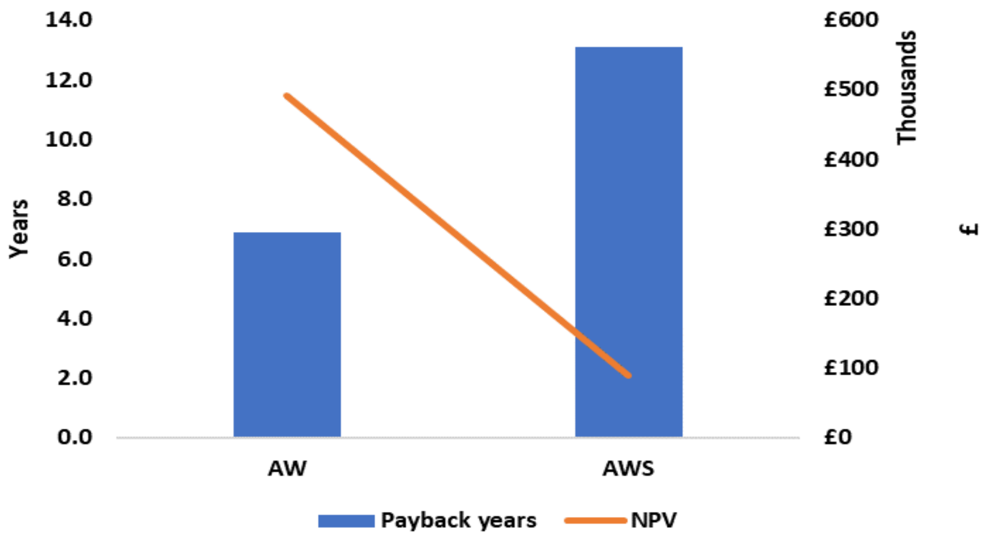

Figure 7.12: Comparison of calculated capital investment repayment period for AW and AWS trommel fines 1000 kg h^{-1} fast pyrolysis system

AW – Agitated Washing; AWS – Agitated Washing with Surfactant (Decon Neutracon)

The decrease in NPV with the AWS trommel fines samples resulted in a higher capital investment repayment period (13.1 years) with AW having an earlier repayment period of 6.9 years (Figure 7.12).This preliminary work suggests that the wet pre-treatment process (AW and AWS) is an effective process to help make the trommel fines feedstock suitable for fast pyrolysis and further improve the feasibility of the trommel fines fast pyrolysis process, at a lower processing capacity of 1000 kg h^{-1} when compared to the minimum processing capacity of 2000 kg h^{-1} for the dry pre-treatment process (PT, refer to section 7.3.1.1). However, this preliminary work also suggests that the addition of a surfactant (Decon Neutracon) to the washing process may not be necessary as the total capital repayment period increased with the AWS trommel fines sample (13.1 years) when compared to the total capital repayment period of 6.9 years observed for the AW trommel fines sample at 1000 kg h^{-1} processing capacity (Figure 7.12). These analyses suggest that the minimum process capacity of a fast pyrolysis systems for energy production from trommel fines may be above 600 kg h^{-1} but certainly below 1000 kg h^{-1}.

7.4 Summary

This study presents the first economic evaluation for an integrated trommel fines fast pyrolysis and energy production system. The evaluation is carried out at system capacities of up to 2000 kg h^{-1} of dry physically pre-treated trommel fines sample (PT) throughput based on calculated

PT trommel fines fast pyrolysis process conversion efficiency (refer to section 3.10) at optimum processing conditions. The results of the economic evaluation show that for the PT trommel fines fast pyrolysis system potential total energy revenue (combine electricity and heat output) per year is greater than the cost of landfilling PT trommel fines per year at all the system capacities evaluated (up to 2000 kg h^{-1}). However, the capital and operating costs are greater than the total energy revenue per year at system capacity of less than 1000 kg h^{-1}, resulting in the PT trommel fine fast pyrolysis systems only becoming economically feasible from 2000 kg h^{-1} system capacity with a capital investment payback period of 8.6 years at 20% interest rate.

