DOCTOR OF PHILOSOPHY

Increase of energy recovery from sewage sludge

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Aston University

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THESIS SUMMARY

The use of the pyrolysis process to obtain valuable products from biomass is amongst the technologies being investigated as a source for renewable energy. The pyrolysis process yields products such as biochar, bio-oil and non condensable gases. The main objective of this project is to increase energy recovery from sewage sludge by utilising the intermediate pyrolysis process. The intermediate pyrolysis has a residence time ranging from 5 to 10 minutes. The main product yields from sewage sludge pyrolysis are 50 wt% biochar, 40 wt% bio-oil and 10 wt% non condensable gases.

The project was carried out on a pilot plant scale reactor with a load capacity of 20 kg/h. This enabled a high yield of biochar and bio-oil. The characterisation of the products indicated that the organic phase of the bio-oil had good fuel properties such as having high energy content of 39 MJ/kg, low acid number of 21.5, high flash point of 150 and viscosity of 35 cSt. An increase in pyrolysis experiments enabled large quantities of pyrolysis oil production.

Co-pyrolysis of sewage sludge was carried out on laboratory scale with mixed wood, rapeseed and straw. It found that there was an increase in bio-oil quantity with rapeseed while co-pyrolysis with wood helped to mask the smell of the sludge pyrolysis oil.

Engine test were successfully carried out in an old Lister engine with pyrolysis oil fractions of 30% and 50% blended with biodiesel. This indicates that these pyrolysis oil fractions can be used in similar engine types without any problems however long term effects in ordinary engines are unknown. An economic evaluation was carried out about the implementation of the intermediate pyrolysis process for electricity production in a CHP using the pyrolysis oil. The prices of electricity per kWh were found to be very high.

Keywords: Sewage sludge, Pyrolysis, Intermediate pyrolysis, Co-pyrolysis, Stability, Engine tests, Economic evaluation

DEDICATION

TO

AL-HAYYUL-QAYYUM

"Without you, this would not be possible"

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CHAPTER 1: INTRODUCTION AND BACKGROUND

1.1 INTRODUCTION

The increase in industrialisation of several countries has led to an increase in demand for fossil fuels consumption [1]. The fossil fuels reserves are limited and expected to run out in the near future [1]. The lack of an alternative fuel to complement the use of fossil fuels would be disastrous for many economies. There has also been increasing concerns about the impact of fossil fuels to the environment. The use of fossil fuels is one of the major sources of global warming. These aspects have prompted the European Union to urge its member states to explore renewable energy sources that are sustainable and environmental friendly [1]. The UK has pledged to increase its energy from renewable sources by 15 % by 2020 [2]. This necessity coupled with the increase in renewable energy incentives has prompted investments into biomass to power production.

There is a current need to help save the environment by reducing the emissions caused from different sources. Dumping of waste on landfill sites has been among the sources of emissions for green house gases. Sewage sludge has been previously dumped on landfill sites as a way of disposing of the large volumes generated by waste treatment plants. However sewage sludge has been identified as a potential biomass that could be used for energy production. It is sustainable and large volumes are created on a daily basis by several companies. Its use would help companies reduce the need for finding disposal options. The pyrolysis process is among the key technologies that can be used to obtain value products from sewage sludge. The pyrolysis process decomposes constituents into bio-oil, biochar and non condensable gases with the absence of oxygen. These products can be applied in a combined heat and power system such as internal combustion engine to generate heat and power.

In the UK, the pyrolysis process is one of the technologies that are recognised by the Renewable Obligation Certificate (ROCs) to receive incentives for power generation. In order to implement the pyrolysis process as a source for energy generation, it must comply with the emission limits and operation set out by the waste incineration directive 2000/76/EC which regulates the waste and waste derived material [3].

1.2 BACKGROUND

1.2.2 SEWAGE SLUDGE AS A POTENTIAL FUEL

Cartmell et al [4] mentions that there are targets set by the EU and UK government to increase power generation from the renewable sources. The new legislation and policy initiatives such as the renewable obligation certificate and the Climate Change Levy aim to stimulate the take up of renewable sources and are creating a more favourable climate for sludge to be considered as a fuel [4]. In addition to this, the authors [4] state that combusting sewage sludge with another material has the potential to generate energy. Fonts et al [5] adds that 'sewage sludge can be considered as a biomass resource for the recovery of energy'.

In order to determine whether a material will be suitable as a fuel, the higher and lower heating value of that material has to be determined. The higher heating value is the amount of heat released by a specific substance or material once it is combusted with condensing of the water produced. The higher the heating value, the better a material makes as a fuel. Table 1.1 shows fuels and other potential materials that can be used as energy with the corresponding heating values. In order to use sewage sludge to obtain fuel through the combustion process, it would have to be dried to some extent to remove the excess water.

Table 1.1: Heating values of various biomass and fuel [6]

It is clear from Table 1.1 that the dried sewage sludge has a higher energy content compared to other materials such as wood. The energy content of dry sewage sludge competes with that of wood and plastics. Therefore the potential of extracting heat and power from sewage sludge is a reality although ways of achieving this may differ within organisations.

1.3 MOTIVATION OF THE PROJECT

1.3.1 SEVERN TRENT WATER

This project is a CASE base from Severn Trent Water that aims to investigate whether the use of intermediate pyrolysis can increase energy recovery from sewage sludge. At present, Severn Trent Water collects biogas produced from their anaerobic digestion system which is used to generate electricity used on site and the surplus is sold to the national grid. The residue from the anaerobic digestion system is then dewatered and collected in an allocated area. This residue is known as sewage sludge.

Sewage sludge is used as a fertilizer on various farms in the UK. The average cost of sewage sludge is £2 per tonne [7]. Although sewage sludge is used as a fertilizer, there is surplus of this waste that is not fully utilised. In the UK, over one million tonnes of dry solids per year are produced by waste water treatment plants [8]. This dry matter can be utilised to recover energy. The use of the intermediate pyrolysis process can increase the potential benefits of sewage sludge and also act as a means of reducing the sludge volumes.

1.3.2 NEW TECHNOLOGY – REACTOR SYSTEM

A new reactor known as the pyroformer under patent [9] applies intermediate pyrolysis (Fig. 1.1). This type of reactor is different to other types of reactors that have been employed. It is a horizontal cylindrical shaped unit made from carbon steel. It is 180 cm in length and has an internal diameter of 20 cm. It is designed with a maximum feeding rate of 20 kg/h. It has two screws, one inner and outer screw that rotates in opposite directions as shown in Fig.1.2. The inner screw is fitted inside the outer screw. The inner screw takes material in while the outer screw transports the char backwards for cycling through the reactor. The char also acts as a heat transfer medium to the fresh feedstock. This allows cracking of high molecular compounds preventing tar formation. The screw design facilitates total breakdown of material inside the reactor. The screws are driven by metal chains attached to the motor. Sewage sludge has never been applied to this type of reactor and the potential products from this system need to be explored.

Figure 1.1: The intermediate pyrolysis reactor [9]

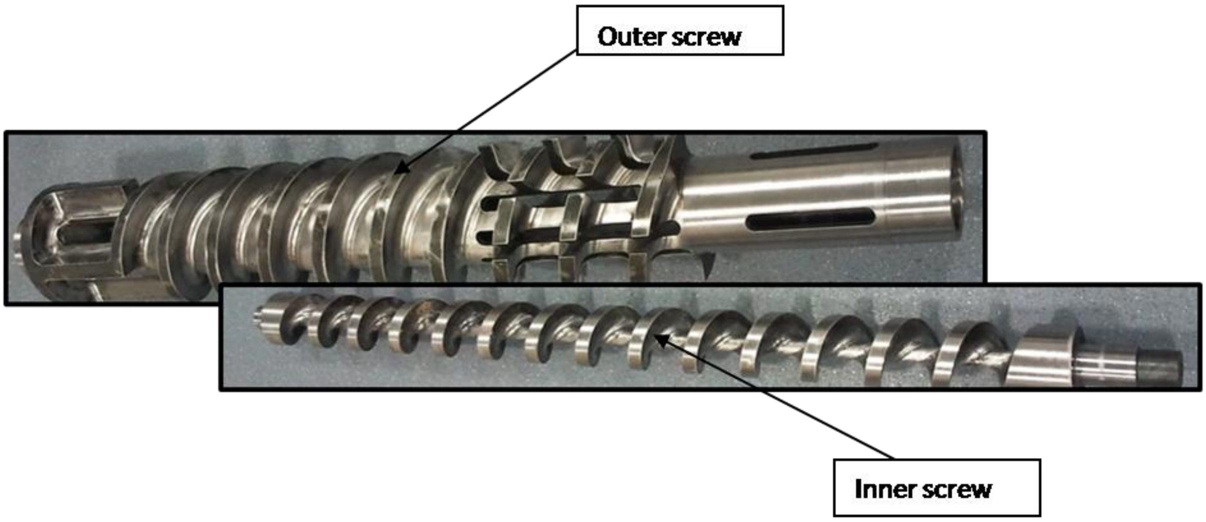


Figure 1.2: The inner and outer screw of the reactor

1.4 OBJECTIVES OF THE PROJECT

The purpose of this project is to investigate the use of the pyrolysis process as an alternative for the energy conversion of sewage sludge and these are the objectives that had to be met,

- Study the pyrolysis behaviour of sewage sludge under intermediate pyrolysis conditions. This will include studying the principle decomposition behaviour of sewage sludge to characterise the chemical compositions of the pyrolysis char, liquid and gases

- Undertaking pyrolysis of sewage sludge at a lab scale to obtain liquid, char, and gases samples to investigate the feasibility for use in a combined heat and power system such as a diesel engine

- Explore the potential to combine sewage sludge with other forms of biomass (e.g. wood chips) for co-pyrolysis

- Undertaking an economic evaluation of turning pre-dried sewage sludge in energy or intermediates at a technical scale site at Severn Trent Water.

1.5 STRUCTURE OF THE THESIS

This thesis is arranged into individual chapters discussing in detail the various aspects involved under every subheading:

Chapter 2: Literature review

This chapter explores the sewage treatment processes, disposal routes for sewage sludge and alternative processes that can be utilised. This chapter also details some of the previous work that has been carried out on the pyrolysis of sewage sludge.

Chapter 3: Equipments and methods

This chapter details the equipments and analysis methods used for investigations carried out in this thesis. The methods are divided into three; Liquid analysis, Solid analysis, Liquids and solids then gas analysis measurements.

Chapter 4: Characterisation of various sludges using the TGA

This chapter explains the characteristics of sludges obtained at different sources of the sewage treatment process. It details the behaviour of the sludges and explains reasons for the differing characteristics. It also explains the choice of the sludge used for the primary investigation in this project.

Chapter 5: Intermediate pyrolysis of sewage sludge

This section explores the use of intermediate process from sample preparation to the products obtained from the pyrolysis process. It discusses the products from the pyrolysis process such as bio-oil, char and gases. This chapter forms the basis of work undertaken in other chapters.

Chapter 6: Co-pyrolysis of sewage sludge

The sewage sludge organic phase showed good fuel characteristics, however it had some drawbacks. In order to improve some of characteristics, sewage sludge was pyrolysised with 40 wt% wood, 40 wt% straw and 40 wt% rapeseed. The bio-oil and char obtained from the co-pyrolysised was analysed and compared to sewage sludge organic phase.

Chapter 7: Potential benefits of sewage sludge bio-char for agriculture

Biochar is the largest product obtained from the intermediate pyrolysis of sewage sludge. This chapter investigates the properties and possibilities of utilising the biochar for agricultural use. It also forms a basis for any future work that could be carried out in this area.

Chapter 8: Stability of the sewage sludge pyrolysis oil

The pyrolysis bio-oils are known for their instability so this chapter investigates the stability of the pyrolysis oil (organic phase) obtained from the intermediate pyrolysis process. It investigates the stability in biodiesel and methanol under thermal heat at 80 and 60 °C for a period of 3 and 7 days.

Chapter 9: Engine tests with sewage sludge pyrolysis oil blends

One of the aims of this research is to investigate the applicability of the pyrolysis oil in an engine for the production of heat and power. This chapter discusses the engine tests carried out. The sewage sludge oil phase was blended with biodiesel and the performance of the mixtures was compared to diesel and biodiesel.

Chapter 10: Economic evaluation of electricity production from sewage sludge pyrolysis oil

This chapter examines the investment costs that could be needed to implement such a process. It highlights the operating costs and cost per kilowatt of electricity that would be required in order to break even. It also analyses the profitability of the process.

CHAPTER 2: LITERATURE REVIEW

This chapter explores sewage sludge treatment processes, disposal routes, alternatives technologies that can be applied and various works undertaken by various authors on the pyrolysis of sewage sludge.

2.1 SEWAGE SLUDGE

Sewage sludge is a by-product of sewage treatment plants. Werther & Ogada [10] state that waste is a combination of the liquid or water-carried waste removed from residential, commercial or industrial establishment. It contains compounds of agricultural value and pollutants [11]. The compounds that are essential for agriculture are organic matter, nitrogen, phosphorus and potassium. The pollutants found in the sludge include heavy metals, organics and pathogens [11]. Sludge treatment is essential as it destroys pathogens, stabilises and dewaters the sludge. The sludge composition also differs from one treatment plant to another; this is because different sources and treatment operations are applied [11]. An example of the composition of the sewage sludge is shown in Table 2.1.

Proper treatment of sludge is necessary to reduce the volume and minimise the potential hazards posed by sewage sludge disposal. The treatment of raw sewage involves effective separation of suspended organic matter from the liquid stream by settlement in primary, secondary and tertiary stages. The aim of such treatment is to reduce the water content, the potential for fermentation and to reduce the presence of pathogens [12].