The sensitivity analysis on the economic evaluation to study the effect of feedstock pre-treatment method on the revenue from energy sales and total repayment period showed that the annual total energy revenue potential and operating cost increased with the wet physically pre-treated trommel fines samples (AW and AWS) and the total capital investment payback period decreased with the wet pre-treated trommel fines samples with AW trommel fines sample having the lowest payback period of 2.7 years. The economic evaluation to determine the minimum processing capacity for the AW and AWS trommel fines samples showed that both AW and AWS trommel fines samples were both economically feasible from 1000 kg h^{-1} processing capacities with payback periods of 6.9 and 13.1 years respectively.

In this study, the solid residues from the trommel fines fast pyrolysis process were not included within the scope of this model. Compared to the existing electricity and heat markets, the markets for the solid products and especially those from heterogeneous and complex feedstocks such as trommel fines are less well established and therefore highly sensitive to market factor. However, it would be interesting to observe the importance of the solid product utilization on economic performance. Further work should review the current and future markets for pre-treated trommel fines fast pyrolysis solid products as it can significantly improve the case for the pre-treated trommel fines fast pyrolysis energy system. The pre-treated trommel fast pyrolysis system can offer environmental benefits and has the potential to reduce landfill costs, but for the system to be viable, attention must be paid to improvements in trommel fines ash reduction, the solid residue applications for higher value markets, reactor cost reductions and improvements in liquid fuel yield, quality and use ability for CHP production.

8 Conclusion and Recommendation

Based on the study reported in this thesis, a number of conclusions have been reached and are presented in this chapter. Similarly, recommendations on further work that should be undertaken in continuation to this research are also suggested. The nature of the study meant that two sets of conclusions were reached. The first concerns the unreported trommel fines feedstock and their products and the second relates to the commissioned 300 g h^{-1} fluidised bed fast pyrolysis reactor to process trommel fines. All measurable aims were achieved.

The outcome of this research project in combination with the recommendations should provide enough information for a complete evaluation of the application of bubbling fluidised bed fast pyrolysis as a thermal conversion technology for trommel fines. Furthermore, the data on dry and wet physically pre-treated trommel fines fast pyrolysis process and ash control methods to reduce the inorganic content within trommel fines feedstock prior to fast pyrolysis are all new and can form the basis for future research into process development. In particular, the effect of ash control on fast pyrolysis processing of trommel fines, mass balance yields and liquid product quality as well as process economics are provided for the first time.

8.1 Trommel fines feedstock preparation

A batch of trommel fines obtained from a UK Waste Management company, used in this study, showed a wide range of particle sizes and contained mixtures of different materials from plastics, paper and cardboard to stones and pieces of bricks. The raw trommel fines feedstock was physically pre-treated to obtain suitable characteristics for an existing fluidised bed reactor system. Pre-treatment yields two main feedstock types; dry (grinding, sieving, manual separation etc.) and wet (agitated washing and agitated washing with 1.00 vol. % Decon Neutracon surfactant). The raw trommel fines and the physically pre-treated feedstocks were characterised in terms of elemental composition, heating values and thermal degradation behaviours. The results showed that although the physically pre-treated trommel fines feedstocks (PT) had high ash contents compared to a normal 'RDF' or more conventional biomass, the energy contents were also high. The characterisation results also showed that the physically pre-treated trommel fines feedstocks contained volatile matter of more than 45% that can be exploited for energy purposes.

The ash content decreased with the wet (aqueous) physically pre-treated trommel fines feedstocks (AW and AWS) but the addition of a surfactant (Decon Neutracon) had no effect on the ash content. The decrease in ash content was solely due to the elimination of the inorganics by sedimentation. The inverse pattern was observed with the volatile content, which increased with the AW and AWS feedstocks. The thermal degradation behaviours investigated via thermogravimetric analysis during this research also showed that fast pyrolysis is an appropriate technology in exploiting the energy potential of all the pre-treated trommel fines feedstocks.

Over the temperature range investigated (400 - 700 ºC), it was shown that at a temperature window of between 500 °C and 550 ºC was the optimum temperature range for obtaining maximum organic liquid yields for PT and the highest process conversion efficiency. However, the solid residues were the highest yield of products obtained from fast pyrolysis of PT feedstock because of the high ash content of the feedstock. An increased in feedstock moisture content (from <3 to 10 wt%) lead to a decrease in organic liquid yields and the highest organic liquid yield was observed at <3 wt% feedstock moisture content.

The organic liquid yield and the process conversion efficiencies increased with AW and AWS feedstocks at optimum processing conditions with the highest organic liquid yield and highest process conversion efficiency obtained with the AW trommel fines feedstock. The inverse pattern was observed with the solid residue yields and the solid residue yields decreased with the AW and AWS feedstocks.

The primary condensate organic liquid product from all the pre-treated trommel fines (PT, AW, and AWS) feedstocks showed high energy contents above 30 MJ kg^{-1} and were found to contain higher energy for exploitation than bio-oil obtained from more conventional biomass feedstocks. Analysis of the liquid products showed the presence of nitrogen-containing organic compounds with PT feedstock. However, the presence of these nitrogen-containing organic compounds decreased with AW and AWS. The same observations were also made with the elemental analysis of the liquid product which also showed a decrease in nitrogen content with the AW and AWS.

Analysis of all the solid products showed that ash was the main components of the solids produced, however, the ash content decreased while the char content in the solid products increased with AW and AWS. The increased char proportions in AW and AWS solid residues also significantly increased the HHV of the solid residues.

The economic evaluation of the pre-treated trommel fines fast pyrolysis system showed that the PT trommel fines fast pyrolysis systems only become economically feasible from 2000 kg h^{-1} with a total capital investment payback period of 8.6 years at 20% interest rate due to the high operating cost associated with running the facility. The NPV increased with the AW and AWS feedstocks, resulting in a reduced capital investment repayment period with AW trommel fines feedstock having the highest NPV and the earliest repayment period.

The economic evaluation of the AW and AWS trommel fines feedstocks to determine their minimum processing capacities showed that both AW and AWS trommel fines samples were both economically feasible from 1000 kg h^{-1} processing capacities with AW trommel fines feedstock having a higher NPV (£4.1 million) and an earlier repayment period (2.7 years).

8.2 Trommel fines fast pyrolysis process

The 300 g h^{-1} bubbling fluidised bed fast pyrolysis reactor unit which has never been commissioned to process feedstocks such as Trommel fines was commissioned and shown to be capable of performing fast pyrolysis experiments. The reactor unit showed that the initial design of the system was indeed capable of processing biomass to liquids and modifications had to be made to accommodate the processing of feedstock with very high ash content. The results from the pre-treated trommel fines fast pyrolysis studies also showed that there were reduced liquid yields as a result of poor operation caused by design flaws. The less than optimal operation of the feed and reactor system meant that the unit as whole could not be operated to full a capacity. One of the important lessons of this research is that the incompatible design of individual units of the fast pyrolysis process affected the operability of the entire process. Serious care must be taken in the design and operation of processing units to suit feedstock characteristics.

The poor operation of the feed system greatly affected the operability of the unit. The bridging and premature pyrolysis of pre-treated trommel fines feedstocks prior to reactor entry was caused by the design of the feeding system not being compatible with feedstocks like trommel fines. As a result of the feeding problems, an alternative feed system design incorporating parts of the initial feed system has been proposed in this work. The alternative design of the feed system incorporated the initial metering unit with gravimetric capabilities and a proposed new varying pitch plug fast screw for efficient feeding. The alternative feed system has the capabilities to eliminate the problems caused by its predecessor.

Optimum hydrodynamic parameters were never achieved using the 300 g h^{-1} bubbling fluidised bed reactor. The reactor system was shown to be unable to achieve selective entrainment of particles because of geometric limitation and the nominal throughput of 300 g h^{-1} unit as designed for the process was never achieved. The reactor unit modifications are necessary to optimise the process and have been proposed. The proposed design has been based on experience gained using the initial fast pyrolysis unit and established principles from literature studies. However, more hydrodynamics calculations are required to properly assess this parameter of the reaction system.