Table 2.1: Composition and properties of sewage sludge [11]

2.2 SEWAGE TREATMENT PROCESS

2.2.1 PRETREATMENT

Fig. 2.1 shows the sewage sludge treatment process. Pre-treatment is the first stage in sewage treatment process. Waste from different sources such as industrial and domestic waste is collected in a single section where treatment begins. The process utilises the screening stage that removes heavy debris i.e. sticks, cans, plastics before they damage or block any pipes in the next treatment process. After the screening process, wastewater is sent to the grit chamber where the velocity of the incoming stream is controlled to allow stones, sand and grit to settle at the bottom. Then the treated effluent is sent onto the next step process.

2.2.2 PRIMARY TREATMENT

The treated effluent from the pre-treatment process is then collected in large tanks which allow sludge to settle at the bottom while materials like oil and grease float on top. The floating material is removed. Metcalf and Eddy [13], state that the organic material in primary sludge is comprised of 20-30 % crude protein, 6-35 % fats and 8-15 % carbohydrates. Sedimentation is the most common type of treatment process applied at this stage, due to its simplicity and cost effectiveness [11]. This method allows the settlement of suspended solids under the influence of gravity. The treated effluent is removed from the bottom of the tank and taken onto the next stage.

Figure 2.1: Sewage sludge treatment processes [11]

2.2.3 SECONDARY TREATMENT

Treated effluent from the primary stage is collected in large tanks where microorganisms and bacteria are used to breakdown organic matter into carbon dioxide, water and nitrogen. In this stage, microorganism or bacteria are used to breakdown organic matter contained within the sludge. The organisms also help to precipitate other compounds and materials out of the wastewater. The bacteria are provided with ideal conditions for survival. They feed on the organic matter thereby breaking it down [14]. After the correct state has been reached, the mixture is then sent to a separation tank where the top and bottom residues are removed and sent onto the final stage.

2.2.4 ANAEROBIC DIGESTION

After the secondary stage is complete, the sludge still contains organic matter that needs to be broken down to make it safer for use on land. The effluent is collected in air tight tanks called digesters at 35 ˚C for up to 20 days; this process is known as anaerobic digestion as no oxygen is present [15]. Bacteria are added to the effluent in the tanks to destroy the pathogens by breakdown the organic matter into biogas. Methane makes the largest percentage of the biogas totalling up to 75 wt% [16]. The biogas can be used in two ways; it can be used for heating the digester to the required temperature or it can be passed through fuel gas engines to generate electricity. At Severn Trent Water, a lot of biogas is used to heat the digesters and the rest is used to generate electricity. This stage is very important as it stabilises the sludge by destroying disease causing bacteria.

2.2.5 DEWATERING

Although different methods differ from each waste water treatment, dewatering of the sludge is normally the final stage. Treated sludge contains large volumes of water or solution that need be reduced for easier handling and disposal. The centrifuge and vacuum filters are widely used for dewatering and if less water content is required for further applications like incineration or agricultural use, further drying is done by using filter press or any other method to remove excess moisture. The dewatered sludge cake referred to as sewage sludge is the final product from the sewage treatment process.

2.3 DISPOSAL OF SEWAGE SLUDGE

After the sewage treatment process, sewage sludge has to be applied or disposed of according to specific country regulations. Sewage sludge contains a variety of organic and inorganic compounds; according to Fytili and Zabaniotou [17] the most common ways to treat sewage sludge in Europe are agricultural use (37 %), land filling (40 %), and incineration (11 %).

2.3.1 LAND FILLING

Landfilling is burying of waste in an allocated piece of land. This method of disposal causes pollution to the ground water originating from the decomposition of organic matter within the sludge [18]. It is also a major source of air pollution especially CH_4 and CO_2. Landfilling also produces noise pollution from delivery vehicles [18] and introduces heavy metals into the soil which affect the crops. Approximately 40 % of the sludge produced in the European Union is disposed of through landfilling [18]. This method of disposal is expected to decrease especially with stringent rules and the need to reduce environmental emissions [19]. Landfilling is no longer considered as a sustainable way of disposal from the environmental perspective [20]. The European council directive 1999/31/EC on the landfill of waste encourages member states to implement stricter rules on those carrying out this kind of method.

2.3.2 AGRICULTURAL USE

For several years, dewatered sewage sludge has been used as a fertilizer on agricultural lands. It contains nitrogen and phosphorous that are beneficial to the soil [21]. Due to its benefits, agricultural use is considered to be the best practical environmental option compared to other methods of disposal [21]. Approximately 71 % of sewage sludge in the UK is used for agriculture [21]. The application of sludge on the land is regulated by the Sludge Use in Agriculture 1989 [21]. However, there are concerns over risks from heavy metals and organic contaminants in the sludge [12]. The metals of major concern are arsenic, cadmium, lead, mercury that are toxic to humans while zinc, nickel and copper are poisonous to plants [22]. The European directive 86/278/EEC places restrictions concerning the use of sewage sludge for agriculture and limits concentrations of heavy metals that is to be applied to the soil. The use of sewage sludge as a fertilizer is being phased out, as major supermarkets no longer accept crops that have been grown on land that has used this type of fertilizer.

2.3.3 INCINERATION

It is combustion of waste to form CO_2 and H_2O with the production of ash as a residue. The process allows total destruction of organic matter contained in the sludge [23]. The incineration process has been widely used in the reduction of sewage sludge volumes. In the UK, 21 % of sewage sludge is incinerated [21]. Severn Trent Water still uses this method at Roundhill Sewage Treatment Works to reduce the volume of their sewage sludge [21]. This method minimises the need for disposal space and reduces odour generated from landfilling. However, incineration is quite expensive due to high temperatures required to carry out the process. It also gives of CO_2 and hazardous pollutants that need cleaning before release to the atmosphere. There is a present need to find alternatives to this process. Mininni et al [20] are of the view that sludge incineration is expected to increase in countries where agricultural use is limited.

2.4 THE USE OF PYROLYSIS PROCESS AS AN ALTERNATIVE PROCESS

Pyrolysis is the thermal decomposition of organic matter in the absence of oxygen. Pyrolysis is one of the alternatives used for the treatment of sewage sludge. The process occurs in the temperature range of 300 to 900 ˚C depending on the desired product outcome [11]. The main products from the pyrolysis process are biochar, bio-oil and non condensable gases. The bio-oil can be used as a fuel or raw material for chemical industries, the gas can be used for combustion and biochar can also be burnt as fuel or used as a fertilizer. In addition to this, the pyrolysis process envelopes the heavy metals except mercury into the biochar [24].

Pyrolysis allows recovery of bio-oil with low emissions of nitrogen and sulphur oxides. Werther and Ogada [10] state that, the formation of toxic organic compounds such as dioxins is avoided with low operating costs compared to incineration. It is a source of quality oil that can be used in many chemical processes and a reduction of sewage sludge to small volumes of inert residues [10]. Pyrolysis process conditions can be altered to produce the desired char, gas or oil as an end product [12].

The pyrolysis temperature and heating rate have the most influence on the product distribution. The abundance of sewage sludge across the globe makes sewage sludge a potential raw material for use in the pyrolysis process for product recovery especially with the decrease of fossil fuels [5]. However, Kim & Parker [25] are of the view that using biochar or dried sludges as fuel may have negative environmental impacts due to the formation of dioxins. Pyrolysis is of three types; fast, intermediate and slow pyrolysis.

2.4.1 FAST PYROLYSIS

This is thermal decomposition that occurs from 400 to 500 ˚C with very short residence times of approximately 2 seconds that maximise secondary reactions [26]. The reaction conditions are tailored to give high liquid yields of 75 wt%, 12 wt% char and 13 wt% non condensable gases based on wood [26]. The biomass must be dried up to a moisture content of less than 10 % in order to reduce the water content in the liquid yield. The biomass used for fast pyrolysis must be finely ground powder with particle size < 3 mm to ensure rapid biomass reaction [26]. The fine powder enables high heat transfer and heating rates of the biomass. Several reactors have been utilised by many authors to achieve fast pyrolysis conditions, however the most common types are; bubbling and fluidised bed reactors [27].

2.4.2 INTERMEDIATE PYROLYSIS

Intermediate pyrolysis takes place around 450 to 500 ˚C with a short vapour residence time. It is a new technology in the UK that was developed by [9] that utilises two screws as discussed in chapter 1. The reaction occurs under controlled heating rate which avoids the formation of tar [9]. Tar is heavy residue of substance that contains higher molecular weight than that of benzene; it is undesirable if oil is to be used as fuel. Biomass used for intermediate pyrolysis does not need pre-treatment conditions similar to that of fast pyrolysis. Feed stock can be used in a wide range of sizes ranging from pellets, big chunks to powder (< 5 mm) depending on the reactor feed design. However, drying the biomass is recommended in order to reduce fuel consumption and water content present in the bio-oil. The product yields of this type of process yields more char and less bio-oil as compared to the fast pyrolysis process. The residence time is controlled by the inner screw design and this can be varied to suite various types of biomass. Bio-oil obtained from the intermediate pyrolysis process doesn’t contain any char particulates and this has been realised through the use of a filtration unit after the reactor system. Sperling [28] found the residence time of the intermediate pyrolysis process to range from 1 to 15 minutes.

2.4.3 SLOW PYROLYSIS

The major characteristic of slow pyrolysis is very long residence times and heating rates compared to the intermediate pyrolysis process. The temperature of 450 ˚C and below are utilised although this can differ depending on the desired product outcome [3]. This process favours charcoal production compared to the liquid and gas yields. A comparison of three pyrolysis processes based on wood is shown in Table 2.2.

Table 2.2: Pyrolysis yields (dry mass basis wt%) based on wood [29]

2.5 PREVIOUS WORK UNDERTAKEN ON SEWAGE SLUDGE PYROLYSIS

Sewage sludge has been a major interest for several authors due to its availability and the need to investigate an alternative use for it. Several authors have undertaken the pyrolysis of sewage sludge using fast and slow pyrolysis. Some of the published work undertaken has been highlighted below.

2.5.1 FAST PYROLYSIS OF SEWAGE SLUDGE

2.5.1.1 STUDY OF PYROLYSIS LIQUIDS OBTAINED FROM DIFFERENT SEWAGE SLUDGES [30]

In this study, Fonts et al [30] used a fluidized bed reactor to investigate the properties of pyrolysis liquids obtained from different sewage sludges. The solids were crushed into powder to a range of 250 – 500 mm. The reactor was heated by an electrical furnace with three heating zones (bed, free-board and cyclone), which could be controlled independently. The bed temperature was set at 550 ˚C with a nitrogen flow rate of 4.5 dm^3/min. The solids were fed to the reactor at a rate of 4.5 g/min.

The pyrolysis reaction took place inside the fluidized bed reactor while the product vapours and gases departed the reactor. The bed height was kept at 150 mm by means of a concentric pipe enabling the bed material to overflow and be collected in a solid vessel. A cyclone and a hot filter were placed behind the reactor to remove the fine particles from the gas stream. The condensable gases were collected as liquid in the recovery system.

The results from the analysis showed that different levels of ash content had a big impact on the product yield. It was found that as the ash content increased, the solid yield decreased but the gas and liquid product increased. No significant differences were found in the higher heating values of the pyrolysis bio-oil obtained from different sewage sludges.

2.5.1.2 FLASH PYROLYSIS OF SEWAGE SLUDGE [31]

A mixture of raw and dried sewage sludge was pyrolysised in a fluidised bed reactor. The authors [31] investigated the effects of flash pyrolysis from a temperature range of 400-700 °C. The effects of reaction conditions, char accumulation and deashing on liquids were investigated. A fluidised bed reactor was used. Nitrogen gas was used as a fluidising medium and this entered the system through the bottom. The reactor throughput ranged from 5-100 g/h. The vapours from the reactor were sent through a cyclone that was then connected to two condensers. The apparatus involved with the experiments were weight before and after the experiment. The experiments were estimated to last from 30 to 60 minutes.

The authors [31] found that the maximum organic yield was at 400 °C with 52.8 wt%. It was also found that an increase in pyrolysis temperature increased the gas yield but decreased char yield. This behaviour was found to be typical of lignocelluloses biomass. The highest water production during pyrolysis was found to be at 550 °C.

Overall the optimum pyrolysis temperature for high product yields was found to be between 380-500 °C. The dried raw sludge gave a bio-oil yield of 53 wt%. The bio-oil was found to have a nitrogen content of 5-7 wt% and oxygen content of 10-15 wt%.

The authors found that using different pyrolysis atmospheres that were nitrogen, methane and hydrogen as the fluidising gases at 500 and 650 °C, the following observations were made. In the hydrogen atmosphere at 500 °C, there were higher tar yields and low gas yields. In methane atmosphere at 500 °C, there were high gas yields and lower char yields. In the hydrogen atmosphere at 650 °C, there were increased gas yields and reduced tar yields. There was little difference in product yields at 650 °C in methane and nitrogen atmosphere.

2.5.1.3 PYROLYSIS OF SEWAGE SLUDGE IN A FLUIDISED BED [32]

The authors [32] carried out fast pyrolysis process using a fluidised bed as the reactor. The fluidised bed had an internal diameter of 0.14 m with an internal height of 0.8 m. Nitrogen gas was used to purge the reactor. Sand was used the fluidising medium. The screw feeders were used to feed the sewage sludge into the reactor. Approximately 1 to 5 kg/h was used for the reaction. The first fluidising bed was connected to a second bed that was then connected to a cyclone followed by an electrostatic precipitator. The permanent gases were recycled back to the first reactor with the help of a compressor. The surplus permanent gases were combusted.

The highest bio-oil yield was found to be at 550 °C. The oil phase at this temperature was found to mainly contain Benzene, Toluene, Styrene, and n-C_5 to n-C_9 compounds. The C/H ratio of the oil phase was found to be similar to that of the sewage sludge. The use of a catalyst was found to enhance gas and oil yield. The catalyst also enabled less tar fractions in the bio-oil.