The operation of the condensing unit of the process was also problematic due to high viscous liquid products from pre-treated trommel fines fast pyrolysis that invariably stuck to the walls of the ESP and blocked the exist point of the ESP. Modifications were made to the condensing unit to improve its performance and ease product collection.

8.3 Recommendations

8.3.1. Trommel fines feedstock preparations for fast pyrolysis

Based on this study, it is suggested that a thorough and detailed study on the economic feasibility of pre-treated trommel fines fast pyrolysis system be conducted to include the current and future markets for pre-treated trommel fines fast pyrolysis solid products. This may help improve the case for the pre-treated trommel fines fast pyrolysis system.

The composition of trommel fines depends on the initial composition of MSW. However, the composition of MSW varies greatly from place to place to country as well as varying significantly throughout the year. It is recommended that future generation and composition of trommel fine be forecasted. This can help establish the type and quantity of materials present in waste, allowing collections and waste treatment technologies to be tailored to suit waste arisings.

For further fast pyrolysis processing, the co-pyrolysis of the pre-treated trommel fines feedstock especially the AW trommel fines sample used during this research and another type of waste such paper sludge, plastic waste, forestry biomass etc. be explored as means of further reducing the ash content of the pre-treated trommel fines feedstock and increasing the liquid yield of the products from fast pyrolysis.

While this research has only explored one type of surfactant (Decon Neutracon) for pre-treatment of trommel fines. Further research into other surfactants could identify a suitable one that could further lower the inorganic content in the trommel fines feedstock compared to Decon Neutracon. Surfactants for future research should however, be evaluated on type (non-ionic, anionic or cationic), retention of feedstock, cost and disposal options. Ideally the surfactant should be bio-degradable. It is also recommended that the use of hot water pre-treatment or mild acid washing to reduce the alkali metal contents be investigated. This may likely have a positive impact on the yields of organic liquids, but the costs of such systems require economic evaluation.

During this research, only the dry physically pre-treated trommel fines feedstock (PT) was processed over a temperature and feedstock moisture content range. The impact of temperature and feedstock moisture content was not explored on the wet physically pre-treated trommel fines feedstocks (AW and AWS). It is recommended that the impact of temperature and feedstock moisture content on the AW and AWS feedstocks be investigated as they may behave differently from the PT; (e.g. they may be more application for pyrolytic gasification, etc.).

Viscosity, pH and aging analysis should be performed on all the liquid products produced from PT, AW, and AWS feedstocks. This would highlight the stability and acidity exhibited by the liquid products. It is also recommended that more analytical techniques (TAN analysis, gel permeation chromatography (GPC), nuclear magnetic resonance spectroscopy (NMR), and Fourier transform infrared spectroscopy (FTIR) be employed to understand the chemistry of components in the liquid products. An extended insight into the chemistry of the liquid will be very beneficial to the upgrading of the liquid products.

8.3.2. Trommel fines fast pyrolysis process

The design of feed systems especially the single fast screw feeder into the reactor was identified as one of the culprits for the poor operation of the entire fast pyrolysis process. It is recommended that the single fast screw feeder to be replaced with a varying pitch plug screw which will operate at high speed to facilitate rapid and unhindered transportation of the pre-treated trommel fines feedstock in to the reactor. This may be beneficial for heterogenous feedstocks such as trommel fines.

The commissioned fluidised bed reactor was designed to handle a throughput of 300 g h^{-1}. However, this was not achieved because of geometric limitations of the fluidised bed reactor system. It is recommended that the fluidised bed reactor be modified to include a vertical tube opening just above the distributor plate with a knife gate valve, which would allow for entrainment of higher density materials like the glass, stones etc. found in the trommel fines feedstocks from the reactor bed when there is pressure and bed build up allowing for a continuous process and also allowing for the commissioned fluidised bed reactor to operate at its designed throughput. It is also recommended that further pre-treated trommel fines fast pyrolysis investigations be studied using a different type of fast pyrolysis reactors (e.g. Ablative and fixed bed) that do not use a fluidising medium (sand) so that the mass balance and product characteristics results could be compared to the fluidised bed fast pyrolysis reactor results. This would help identify the type of fast pyrolysis reactor that is best suited for heterogenous and difficult to process waste like trommel fines.

The results from the analysis of the liquid products from all the pre-treated trommel fines (PT, AW and AWS) feedstocks showed the presence of nitrogen and sulphur. These heteroatoms may also be present in the gas phase, however the current gas analysis system does not allow for the monitoring of gaseous compounds of these elements. It is recommended that the gas analysis system be upgraded to detect a wider range of gases (NOx, Sox, chlorine). The need for the fast pyrolysis process units to detect nitrogen- and sulphur-containing gases especially for heterogenous and difficult-to-process solid feedstock such as trommel fines cannot be over emphasised.

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Appendix 1: Publications

Publication arising from this research:

Eke, J & Onwudili, J.A. & Bridgwater, and A.V. Physical pre-treatment of biogenic-rich trommel fines for fast pyrolysis. Waste Management. 10.1016/j.wasman.2017.09.009.

Eke, J & Bridgwater, A.V & Onwudili, and J.A. Influence of temperature on fast pyrolysis of pre-treated trommel fines in a bubbling fluidized bed. Waste Management 2018. Submitted for publication (23/05/2018)

Eke, J, Onwudili, J.A., Bridgwater, and A.V. Influence of moisture content on the fast pyrolysis of pre-treated trommel fines in a bubbling fluidized bed. Waste and Biomass Valorization 2018. Submitted for publication (01/06/2018).

Conference Paper:

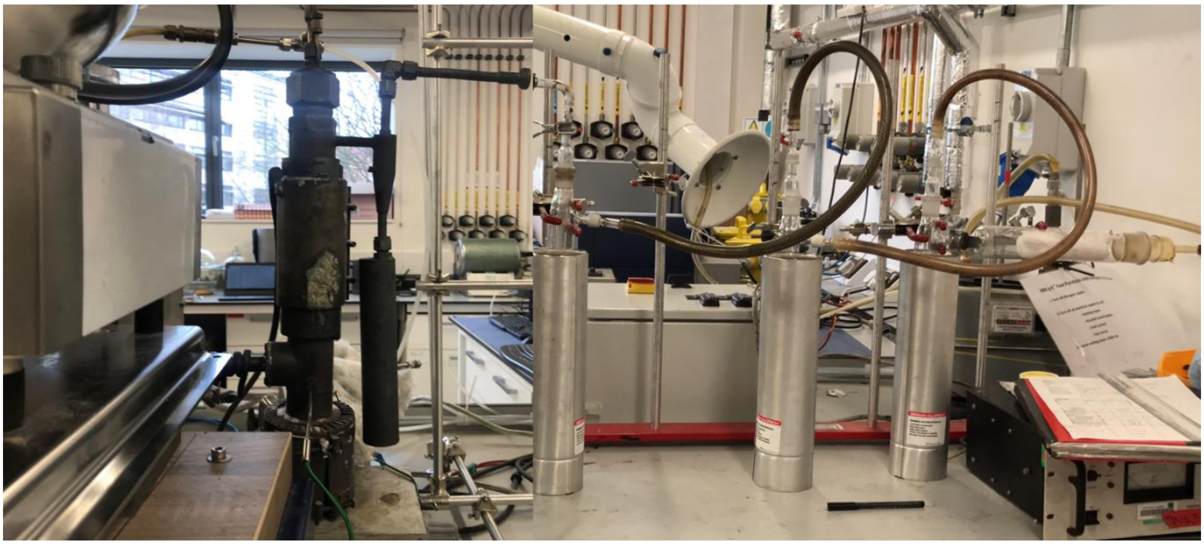
Eke, J, Onwudili, J.A and Bridgwater, A.V. Pre-treatment of biogenic-rich trommel fine for fast pyrolysis. In 6th International Symposium on Energy from Biomass and Waste, November 2016. Venice, Italy

Appendix 2: 300 g h^{-1} fast pyrolysis rig operating procedure

(Joseph Eke and Dr Scott Banks)

Set up

The diagram below shows the set up for the 300 g hr^{-1} pyrolysis rig in Aston University used during this research.