The authors [32] found an increase in pyrolysis temperature increased the gas yield. Large quantities of permanent gases were produced that enabled the recycle to the fluidised bed. The authors found the pyrolysis reaction of sewage sludge to be dependent on particle size. Larger particle sizes ranging from 2 to 3 mm were found to enhance char formation. The product water was found to be lower with increase in pyrolysis temperature especially at temperatures less than 500 °C. The product water was thought to originate from the decomposition of sugars and acid. They also found that the heavy metals were more concentrated in the soot than char. The emission of Cd was found to occur below 600 °C.

2.5.1.4 LIQUID HYDROCARBONS FROM CATALYTIC PYROLYSIS OF SEWAGE SLUDGE LIPID AND CANOLA OIL: EVALUATION OF FUEL PROPERTIES [33]

The authors [33] carried out the pyrolysis of lipids obtained from sewage sludge and canola oil. They used activated alumina as a catalyst for the process. The lipids from sewage sludge were extracted with toluene using the Soxhlet extraction method. The reactor used was a fixed bed made from stainless steel. Before the each run, the reactor was packed with 40 g of activated alumina. The feed was preheated at 200 °C while the reactor was heated to 450 °C. Nitrogen gas was used to purge the system before reaction. The pyrolysis temperature used for the reaction was 450 °C. The toluene extracted lipids were semisolid at room temperature. In order to maintain the liquid state, the semisolids were melted and this state was maintained in a syringe by wrapping a heating coil around the syringe. The extracted lipids were injected into the preheater using 40 ml of sample in a 50 ml syringe. The feeding rate was estimated to be 0.46 weight hourly space velocity. Canola oil was treated in the same way as the semisolids.

The properties of the liquid obtained were compared to those of diesel fuel. It was found that the liquid from the sludge lipid extraction had a very low viscosity of 1.88 cSt @ 40 °C compared to canola and diesel fuel. The lipids also generated a better energy content of 46.18 MJ/kg than that obtained from diesel fuel found to be 45.89 MJ/kg. The lipids also generated a liquid with a low ash content of 0.01 wt% compared to diesel that was 0.02 wt%. The sulphur content from the sludge lipids was found to be the same as that of diesel fuel.

2.5.1.5 ON THE PYROLYSIS OF SEWAGE SLUDGE: THE INFLUENCE OF PYROLYSIS CONDITIONS ON SOLID, LIQUID AND GAS FRACTIONS [6]

The authors [6] studied the effects of various temperatures ranging from 450 to 850 °C on the pyrolysis yield. They used a horizontal quartz reactor that was placed in the electrical laboratory furnace. A sample of 20 g containing 1 to 3 mm particle size was used for the experiment. Helium was used to purge the reactor at a flow rate of 100 ml/min. The pyrolysis temperatures used varied; these were 450, 650 and 850 °C. Heating rates ranging from 5 to 60 °C/min were used.

The authors [6] found that an increase in temperature decreased the char yield while the non condensable gases increased. The authors observed an increase in bio-oil yield as the temperature increased from 450 to 650 °C, however this remained constant at 850 °C. The heating rate was found to have an effect on pyrolysis temperatures that were ≤ 650 °C. There was an increase in ash content of the biochar as the temperature increased from 450 to 850 °C. The ash content was found to be 51 wt% at 450 °C and 88 wt% at 850 °C.

The authors used the centrifugal process to separate the organic from the aqueous phase. The properties of the organic phase were investigated. The aqueous phase was found to be 30 to 40 wt% of the total bio-oil yield. The use of a higher heating rate of 60 °C/min was found to influence higher bio-oil yield at 450 °C compared to a lower rate of 5 °C/min. The heating values of the organic phase were found to range from 22 to 27 MJ/kg.

The composition of the gaseous phase was found to contain CO, CO_2, H_2, O_2, N_2 and C_xH_y. An increase in pyrolysis temperature increased CO and H_2 and a decrease in CO_2 production. The authors found that a reduction in volume of approximately 40 to 50 % of dry sewage sludge using the pyrolysis process can be achieved at temperatures greater than 650 °C.

2.5.1.6 LOW-TEMPERATURE PYROLYSIS OF SEWAGE SLUDGE AND PUTRESCIBLE GARBAGE FOR FUEL OIL PRODUCTION [34]

Shen and Zhang [34] mixed different fractions of putrescible garbage (PG) and sewage sludge and investigated the mechanism, product distribution and best conditions for maximising fuel oil yields under low temperature pyrolysis conditions. A two stage rotary kiln reactor that was heated externally between 400-550 ˚C was used for the experiment. The feed was transported to the reactor via a screw feeder at a rate of 600 g/h; this was heated to the reactor temperature at varying times (20 and 60 min). Primary pyrolysis occurred in this reactor to form volatile matter (fuel oil vapour) and char. Both products were brought into contact with each other again in the second reactor, in which secondary pyrolysis and cracking of the volatile hydrocarbons occurred. The char was retained for the same time in the second reactor. The vapour was condensed in two stages; cooled by air and water cooled by a shell and tube condenser. The non-condensable gases were flared with the aid of a propane-fired burner.

Shen and Zhang [34] found that an increase in the sludge blend influenced the increase in reactor temperature and decreased the retention time. The reason for this increase might be directly linked to the nature and structure of sewage sludge. The highest bio-oil yield was achieved at the temperature of 550 ˚C at 20 min with the mixture of 60:40:50 (PG: Sludge: Ash). Ash was used as a catalyst for the reaction.

PG produced higher viscosity bio-oils while sewage sludge reduced the bio-oil viscosity. The sewage sludge bio-oil produced a higher energy content of 38 MJ/kg compared to that of PG that was 33 MJ/kg. The analysis of the bio-oils showed that both sewage sludge and PG have oxygenated aromatics but the oxygen arrangements were different on the aromatic rings.

2.5.1.7 PRODUCTION OF BIO-FUELS BY HIGH TEMPERATURE PYROLYSIS OF SEWAGE SLUDGE USING CONVENTIONAL AND MICROWAVE HEATING [35]

The authors [35] carried out the drying and pyrolysis of the sewage sludge in a single process. They used the multimode and single mode microwave cavity ovens. A quartz reactor with 40 cm height and internal diameter of 3 cm was used for the experiment. A sample size of approximately 15 g was used in the reaction. Helium at a flow rate of 100 ml/min was used to purge the reactor for 10 minutes before the experiment. The authors used an input power of 1000 W with a frequency of 2450 MHz. Graphite strips from char residue were used as microwave receptors. Graphite of approximately 1 g was blended with 15 g of wet sewage sludge. The sample temperature was monitored using an infrared optical pyrometer.

They found the use of FTIR and GC/MS to be beneficial in characterisation of pyrolysis oil. The composition analysis of the pyrolysis oils by GC/MS indicated that the use of electrical heating in the pyrolysis of sewage sludge produced oil that could have a significant environmental and toxicological impact. Pyrolysis oil from conventional heating contained a high proportion of aromatic hydrogen and small quantities of esters, nitriles and aliphatic hydrogen.

The results from the analysis of the microwave pyrolysis oils by means of FTIR showed that they were made up of aliphatic hydrogen together with ester, carboxylic or amide groups. The authors found that the use of microwave oven preserves some of the functional groups from the original sewage sludge such as aliphatic and oxygenated compounds

The authors [35] found the char to contain 83.5 % ash content with a calorific value ranging from 5000 to 7000 kJ/kg. The char was classified as low grade fuel due to ash content.

2.5.1.8 RECOVERY OF OILS WITH HIGH CALORIC VALUE AND LOW CONTAMINANT CONTENT BY PYROLYSIS OF DIGESTED AND DRIED SEWAGE SLUDGE CONTAINING POLYMER FLOCCULANTS [36]

The authors [36] investigated the properties of dried sewage sludge containing polymer flocculants. The pyrolysis experiments were carried out using a fluidized bed. The dimensions of the reactor had a height of 300 mm and an inner diameter of 80 mm. The reactor had a capacity of up to 1 kg/h and it was electrically heated. The pyrolysis temperatures used ranged from 446 –720 °C. Screw feeders were used to feed the sewage sludge onto the bed material that was made of sand. The reactor was also connected to a char separation system made up of a cyclone and hot gas filter. These were used to capture char fines ranging from 1-10 µm. Quenching columns cooled by water and ethanol were used to collect bio-oil. The permanent gases were recycled back to fluidised bed with the aid of a compressor.

The authors found an increase in the higher heating value of the pyrolysis gas as the reaction temperature increased. The main pyrolysis gases found were CO, CO_2, CH_4 and other light hydrocarbons. The highest value for the gas was found to be 30 MJ/kg. The pyrolysis oils were found to have varying viscosities. The pyrolysis oils obtained at higher temperature was found to be less viscous while those obtained at lower temperatures were more viscous.

The pyrolysis oil was found to contain acids, alcohols, aldehydes and hydrocarbons. The high temperature pyrolysis oils had a maximum higher heating value of 30 MJ/kg while the lower temperature pyrolysis oils were found to be 33 MJ/kg.

2.5.1.9 A TECHNICAL AND ECONOMIC EVALUATION OF THE PYROLYSIS OF SEWAGE SLUDGE FOR THE PRODUCTION OF BIO-OIL [25]

Kim and Parker [25] used a laboratory scale cylindrical batch reactor made from stainless steel for the pyrolysis reaction. The reactor was 16 cm in length and 4 cm in diameter. Nitrogen was used for purging the reactor. Three different types of sludges were used for the analysis. A mass of 5 g of dried sewage sludge was placed in the reactor that was tightly sealed using caps at both ends. Liquid yield was collected at the bottom of the separator while the non condensable gases escaped through the condenser. The results obtained from the experiment are summarised in Table 2.3.

Table 2.3: Summary of pyrolysis bio-oil and char yields [25]

The residence time for the pyrolysis reaction was not mentioned however the gas residence time was 20 minutes. Kim and Parker [25] found that the volatile content and pyrolysis temperature greatly affected the bio-oil and char yields. As the temperature increased from 250 to 400 ˚C, there was an increase in the bio-oil and gas yield. The non condensable gases were estimated to be 9 to 20 % while the energy loss was assumed to be less than 10 %. Different optimum temperatures were found for various sludges; activated sludge was 400 ˚C, primary and digested sludge was 450 ˚C. The primary sludge pyrolysis at 500 ˚C was found to have the best economic benefit.

2.5.1.10 STUDY OF BIO-OILS AND SOLIDS FROM FLASH PYROLYSIS OF SEWAGE SLUDGES [37]

The authors [37] carried out fast pyrolysis using three different sewage sludges. These were; thickened excess activated sludge, dewatered digested sludge and dried excessive activated sludge. The authors [37] used a semi continuous reactor for fast pyrolysis and white sand as the heat transfer medium. The reactor was made of stainless steel with a volume of 2200 ml which was heated externally by an outer jacket. A mass of 200 g of dried sewage sludge sample was used for analysis. The nitrogen gas flow into the reactor was 140 ml/min. The condensable gases were cooled into liquid using a collection vessel that was placed in liquid nitrogen while the non condensable gases escaped through the chimney.

The authors found the bio-oil yields based on ash free basis ranged from 39.2 to 57.5 %. The activated sludge was found to have the best results concerning pyrolysis products. It was found that 57.5 % of organic matter from this sludge was converted to bio-oil which had a calorific value of 24.7 MJ/kg. It also had the lowest water content of 10.3 wt%.

The bio-oil was also found to contain a range of compounds, which included carboxylic acids, alcohols, nitrogen compounds, sulphur, hydrocarbons and steroids. The authors found the organic phase to contain large quantities of fatty acid with lower aliphatic compounds. Pokorna et al [37] also found nitrogenous compounds to range from 27 to 29% from thickened excess activated sludge and 11 to 12% from the dried excessive activated sludge.

2.5.1.11 EFFECT OF PYROLYSIS TEMPERATURE ON THE COMPOSITION OF THE OILS OBTAINED FROM SEWAGE SLUDGE [38]

Sanchez et al [38] investigated the effects of composition of sewage sludge pyrolysis oil at temperatures of 350, 450, 550 and 950 °C. The reactor was made from quartz; it was 7 cm in diameter and 40 cm in length. A sample size of 30 g was placed in the middle to the reactor before the pyrolysis experiment. Helium was used to purge the reactor to ensure inert conditions. A flow rate of 100 ml/min was used and this lasted for 30 minutes before the start of the experiment. The heating rate of 30 K/min was used to reach the required temperature. GC-MS was used for analysis of the bio-oil samples.

The authors [38] observed a decrease in char yield as the temperature increased from 350 to 950 °C. This decrease is attributed to increasing de-volatilization of solid hydrocarbons in the char. The maximum pyrolysis oil yield was achieved at 450 °C with a 13 wt%, then decreased at 550 °C and then remained constant at 950 °C.

The authors found an increase in water content during pyrolysis with all the pyrolysis temperatures despite low moisture content from sewage sludge. The water production during pyrolysis was thought to be due to the breaking up of functional groups from the volatile compounds.

The authors reported no significant changes of gas yield from 350 to 550 °C. However there was increase in gas yield at 950 °C, this was attributed to secondary cracking of pyrolysis vapours.

The authors found that as the temperature increased from 350 to 950 °C, there was an increase the in the concentration of mono-aromatic hydrocarbons. On the other hand, there was a decrease of the phenol and its alkyl derivatives as the temperature increased.

CHAPTER 3: EQUIPMENTS AND METHODS

This chapter describes the laboratory scale equipments used and analytical methods applied to obtain the results reported in this thesis. The first section describes the liquid analysis, second set describes solids and the last part explains the gas analysis in detail.

3.1 LIQUID ANALYSIS

3.1.1 GAS CHROMATOGRAPHY- MASS SPECTROMETRY (GC/MS)

This equipment analyses compositions of various liquid samples. GC-MS analysis was carried out on HP 5890 series 11 with an Agilent auto sampler and coupled to HP 5972 series detector (TCD) (Fig. 3.1). The column used is a fused silica capillary column (14 % cyanopropylphenyl-86 % methylpoxysiloxane, 60m x 0.25mm x 0.25µm). The oven was raised from 40 ˚C to 290 ˚C at a rate of 3 ˚C/min and held for 20 minutes. Helium was used as a carrier gas a rate of 1 ml/min in a split ratio of 50:1. The injector temperature was held at 310 ˚C with a volume of 5 µl. The compounds were identified using NIST mass spectra library. The samples were diluted with chloroform to a ratio of 1:100.

Figure 3.1: The gas chromatograph mass spectrometry 5890 series

3.1.2 VISCOMETER

The viscometer was manufactured by Rheotek and had model no; BS/U 60 – 300. Three types of viscometers were used for analysis; size 100 measuring from 3 to 15 cSt, size 150 for 7 to 35 cSt and size 200 for 20 to 100 cSt. Sample preparation was made according to the British standard method BS 188:1977. The water bath was filled with water and heated to the required temperature with the aid of the controller and immersion heater (Fig. 3.2).

Figure 3.2: Experimental setup for viscosity measurement

The viscometer was charged with the sample using a long pipette to minimize any wetting of the tube (Fig. 3.2). The viscometer was then placed in a holder which was attached and immersed in the bath. The viscometer was allowed to reach the same temperature as that of the bath for approximately 10 -15 minutes. The level of the sample was adjusted by suction about 5 mm above the upper timing mark. Suction was controlled by a rubber tube that was connected to an open end of a viscometer.

A timer was set once the sample begun to flow freely from the first measuring point to another. The viscosity was measured using the Equation 3.1.

$$V = C * t \qquad \textit{Equation 3.1}$$

Where; V is the viscosity in centistokes (cSt), C is the viscometer constant, t is the time taken for a fluid to flow from one point to another (seconds).

3.1.3 KARL FISCHER TITRATOR

The Karl Fischer Titrator is used to determine the water content within a liquid sample. It utilises the quantitative reaction of water with Iodine and Sulphur dioxide in the presence of lower alcohols such as Methanol and an organic base i.e. Pyridine [39]. The Karl Fischer Titrator model used for titration is the V20 volumetric Titrator in accordance with ASTM E203. The titration beaker was filled with KF solvent and equipped with a magnetic stirrer.

The system first performs a pre-titration as a basis for a water free solvent. The measured sample is then injected into the titration beaker and weight is entered into the system. The water content is then measured according to the weight of sample used for analysis.

3.1.4 ACID NUMBER TITRATOR

The Mettler Toledo G20 compact Titrator is used for the determination of acid number in oils samples. It uses the ASTM method D664-04 by potentiometric titration with potassium hydroxide in 2-propanol [40]. The sample weight is chosen according to ASTM D664-04. The known amount of sample is dissolved in a portion containing the mixture of solvents Toluene, 2-propanol and water in a ratio of 500: 495: 5 ml [40]. The dissolved sample is then attached to the titrator for analysis. The electrode is rinsed with the solvent such as ethanol before the start of another titration.

3.1.5 FLASH POINT

The flash point measurements were carried out using the Seta flash Series 3 plus Closed Cup according to ASTM D7236. The equipment was preheated for approximately 5 minutes before analysis (Fig.3.3). The flame candles are lit and start temperature is set for the test. The test sample of 2 ml is injected onto a hot plate and temperature is ramped up gradually with 10 °C increments while manually flicking the flame onto the oil. The flash point is detected automated by the apparatus.

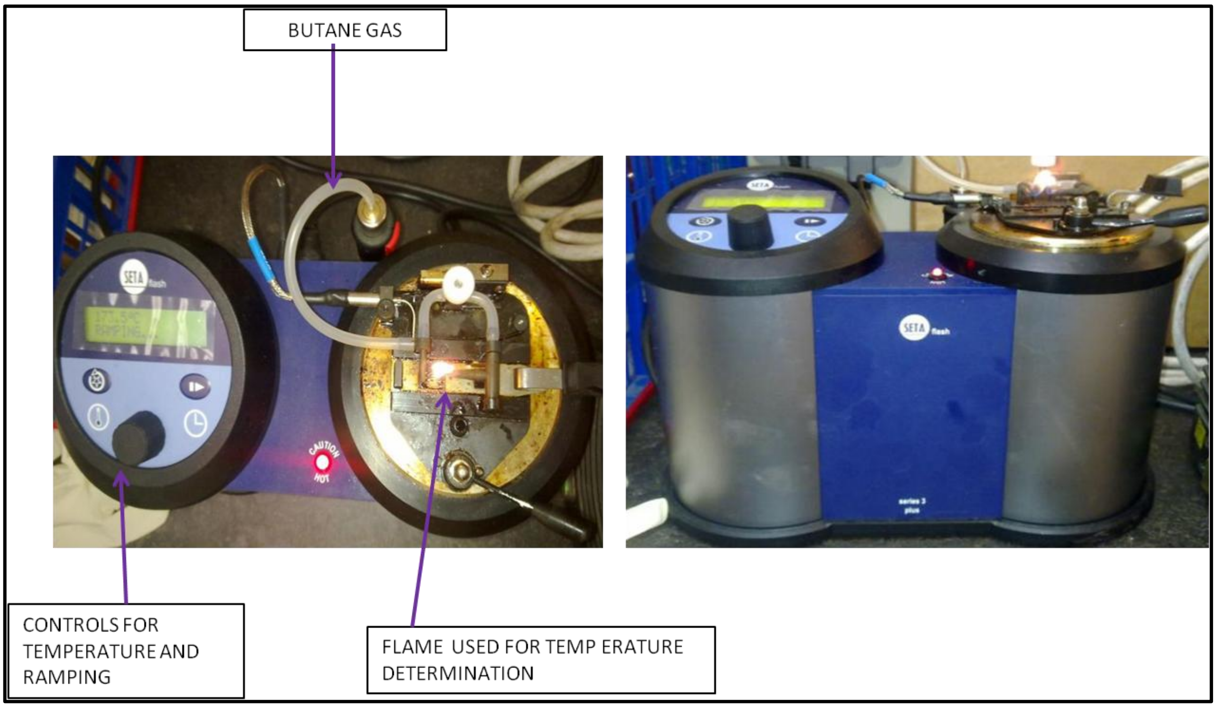
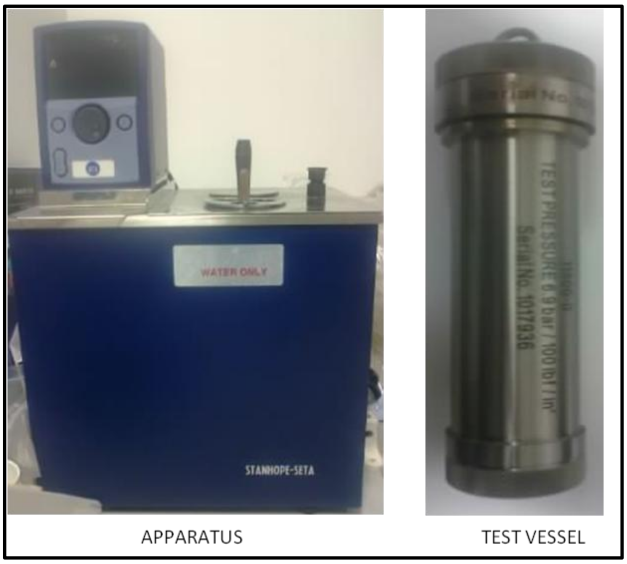


Figure 3.3: The Seta flash point tester used for flash point determination

3.1.6 COPPER CORROSION TEST

The copper corrosion test was determined using the Stanhope-SETA apparatus (Fig.3.4) in accordance with ASTM D130. A polished copper stripe was inserted into a copper corrosion test vessel that contained the test oil. The vessel was then immersed into an oil heating bath at 40 ˚C. The test was carried out at varying times from 1 hr to 12 hrs. The experiments were repeated three times for accuracy. The results obtained were compared to the ASTM D130 corrosion standard board supplied with the equipment.



APPARATUS TEST VESSEL

Figure 3.4: The Stanhope Seta equipment for the copper corrosion test

3.1.7 pH MEASUREMENT

The pH of the bio-oils was measured using a glass electrode connected to Sartorius pH meter. The pH meter was calibrated using three standardised buffer solutions (acidic, neutral and alkaline) obtained from Fisher Scientific used in accordance to ASTM D7544.

3.1.8 ASH CONTENT OF THE BIO-OIL

The ash content of the oil sample was determined in accordance with ASTM D482.The sample was preheated in the oven at 105 °C for 1 hour to remove water. The sample was then combusted in the muffle furnace at 775 ˚C for ten minutes. After cooling, the ash content was determined using the following equation [41];

$$Ash\ content = \frac{(A\ x\ 100)}{W} \qquad \textit{Equation 3.2}$$

Where; A is mass of sample after heating, W is the initial mass in grams.

3.2 SOLID ANALYSIS

3.2.1 THERMOGRAVIMETRY MASS SPECTROMETRY (TG-MS)

This technique was used to study the thermal decomposition of solids and possible reactions that might take place. The TG/MS technique was applied to sewage sludge samples in order to determine the decomposition behaviour during pyrolysis. This technique was also applied to determine the amount of moisture, volatiles, char and ash contained within the sewage sludge. The TGA model used for the experiments is the Mettler Toledo TGA/DSC1 (Fig. 3.5). This records the weight loss of a sample in relation to temperature change. In order to analyse a sample, a crucible was filled with a sample not greater than 15 mg which is then placed onto the sample holder. An empty crucible was then placed next to the sample crucible to maintain the correct balance. The furnace was then closed and purged with helium gas. The flow rate of the gas was set at 60 ml/min.

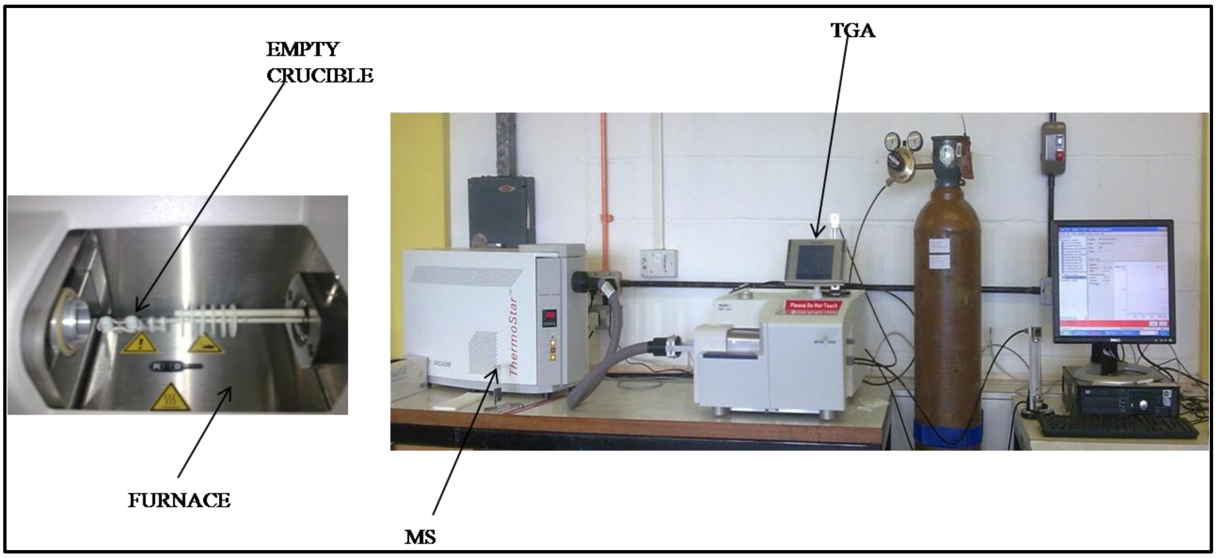


Figure 3.5: The setup of the Thermogravimetric Mass Spectrometry (TG-MS)

3.2.2 SCANNING ELECTRON MICROSCOPE (SEM)

This is a measurement tool that uses high energy electrons that focuses at the surface of a solid to reveal structure, arrangement and texture. Scanning electron microscope images were taken for the sewage sludge char and the co-pyrolysis biochar obtained from 40% wood, 40% straw and 40% rapeseed. The analysis was carried out at sub-company based at Aston University. The x-ray images of the char samples were carried out with the help of the expert based at the company. The expert used a Cambridge S-90 scanning electron microscope with digital imaging at various ranges.

3.3 LIQUIDS AND SOLIDS

3.3.1 BOMB CALORIMETER FOR HIGHER HEATING VALUE

The calorimeter measures the heat of combustion given out when the sample is burnt in the presence of oxygen. The heat capacity of the sample and the difference in temperature rise between maximum and minimum are then used to determine the higher heating value of the sample. The calorimeter used is the automated Parr 6100 calorimeter manufactured in the USA (Fig. 3.6). Benzoic acid is used to calibrate the calorimeter. The calorimeter uses 2000 g of distilled water and takes sample pellets of less than 1.10 g. The bomb itself takes 10 mm length of wire that was folded into a loop but doesn't touch the sample. The calorimeter was switched on and allowed to warm up for 20 minutes. The bomb was set on a support stand and fuse wire was attached between the electrodes. The sample was placed into the sample holder and a very little amount of water was placed in the bomb cylinder. This was closed and pressurised with oxygen at 45 psi and 3000 psi. This was then closed and the experiment was started by pressing on the screen of the calorimeter. The higher heating value is displayed on the calorimeter after completion.