Pre-Start up

1. Put a pre-determined amount of feedstock to be pyrolysed into the feeder and close it.
2. Put a measured amount of sand (about 150g, particle size: 500 - 600µm) into the reactor and then close it.
3. Weigh char pot and attach it to the reactor (Anti-seize is applied to all the joints of the reactor and the metal components i.e. the char pot, the reactor threading and to the ball and socket joint between the transition pipe and the metal transition pipe. This is done to prevent the glassware and metal components from getting stuck after the run.).
4. Sufficiently insulate the reactor to avoid any significant heat losses to the surroundings.
5. Ensure there are no combustible materials e.g. paper, organic solvent etc. around the vicinity of the rig.
6. Ensure rig is clean and properly assembled; all nuts and bolts should be tight enough and clamps should be used where appropriate to prevent leakages.
7. Open fluidising gas and set flow rate to 5 l min^{-1}.

8. Open the feeder top nitrogen gas and set flow rate to 2 l min^{-1}.
9. Using a leak detector or soap solution, check for leakages at all joints and connections.
10. Ensure that all temperature and pressure displays are identified.
11. Ensure that the electric insulation plastics of all wires are not contacted with hot surface.
12. Check that all electric connections are appropriate and are isolated from the hot area of the fluidised bed
13. Check that the entire system is adequately earthed.
14. Check that the venting system connected to the rig is working. A piece of paper can be placed near the port, if the paper is sucked in, the venting system is working.
15. Check the Micro GC to make sure it is ready to accept gas samples.
16. Make sure that the secondary condensers are filled with dry-ice/acetone mixture.

Start up

1. Open the cooling water valve. The flow rate should be set to make sure that the wall of the feeder close to the reactor is not more than 50 °C.
2. Turn on the nitrogen pre-heater and let the temperature reach set point of about 300 °C This will usually take just a few minutes.
3. Switch on the first slip-on heater, wait for about 2 minutes and switch on the second slip-on heater. The temperature of the heaters should be set to about 150 °C above the target pyrolysis temperature.
4. Allow enough time for the bed temperature to become stable at the targeted pyrolysis temperature, usually takes between 1-2 hours.
5. When the reactor temperature becomes steady at pyrolysis temperature, turn on the screw feeder and adjust to a pre-determined rotating speed. Simultaneously, start a stop watch to monitor the time of the experiment, increase the fluidising gas and set flow rate to 8 l min^{-1} and increase the feeder top nitrogen gas and set flow rate to 10 l min^{-1}.

Operation

1. Record the system parameters every 5 minutes. The items to be recorded are bed temperature, freeboard temperature, feeder pressure, pressure difference across the bed and gas count.
2. Check the screw feeder regularly to make sure there is no noise.
3. Take sensible actions according to the physical observations and measurements during the running period such as the nitrogen flow rates. Valves can be adjusted manually to correct such changes.

4. A high feeder pressure indicates a blockage in the system. The rig must be stopped according to the emergency shutdown procedure.

Shut down

1. Turn off the slip-on heaters.
2. Close all nitrogen gas flow.
3. Turn off the GC pump.
4. Close the cooling water valve.
5. Separate the glass transition pipe from the metal transition pipe as it may otherwise become stuck.
6. Leave the system to cool down to room temperature.

Dismantling and cleaning

1. Take off all insulation material from the rig.
2. Dismantle char pots and transition pipe from the condenser.
3. Weigh all parts of the rig for mass balance purposes.

Emergency shut down

1. Turn off feeder screw.
2. Turn of the power from the mains.
3. Follow procedure for normal shut down.