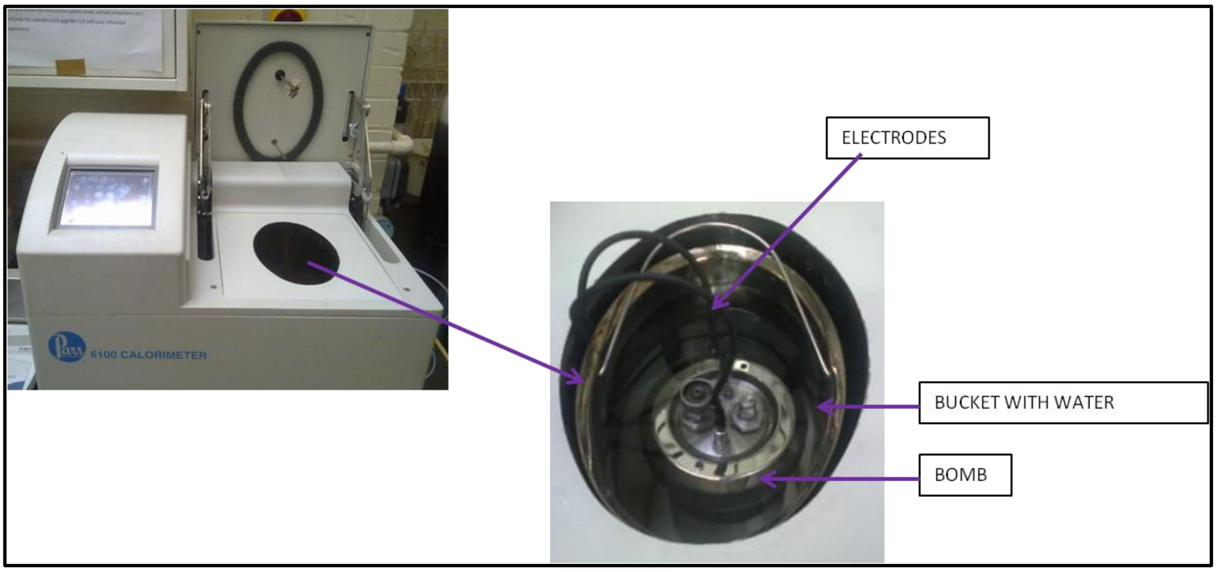


Figure 3.6: The experimental setup of the bomb calorimeter

3.3.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

It measures the amount of energy that was absorbed at each wavelength and this enables identification of chemical bonds in a molecule by producing an infrared absorption spectrum. The FT-IR used for analysis was manufactured by Perkin Elmer model spectrum ux (Fig. 3.7). In order to make an FTIR analysis, 10 mg of potassium bromide (KBr) was finely ground using a motor and paste.

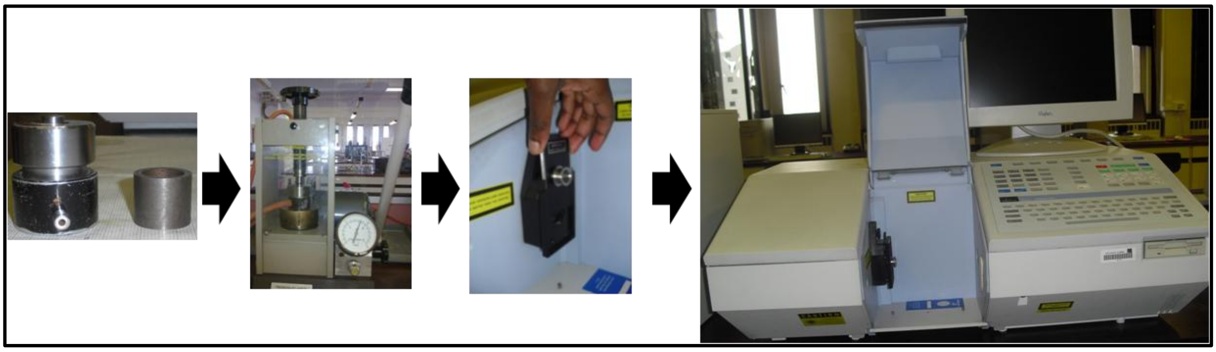


Figure 3.7: Sample preparation and Fourier Transform Infrared Spectroscopy (FT-IR)

Approximately 0.5 mg of the sample was mixed with potassium bromide using a motor and paste. A small quantity of the mixture was then into a holder and placed into the hydraulic press to make a pellet. The pellet was placed into the sample holder of the FTIR and slid into position. The analysis was then started using the FTIR software. A total of six sample runs were made.

3.3.3 ULTIMATE ANALYSIS

The elemental composition was determined by the ultimate analysis. The composition is made of carbon, hydrogen, nitrogen, oxygen and sulphur. The elemental analysis was carried out externally by [42]. They used the Carlo-Erba elemental analyser to carry out the tests. The errors in the values were given by the company to be ±0.03%.

3.3.4 INORGANIC COMPOUNDS

The inorganic compounds found in ash such sodium, calcium, potassium, phosphorus were measured externally by MEDAC Ltd [42]. They used the inductively coupled plasma-optical emission spectrometer technique to determine the inorganic compounds. The errors in the inorganic are given by [42] to be ± 0.3%.

3.3.5 MOISTURE ANALYSER

The moisture analyser used is an electronic unit known as the Sartorius moisture analyzer model MA35. It uses the infrared radiation from a tubular metal heating element to heat a sample. The equipment takes approximately 1 g of a sample with accuracy ± 0.2 % [43]. The apparatus is allowed to warm up for at least 30 minutes before the experiment. The sample is evenly spread on the pan for analysis. The weight of sample is entered and moisture content is determined after a few minutes.

3.3.6 DRYING OVEN

The analysis of the moisture content is carried out in a specialised oven. The method used is the ASTM D3174-87 that recommends a temperature of 105 °C for one hour. The sample weighing 1 g is measured and placed into the oven. After an hour, the sample is allowed to cool in the desiccator for about 30 minutes. The moisture content is then calculated from the equation below;

$$Moisture\ content(\%) = \left(\frac{A-B}{A}\right) x\ 100 \qquad \textit{Equation 3.3}$$

Where A is the weight of the sample before the experiment (g) and B is the weight of the sample after the experiment (g).

3.3.7 ASHING AND VOLATILES OVEN

The muffle oven is specially designed to allow measurements for ash and volatile content measurements. It has an outlet flange that is closed for measurement of volatiles and opened for measurement of ash content. Ash content is determined according to standard ASTM D3174-93. The experiment takes place in an oven whose temperature can rise up to 1000 °C. For this experiment, 1 g of sample was measured in a crucible and partially covered to allow some amount of air to enter. Replicates are made to determine consistency of the results.

The crucible was placed in the oven and temperature gradually from 100 to 750 °C every hour. After completion, the crucible was removed and cooled in a desiccator. Equation 3.4 was used to determine the ash content [44].

$$Ash\ content(\%) = \left(\frac{(A-B)}{C}\right) x\ 100 \qquad \textit{Equation 3.4}$$

A is weight of crucible, cover and ash residue (g), B is weight of empty crucible and cover (g) and C is weigh of analysis sample used (g).

The British standard for measurement of ash content was also used. It uses the BS EN 14775:2009 method and utilises a maximum temperature of 550 ˚C instead of 750 ˚C. The furnace temperature is raised to 250 ˚C with a heating rate of 7.5 ˚C/min and maintained at this temperature for one hour to allow volatile to escape [45]. The furnace is then raised to 550 ˚C at a heating rate of 10 ˚C/min [45]. This temperature is maintained for 2.5 hrs. The ash content is measured on dry basis using the following equation [45];

$$A = \frac{m_3-m_1}{m_2-m_1}\ x\ 100\ x \frac{100}{100-m_d} \qquad \textit{Equation 3.5}$$

Where m_1 is the mass (g) of the empty dish, m_2 is the mass (g) of the dish plus the test sample, m_3 is the mass (g) of the dish plus ash; M_d is the moisture content of the test sample and A is the ash content.

The Volatile contents were also measurement using the British standard BS EN 15148:2009. This method requires preheating the empty crucibles in the oven at 900 ˚C for 7 min [46]. These are cooled and the test sample is placed into the crucible. The test samples are then transferred to the oven at 900 ˚C for 7 min [46]. These are then taken out and allowed to cool to an average temperature before transfer to the desiccator. The volatile contain is then measured using the equation below [46];

$$V = \left[\frac{100(m_2-m_3) \quad -m_{ad}}{m_2-m_1}\right] x \ \frac{100}{[100-m_{ad}]} \qquad \textit{Equation 3.6}$$

Where m_1 is the mass of the empty crucible and lid, m_2 is the mass (g) of the crucible and lid and test portion before heating, m_3 is the mass (g) of the crucible and lid and contents after heating; M_{ad} is the moisture content of analysed sample and V is the volatile contents.

3.4 GAS ANALYSIS

3.4.1 PERMANENT GAS ANALYSIS

The analysis of the gases was carried out using the gas chromatograph (GC). The model number is 5890 series 11 gas chromatograph (Fig.3.8). The thermal conductivity detector (TCD) was used as the detector. Helium was used as the carrier gas for GC. The GC was calibrated using a mixture of permanent gases such as CH_4, H_2, N_2, and CO_2. A gas meter was used to determine the volume of non condensable gases produced. The gases were analysed by the system using the residence time that corresponded with particular calibration gases. Therefore, any gases found in the pyrolysis stream that was not used for calibration, cannot be detected by the system.

Figure 3.8: Gas chromatograph for permanent gas measurements

CHAPTER 4: CHARACTERISATION OF VARIOUS SEWAGE SLUDGES

This chapter investigates the properties of different sludges obtained at various stages in the waste treatment processes. Standard ASTM methods are used for proximate and ultimate analysis. Thermogravimetric mass spectrometry analysis (TG-MS) is to determine the amount of volatile, ash and study the decomposition rate of the sludge samples using DTG curves.

4.1 METHODOLOGY

4.1.1 THE SLUDGE SAMPLES

The sludge samples used for analysis are collected at various stages in the waste treatment process. Fig. 4.1 shows the location of the sludge samples and a description is given below. The samples were selected for analysis in order to understand the characteristics and impact of each stage. For the purpose of this investigation the sludge samples are grouped into two categories; the undigested and digested sludge.

Table 4.1: The origin and categories of the undigested and digested sludge

UNDIGESTED SLUDGE	SYMBOL	DIGESTED SLUDGE	SYMBOL
Crude Primary Sludge (Primary + Imports)	**A**	Post Digestion Liquid Sludge	**D**
Surplus Activated Sludge (SAS) – Biological Treatment	**B**	Post Digestion De-watered Sludge Cake	**E**
Anaerobic Digestion Feed (Mix Primary + Imports + SAS)	**C**	Dried Digested Sewage Sludge (~90% Dried Solids)	**F**
Dried Raw Undigested Sewage Sludge (Primary + Import + SAS)	**G**		

4.1.2 PREPARATION

All the samples with the exception of sludge F and G were received in form of a slurry with high moisture content. The samples were dried in the oven to obtain a solid residue. The solids were ground into powder using a motor and paste.

Figure 4.1: Sewage sludge treatment process and origin of samples various sewage sludges (obtained with permission from Severn Trent Water)

4.1.2 ANALYTICAL MEASUREMENTS

4.1.2.1 PROPERTIES OF THE SLUDGES

Analysis of different sewage sludges obtained from different stages within the sewage treatment processes were tested for moisture, char and ash on a dry basis and the results are recorded in Table 4.2. The moisture, char and ash content were determined on dry basis using the standard ASTM D3174-87, D3174-93. The ultimate analysis for the sludges was done externally by [42]. All the results are presented on a dry ash free basis. The higher heating values were obtained using a bomb calorimeter as described earlier.

4.1.2.2 PROXIMATE ANALYSIS BY TG-MS ANALYSIS

This technique was also applied to determine the amount of moisture, volatiles, char and ash contained within the sewage sludge. The TGA model used for the experiments is the Mettler Toledo TGA/DSC1.

4.1.2.3 DTG CURVE USING TG-MS

This technique was used to study the thermal decomposition of solids and possible reactions that might take place. The TG-MS technique was applied to sludge samples in order to determine the decomposition behaviour during pyrolysis. In order to ensure pyrolysis conditions, the furnace was purged with Helium gas at a rate of 60 ml/min.

4.2 RESULTS AND DISCUSSION

4.2.1 PROPERTIES OF THE SLUDGES

4.2.1.1 PROXIMATE ANALYSIS

Table 4.2 shows the characteristics of sludge obtained at various locations from the waste treatment process. The proximate analysis of the sludges was characterised using standard ASTM D3174-93 and D3175-11. Further details are given in Appendix 1. On average the undigested sludge has the highest amount of volatile matter compared to the digested sludges. The trend of the sludge is expected, this is because the digested sludge undergo decomposition by microorganism that utilise most of the organic matter. This results into having less volatile matter and high ash content has shown in Table 4.2.

4.2.1.2 ULTIMATE ANALYSIS

The undigested sludge has the highest amount of carbon content compared to the digested sludge. This is because the carbon compounds are given of as CH_4 and CO_2 during anaerobic digestion while the nitrogen is given of as NH_4. In addition to this, the digested sludge had slightly higher levels of sulphur content compared to the undigested sludge.

4.2.1.3 HIGHER HEATING VALUE

Table 4.2 shows that the higher heating values of the undigested and digested sludges increase with increasing carbon content. The undigested sludge has the highest heating values compared to the digested sludges. The highest value recorded for the undigested sludge is 17.5 MJ/kg while the lowest value for the digested sludges was only 12.38 MJ/kg. The amount of ash present in the sewage sludge also affects the higher heating value. The undigested sludge (G, A, C, B) have lower ash contents and more organic compounds. This implies that they have more combustible material and less inorganic compounds than the digested sludge (D, E, F) that have more inorganic compounds. During anaerobic digestion, the organic materials are broken down by micro-organisms that also form CH_4 and CO_2. This results in having more inorganic compounds in the digested sludge.

Table 4.2: Characterisation of various sludges

	UNDIGESTED SLUDGE				DIGESTED SLUDGE		
	G	**A**	**C**	**B**	**D**	**E**	**F**
Proximate analysis (±1)(wt %)[a]							
Moisture	9.53	4.96	4.53	6.12	4.69	6.11	10.05
Ash	27.80	33.04	35.18	36.86	41.33	42.18	43.00
Volatile matter	62.67	62.00	60.29	57.02	53.98	51.71	46.95
Ultimate analysis (±0.03)(wt %)[b]							
C	36.58	35.8	35.01	31.25	31.01	27.9	28.25
H	5.95	5.81	5.69	5.26	5.01	4.7	4.83
N	3.86	4.44	4.64	5.66	3.94	3.89	3.81
O	29.12	27.5	26.41	32.22	26.59	25.68	27.13
S	1.03	1.01	1.15	0.9	1.4	1.36	1.41
HHV (±0.001)(MJ/kg)	17.5	17.10	15.98	14.50	13.40	12.74	12.38

[a]Weight percentage based on dry basis

[b]Weight percentage based on dry and ash-free basis (results obtained externally)

4.2.2 PROXIMATE ANALYSIS BY TG-MS ANALYSIS

The samples were ground and sieved so an assumption has been made that the samples used are a true presentation of the sludge before sieving. Table 4.3 shows the moisture, volatiles, char and ash content on a dry basis calculated from the pyrolysis and combustion of sludge samples. It was found that the undigested sludges have the higher moisture content on average compared to the digested sludges.

4.2.2.1 VOLATILES

In general, the undigested sludges have the highest rate of volatiles compared to the digested sludge. The undigested sludge G showed the highest amount of volatiles among the undigested sludge. Since sludge G is dried raw undigested sludge, it contains a lot of organic compounds that decompose when heated resulting into high rates of volatiles compared to other sludge.

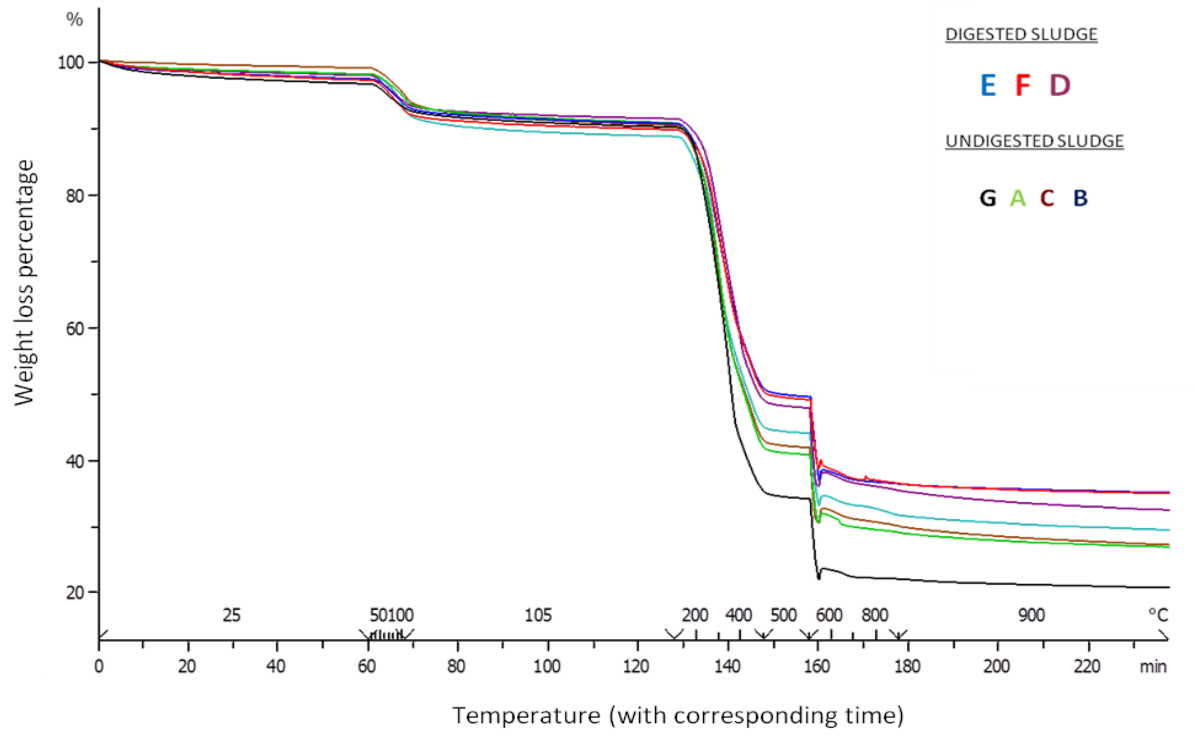


Figure 4.2: Thermogravimetric (TG) curves for the digested and undigested sludges used to obtain the proximate analysis results shown in Table 4.3

Table 4.3: Proximate analysis results obtained from the TG-MS

	Pyrolysis			Combustion	
	Average Yields of 105 – 500 °C			Average Yields of 500 – 900 °C	
	Moisture	Volatiles	Char	Char	Ash
Undigested sludge					
G	10.32	56.17	33.54	13.24	20.29
A	9.23	50.59	40.19	14.44	25.74
C	9.72	48.52	41.80	14.76	27.04
B	11.08	45.13	43.82	14.43	29.38
Digested sludge					
D	8.25	43.43	48.31	15.29	33.03
E	9.51	41.08	49.41	15.12	34.24
F	11.59	40.00	48.42	13.96	34.55

[a]Weight percentage on dry basis (±0.04 wt.%)

4.2.2.2 ASH CONTENT

Overall the digested sludges have the highest ash content compared to the undigested sludges. The digested samples E and F have the highest ash content while the undigested sludge G has the lowest ash content. This trend is in agreement with the results obtained from Table 4.2. The results are expected because the undigested sludge contains more organic compounds while these are broken down during the anaerobic digestion for the digested sludge. This leads to a lower volatile and higher ash content. Kim and Parker [25] found similar results with various types of sewage sludges. Other authors [6] [30] [37] have focused on the digested sludges due to large volumes and for safety purposes.

4.2.3 DTG CURVE USING TG-MS

The TGA curve shows a plot of mass against temperature that is converted into a DTG curve, which measures the rate of mass loss against temperature (dm/dt). The analytical method is given in Appendix A1.3. DTG allows identification of various mass losses at different temperatures. The peaks from the DTG curves give an indication of the decomposition temperature of compounds found in sewage sludge. Fig. 4.3 shows the curve for the digested and undigested sludges indicating different decomposition behaviour.

The observed weight loss from 50 to 200 °C occurs due to evaporation of water molecules contained within the sludges. At a temperature range of 200 to 400 °C, most of the organic matter is degraded resulting into high decomposition peaks shown in Fig. 4.3. The undigested sludges undergo more decomposition during pyrolysis than the digested sludge. Sample G (undigested sludge) has the highest rate of mass loss occurring over a broad temperature range between 180 to 400 °C which reflects degradation of organic compounds.

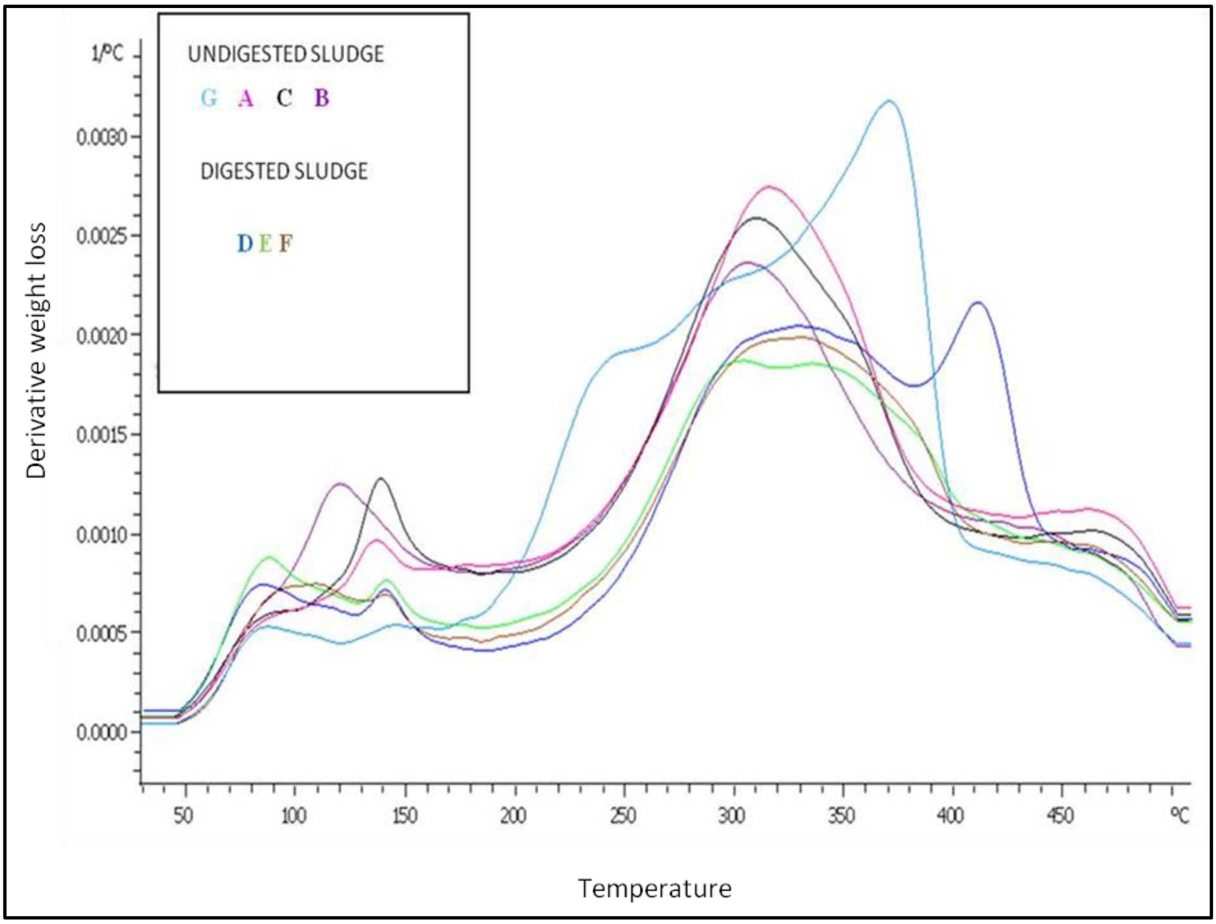


Figure 4.3: DTG curve showing the decomposition rate of the digested and undigested sludges against temperature

The undigested sludges A, C and B show similar pattern of the DTG curve and peaks occur within the region of 300 to 340 ˚C. The digested sludges E and F have peaks within the temperature range of 290 to 360 ˚C while sample D shows peaks between 290 to 370 ˚C and then at regions of 410 to 430 ˚C. Most of the sludge decomposition occurs by 450 °C although there are some reactions that occur between 450 and 500 °C. Any of these two temperatures would therefore be ideal for pyrolysis of sewage sludge although 500 °C would be more suitable.

In general, the undigested sludge undergoes more decomposition than the digested sludge. This is due to the presence of high amounts of organic content and volatile matter present within the undigested sludge that decompose various temperatures.

4.3 SUMMARY

The dried raw undigested sludge named as sample G, has the best higher heating value of 17.5 MJ/kg, it also has the highest amount of volatiles and lowest ash content. This sludge would be ideal as a raw material for the pyrolysis process as it would be predicted to give higher bio-oil content due to the presence of a high organic content. However due to the presence of pathogens and other unknown micro-organisms that are present in the undigested sludge, it was not possible to work with this material on a larger scale. The digested sludge on the other hand has been rigorously regulated and tested by the Environmental Agency. It poses less risks compared to the undigested sludge and due to high volumes being generated on a daily basis, this material offers great opportunity for investigations.

The decomposition curves show that highest degradation of the organic compounds found in the digested sludge occurs in the range of 280 to 450 °C. Therefore a pyrolysis temperature of 450 °C could be sufficient to degrade all the organic compounds. Fonts et al [47] found that many authors had found the best pyrolysis temperature for sewage sludge to be 450 and 500 °C.

CHAPTER 5: INTERMEDIATE PYROLYSIS OF SEWAGE SLUDGE

This chapter describes the use of the intermediate pyrolysis process to obtain bio-oil, biochar and non condensable gases from sewage sludge. It describes the preparation steps of the feedstock for analysis to the operation of the reactor used to carry out the process. It also investigates the properties of bio-oil, biochar and the gases compared to other processes.

5.1 METHODOLOGY

5.1.1 FEEDSTOCK

It should be noted that the sewage sludge used for the intermediate pyrolysis process is from a different site (Netheridge, UK) to that reported in chapter 4 although all the samples are from the same company. The sludge used for the pilot plant scale is maintained throughout this thesis. The sludge used for intermediate pyrolysis is the residue collected after the anaerobic digestion process from the domestic waste treatment. This residue is commonly known as the digested sludge. For the purpose of this report, the digested sludge will be referred to as sewage sludge, since this is the name commonly used by industry and regulatory authorities to refer to the end product from the waste treatment process.

5.1.2 SEWAGE SLUDGE PREPARATION

The feedstock requirement for intermediate pyrolysis can be any form or size depending on the size of the feeding chute of the reactor except powder form. The reactor used to carry out the pyrolysis process can only take sample sizes ranging from 3.5 to 11.5 mm; any particles smaller or larger than this creates blockage problems from the screw feeder to the reactor.

The sewage sludge used for analysis is dewatered by the centrifugal process. It contains a high water content and difficult to handle in this state. In order to ensure uniformity of the samples, the sewage sludge undergoes through the following preparation stages (Fig.5.1);

5.1.2.1 DRYING

Sewage sludge is received in a wet sticky form. The material is dried in the oven by placing it on large trays. It was dried at 60 °C from 5 to 7 days until the sludge was less than 10 % moisture content. The dryer has an extractor connected to it that enabled the escape of odour and moisture that arouse from the sludge.

5.1.2.2 HAMMERING

After the drying process, the sewage sludge was in the form of hardened material similar to dried clay. A hammer was used to breakdown the big chunks of material into smaller particles. This process is very tedious and takes several days to complete.

5.1.2.3 GRINDING

The sewage sludge particles are then ground into powder using a kitchen blender. This stage prepares the materials for the next process and also ensures uniformity of the material. It is very time consuming and takes several weeks as the blender used over heats and breaks down continuously due to the nature material.

5.1.2.4 PELLETIZING

The sewage sludge powder is then mixed rigorously with 10 wt% water. The adding of water is necessary and it acts as a binding agent for the formation of pellets. The mixed material is placed in the pelletizer in small amounts. The pelletizer has two rollers fixed with screws on both ends. The screws rotate forcing the material through the outlet holes thus forming pellets.

Figure 5.1: Sewage sludge preparation from drying to pelletizing

5.1.3 MAJOR COMPONENTS FOR INTERMEDIATE PYROLYSIS

The pyroformer is a reactor used to perform the intermediate pyrolysis process. The reactor is a horizontal cylindrical shaped unit made from carbon steel. It is 180 cm in length and has an internal diameter of 20 cm. It has two screws, one inner and outer screw that rotates in opposite directions. The inner screw takes material in, while the outer screw transports the char backwards. The reactor contains many components but some of the major parts as shown in Fig. 5.2 include; the mains control, control panel, feeding chute, condensers and electrostatic precipitator. The power for the reactor is supplied through the mains supply. The control panel is the main control box for the feeder systems and reactor components. The movement of the two screws are facilitated by the motor attached to the reactor. The outer and inner screw rotations were set at 4 revolutions per minute (rpm) for outer and 1.25 rpm for the inner screw. The temperature in the reactor was set gradually up to 450 ˚C.

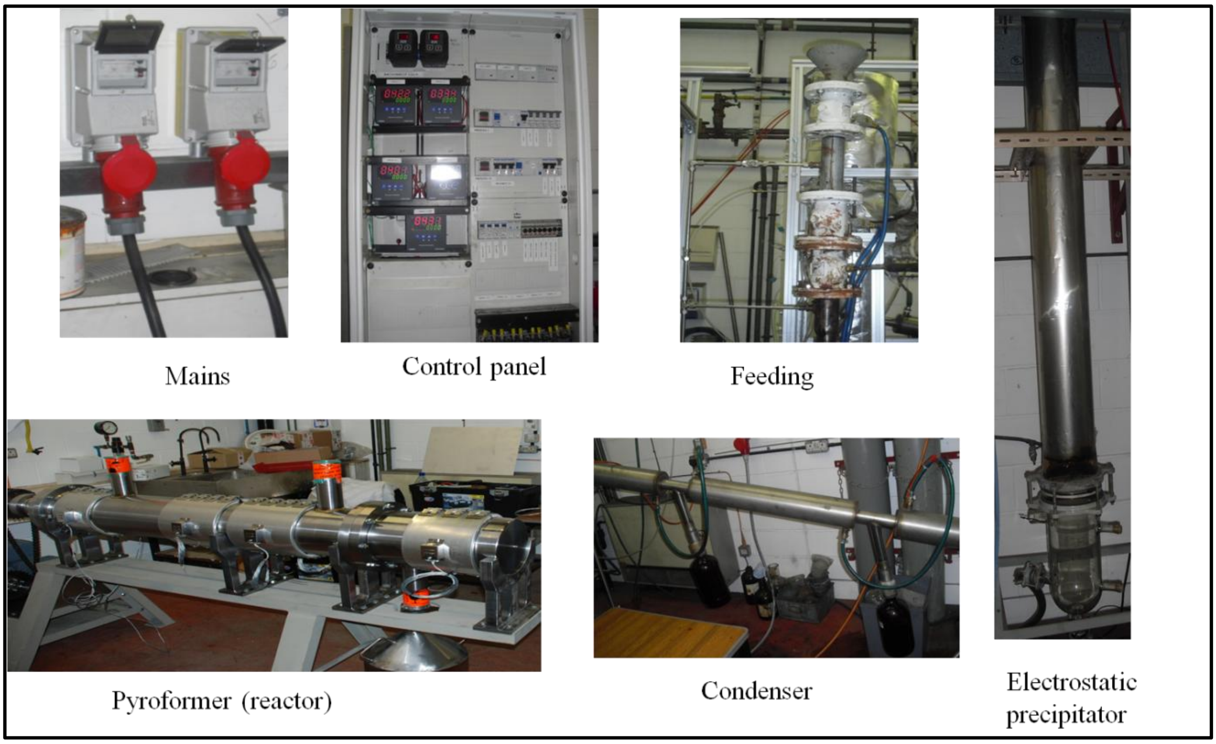


Figure 5.2: Major equipments used for the intermediate pyrolysis process

Nitrogen was purged through the reactor before the start of the experiment to remove any presence of oxygen to ensure that pyrolysis conditions are met.

5.1.4 INTERMEDIATE PROCESS REACTION

The sewage sludge pellets were fed through the feeding chute into the reactor (Fig.5.3). The pellets were fed at a rate of 4.5 kg/hr. The vapours produced in the reactor were then sent through the hot gas filtration to remove any impurities and the rest of the condensable vapours were cooled with water in the condenser to form bio-oil. The non condensable gases were expelled through the Electrostatic precipitator (ESP) that removes aerosols and also collects some of the bio-oil residues.

Figure 5.3: The pilot plant experimental setup of the intermediate pyrolysis process [48]

1. Reactor 2. Feeding hopper 3. Feeding chute 4. Heating unit 5. Inner screw 6. Outer screw 7. Screw driving motors 8. Pyrolysis vapour outlet 9. Reactor stands 10. Char pot 11. Hot gas filter, 12. Shell and Tube condenser 13. Electrostatic precipitator 14. Gas vessel 15. Exhaust system.

5.2 INTERMEDIATE PYROLYSIS RESULTS AND DISCUSSION

5.2.1 SEWAGE SLUDGE CHARACTERISATION

The characteristics of sewage sludge are reported in Table 5.1. This shows the ultimate and proximate analysis of the sewage sludge. It should be noted that sewage sludge composition will vary slightly even if it is produced from the same treatment process.

5.2.1.1 VOLATILES

Sewage sludge has a high volatile content due to the presence of various types of organics. The high volatile content enables the use of sewage sludge as a potential fuel. The organic compounds are broken down during the pyrolysis process to yield bio-oil. The presence of organic compounds in sewage sludge enables it to be used as a fertilizer on farms. The micro-organisms present in the soil are able to breakdown the organic molecules and extract nutrients.

5.2.1.2 ASH CONTENT

The ash content found in sewage sludge was found to be 32.6 wt%. Sanchez et al [38] found a similar value of 32.4 wt% of the digested sludge. Fonts et al [30], Piskorz et al [31], Stammbach et al [32], Pokorna et al [37], Kaminsky and Kummer[49], found higher ash contents ranging from 39 - 47.5 wt%. The ash is mainly composed of inorganic compounds such as CaO, P_2O_5, Al_2O_3, Fe_2O_3, K_2O, and ZnO as shown in Table 5.1. The most abundant of the inorganic compounds are Si, P and Ca. The ash content in the biomass influences the pyrolysis reaction and has a great impact on the product yield especially potassium and calcium [50].

5.2.1.3 CARBON AND HYDROGEN CONTENT

As a raw material, sewage sludge as a high carbon and hydrogen content although some of this is lost during the anaerobic digestion process as CH_4 gas. The high carbon content of 35.6 wt% with a 5.2 wt% contributes greatly to its energy content. Stammbach et al [32], Park et al [36] found higher values for the carbon to range from 50.3 - 55.45 wt% while the hydrogen content ranged from 7.1 - 8.2 wt%. However, Fonts et al [30] found the carbon to be 27.7 wt% and hydrogen content to be 4.4 wt%. The variation in carbon and hydrogen content is due to composition of the sewage sludge. This will vary from batch to batch, country to country and region to region.

5.2.1.4 NITROGEN CONTENT

Sewage sludge contains a high nitrogen content of 4.3 wt% compared to lignocellulosic biomass such as wood and straw. However, Stammbach et al [32], Dominguez et al [35], Park et al [36], found the nitrogen content to be much higher, this ranged from 6.1 to 7.42 wt%. The high nitrogen content originates from impurities such as dead bacteria and microbes that contain proteins and peptides [5]. The high nitrogen content from the sewage sludge enables it to be used as a fertilizer.

5.2.1.5 HIGHER HEATING VALUE

Sewage sludge has a relatively high energy content of 15.3 MJ/kg. Park et al [36] found the same value for the digested sludge in Korea to be 15.2 MJ/kg while Fonts et al [30] found this to be 11.9 MJ/kg. The energy content is greatly affected by the water content, so low water content will have high energy content. It is also affected by the type of sludge; digested sludge will have a lower energy content compared to the undigested sludge as these have more combustible or organic matter present. The higher heating value of the sludge is also slightly less than lignocellulosic biomass such as mixed wood that has energy content of 17 MJ/kg. The availability of this energy in the sewage sludge makes it an ideal biomass for energy recovery through various sources.

Table 5.1: Proximate and ultimate analysis for sewage sludge

	Sewage sludge
Proximate analysis(±1) wt.%[a]	
Moisture	4.7
Volatiles	63.7
Ash content	32.6
Ultimate analysis(±0.03) wt.%[b]	
C	35.6
H	5.2
N	4.33
O [c]	53
S	1.87
Ash analysis(±0.3) wt.%[b]	
SiO_2	6.37
P_2O_5	5.15
CaO	4.00
Fe_2O_3	2.39
Al_2O_3	2.12
K_2O	0.52
ZnO	0.20
CuO	0.15
HHV (±0.001)(MJ/kg)	15.3

[a] Weight percentage on dry basis

[b] Weight percentage on dry and ash-free basis (values obtained externally)

[c] Obtained by difference

5.2.2 INTERMEDIATE PYROLYSIS YIELDS

The products obtained from the sewage sludge intermediate pyrolysis process are summarised in Table 5.2. The product yields are estimated from the mass outputs of bio-oil and biochar. The non condensable gases are estimated by difference.

Table 5.2: Product yield from intermediate pyrolysis of sewage sludge

Total mass in(kg)(±0.5)[a]	Char out	Bio-oil	Permanent gases (by difference)
10.5	5.2	4.2	1.1

[a] Weight percentage on dry mass basis

5.2.3 BIO-OIL CHARACTERISATION

The bio-oil produced for the pyrolysis of sewage sludge consists of two layers; the pyrolysis oil (organic/upper phase) and aqueous phase (Fig.5.4). The pyrolysis oil is dark in colour and less dense while the aqueous phase is clearer and denser. These two properties make the separation of the two phases by decantation easier. Dominguez et al [35] used the same method of phase separation while Inguanzo et al [6] used the centrifugal process to separate the organic from the aqueous phase. The phases are analysed separately for physicochemical properties and composition.

The quantity of pyrolysis oil obtained from the intermediate pyrolysis process was 33 wt% of the total bio-oil yield. This is much lower than the values reported by Pokorna et al [37] to be 44 wt%, Park et al [36] to range from 52-57 wt% and Inguanzo et al [6] to be 60 wt%. The reason for these differences is because these authors used fast pyrolysis processes on sewage sludge that enabled higher pyrolysis oil yields. It should also be noted that these authors [3][6][36] used varying reaction conditions.

The aqueous phase from the intermediate pyrolysis process was found to be 67 wt% of the total bio-oil yield. Inguanzo et al [6] found to this to range from 30 to 40 wt% at various temperatures. This is much lower than that obtained from the intermediate pyrolysis process.

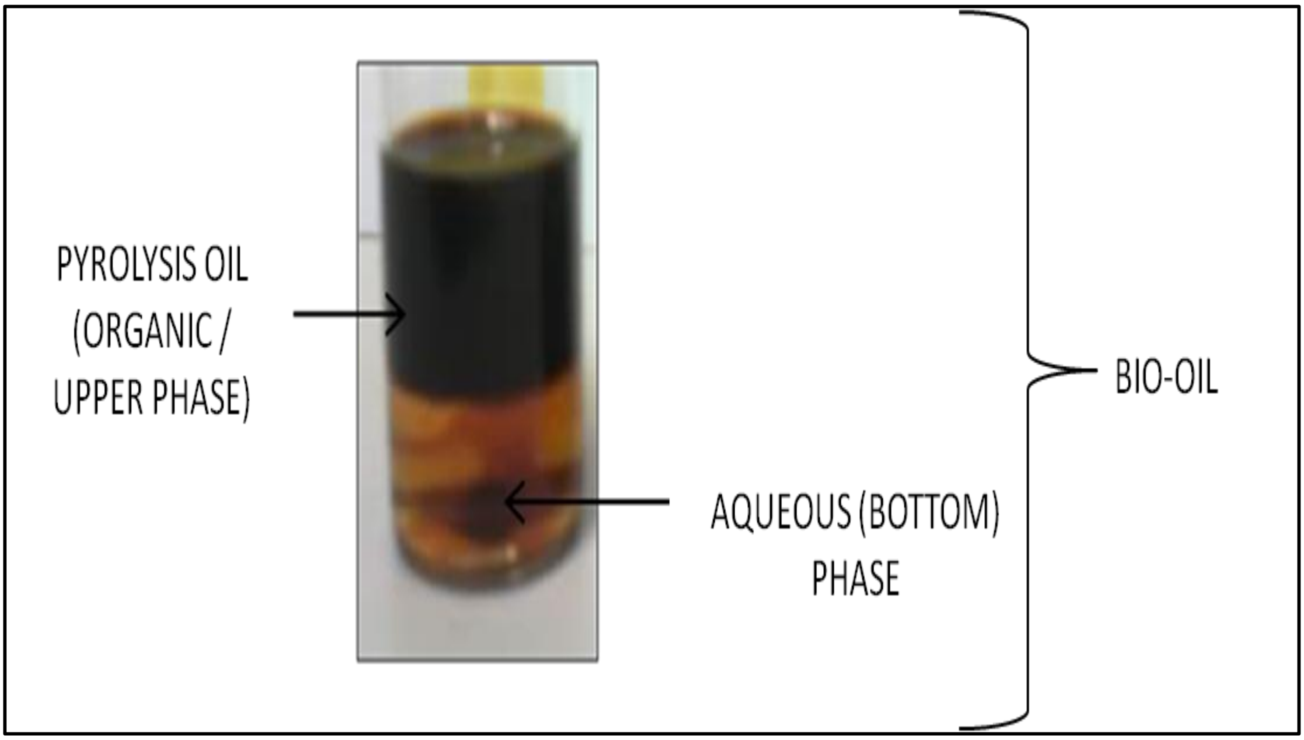


Figure 5.4: The sewage sludge bio-oil obtained from the intermediate pyrolysis process

5.2.4 THE PHYSICOCHEMICAL PROPERTIES OF SEWAGE SLUDGE PYROLYSIS OIL

The characteristics of the pyrolysis oil of sewage sludge bio-oil are summarised in Table 5.3. These are compared to biodiesel and diesel.

5.2.4.1 CARBON AND HYDROGEN

The sewage sludge pyrolysis oil has a high carbon and hydrogen content as shown in Table 5.3 compared to the sewage sludge. The high carbon and hydrogen contribute greatly to the energy content of the pyrolysis oil. Kim and Parker [25] also found the carbon and hydrogen to be 69–74 wt% and 9.7–9.9 wt%. The results are similar to those obtained from the intermediate pyrolysis process.

5.2.4.2 OXYGEN CONTENT

The sewage sludge pyrolysis oil has a relatively low oxygen content ranging from 8.0 to 12.8 wt% compared to those reported in literature by Inguanzo et al [6] and Park et al [36]. The former found this to range from 20.4 to 34.9 wt% while the latter found this to be 24.6–45.7 wt%. In general, pyrolysis oils have a higher oxygen content compared to diesel and biodiesel. The amount of oxygen present in the bio-oil depends on the composition. The presence of high oxygenated compounds will increase the oxygen in the bio-oil. The high oxygen content in the pyrolysis oil is an advantage during combustion in a diesel engine as this aids the formation of CO_2 instead of CO, which is due to incomplete combustion.

5.2.4.3 NITROGEN CONTENT

The sewage sludge pyrolysis oil has a high nitrogen content ranging from 5.1-5.8 wt% compared to biodiesel and diesel. However, Fonts et al [30] and Pokorna et al [37] found this to be 8 wt%. This is much higher than that obtained from the intermediate pyrolysis process. The amount of nitrogen in pyrolysis oils is dependent on the nature of feedstock used for pyrolysis. Pyrolysis oils intended for fuel applications should have low amounts of nitrogen. Nitrogen in fuels reacts with oxygen at high temperatures to form NO_x that pollutants the environment.

5.2.4.4 SULPHUR CONTENT

It is essential to know the sulphur content in a proposed fuel as this affects the engine performance and emissions. Sulphur is also a major environmental concern as it is converted to SO_X upon combustion that contributes to acid rain. The pyrolysis oil has a high sulphur content ranging from 1.9 to 3.3 wt%. This is higher than the average value obtained by authors in literature [6][30][36][37] who found the sulphur content to range from 0.4 to 2.4 wt%. Large quantities of sulphur are reported to increase carbon deposits in cylinders and on pistons, and cause corrosion in engine cylinders [51]. Due to the major concerns of sulphur in the EU, the sulphur content of diesel fuels was reduced to 0.05 wt% in 1996 [51]. This has been amended according to Council directive 1999/32/EC to a maximum sulphur content of 1% by mass in 2003 [52].

5.2.4.5 WATER CONTENT

The water content found in bio-oil originates from the feedstock and generated during the pyrolysis process [47]. The temperature used for the pyrolysis process greatly affects the water content [47]. The type of separation process between the organic and aqueous phase also contributes to the amount of water present in the pyrolysis oil. Sewage sludge pyrolysis oil has a low water content of 4.12 wt% as shown in Table 5.3. The water content obtained is much lower than that reported by Piskorz et al [31] to be 22 wt %, Fonts et al [30] to be 40 and Sanchez et al [38] to be 58 wt% carried out at 450 °C with fast pyrolysis process. Pyrolysis oils have higher water content compared to biodiesel and diesel fuels (Table 5.3). Pyrolysis oil intended for fuel applications should have little or no water content as this affects the energy content and causes poor ignition.

5.2.4.6 HIGHER HEATING VALUE

The sewage sludge pyrolysis oil has a high energy content ranging from 35 to 39 MJ/kg. Several authors found varying energy content for the sewage sludge pyrolysis oil. Inguanzo et al [6], Pokorna et al [37], Fonts et al [30] found this to range from 22 to 34 MJ/kg while Kim and Parker [25] found to range from 38 to 39 MJ/kg. The pyrolysis of sewage sludge from a refinery was reported by Karayildirim et al [24] to have a high energy content of 45 MJ/kg. These energy contents are much higher than those reported from lignocelluloses biomass such as wood. The varying energy content is affected by the properties of the sewage sludge and pyrolysis conditions. The presence of lipids in the sewage sludge contributes significantly to the high energy content [47]. This energy content makes the pyrolysis oil a suitable fuel for various processes.

Table 5.3: Properties of sewage sludge pyrolysis oil and other fuels

	Units	Sewage sludge pyrolysis oil	Biodiesel	Diesel
Water content	(±1) wt.%	4.12	0.4	N/A
Ultimate analysis	(±0.03) wt.%[a]			
C		64.7-74.2	78.86	85.6
H		9.7-9.9	12.63	13.37
N		5.1-5.84	<0.10	<0.10
O		8-12.8	7.67	0.83
S		1.9-3.3	0.74	<0.10
Viscosity @ 40˚C	(±1) cSt	38-45	4	6
pH	(±0.1)	9.6	7	7
Acid no	(±0.1)mgKOH/g	21.7	0.8	0.01
Copper corrosion test		4b	1a	1b
Density	(±0.1)g/ml	0.990	0.897	0.825
Ash content	wt.%	0.23	0.1	0.01
Flash point	°C	150	160	64
HHV	(±0.001)(MJ/kg)	35.6-39	39	45

[a]Weight percentage based on dry ash free basis

5.2.4.7 KINEMATIC VISCOSITY

The pyrolysis oil has a high viscosity ranging from 38 to 45 cSt compared to diesel and biodiesel. A few authors in literature were able to determine the viscosity of the sewage sludge pyrolysis oil. Shen and Zhang [34] found to range from 102 to 157 cSt while Gil-lalaguna et al [53] found this to range from 400 to 1500 cSt. On the other hand, Bahadur et al [33] found the oil from catalytic pyrolysis of lipids extracted from sewage sludge to have a very low viscosity of 1.88 cSt. Shen and Zhang [34] found that the ash content helped to reduce viscosity. The ash aids in cracking of long chain molecules into shorter molecules and this principle is adapted with the intermediate pyrolysis process with the char cycling within the reactor that enables lower viscosity pyrolysis oil compared to those in Literature [34][33][53].

5.2.4.8 DENSITY

Density provides information about a fuel's performance. Sewage sludge pyrolysis oil has a high density of 0.990 g/ml compared to 0.825 g/ml and 0.897 g/ml for diesel and biodiesel. Fonts et al [30] also found the pyrolysis oil to be 0.94 g/ml. The density of a fuel has an impact on the performance of a diesel engine. This is because the fuel injection system operates on a volume metering system [51]. This implies that since the sewage sludge pyrolysis oil has a higher density than diesel and biodiesel, a greater mass of pyrolysis oil will be injected. The high density of pyrolysis oil compensates for the lower energy content compared to diesel and biodiesel. On the other hand, an increase in fuel density can cause problems such as increased smoke, reduced fuel spray penetration in the cylinder and an advance in fuel injection timing [51][54]. This may lead to engine instability during operation and poor combustion [54].

5.2.4.9 ACID NUMBER AND pH

The acid number differs from a pH test as this provides the concentration of acid or alkaline constituents. These can include weak organic acids such as carboxylic acid, alcohols, phenols, acetic acids and strong inorganic acids i.e. sulphuric, phosphoric and nitric acid. Sewage sludge has a relatively low acid number compared to lignocellulosic biomass such as wood that has been reported to have 50-100 mg KOH/g [55]. The acid number of sewage sludge originates from the reaction of the phenols that are present in the bio-oil. Although the sewage sludge pyrolysis oil has a low acid number it is considered corrosive to carbon steel.

The pH test measures the apparent pH of the sample and gives an indication of the corrosiveness of a sample. Pyrolysis bio-oils have been reported by Bridgwater [26] to be acidic in nature. However, sewage sludge pyrolysis oil is alkaline with a pH of 9. The alkaline state of the pyrolysis oil is due to the presence of nitrogen compounds [35] [49]. Other authors like Kaminsky and Kummer [49] and

Dominguez et al [35] also found the sewage sludge pyrolysis oil to be alkaline. However, Fonts et al [30] found this to be nearly neutral with a pH of 7.8.

5.2.4.10 FLASH POINT

Flash point is the temperature at which the oil produces enough vapour to cause ignition. The flash point of sewage sludge pyrolysis oil is 150 ˚C which is much greater than that of diesel fuel that is 64 ˚C. This means that the pyrolysis oil will ignite at a higher temperature than diesel, making it safer to transport. However biodiesel will ignite at a much higher temperature than the pyrolysis oil. It is essential to know the flash point of an oil as this affects insurance premiums especially during transportation and storage.

5.2.4.11 COPPER CORROSION TEST

The copper corrosion test detects compounds that might be corrosive to copper, the most common element being sulphur. Fig. 5.5 shows the results of the copper corrosion test for sewage sludge pyrolysis oil, biodiesel and diesel. Sewage sludge pyrolysis oil has the highest copper corrosion rate after 12 h at 40 °C. The corrosion rate for sewage sludge pyrolysis oil is classified as 4b which corresponds to a matte black colour as shown in Fig.5.5. The matte black colour indicates corrosion to the copper strip. This implies that the pyrolysis oil would be corrosive to metals such as brass and copper. On contrast, biodiesel has a copper corrosion rate of 1a that corresponds to a light orange colour which indicates a slight tarnish to the copper strip. Diesel fuel has a rate of 1b that corresponds to a dark orange colour. This also indicates a slight tarnish to the copper strip. The results for biodiesel and diesel indicate the presence of little quantities of sulphur compounds that are responsible for aiding corrosion. This is supported by the low values shown in Table 5.3. It should be noted that the presence of masking agents such as sulfolane [56] would prevent the detection of sulphur component present in the oil.

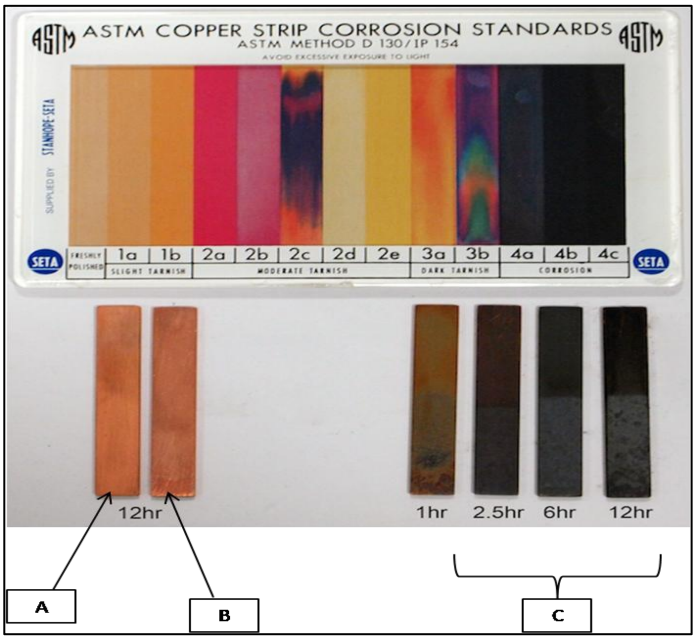


Figure 5.5: Copper strip corrosion results shown for biodiesel [**A**], diesel [**B**] and sewage sludge pyrolysis oil [**C**]

5.2.4.12 ASH CONTENT

Ash deposits are formed on injectors when bio-oil is combusted in a diesel engine. Ash in bio-oils has been reported by Zhang et al [57] to causes corrosion, deterioration and kicking in engines. The pyrolysis oil has an ash content of 0.23 wt%; however the recommended ash content for engine applications should be less than 0.1 wt% [47]. Therefore the combustion of sewage sludge pyrolysis oil will leave deposits on the injector if combusted in a diesel engine. Bahadur et al [33] found the ash content from sewage sludge lipid pyrolysis to be 0.01 wt%. This ash content is very low because extracted lipids were used for pyrolysis and not sewage sludge itself. The sewage sludge pyrolysis oil can be used in a furnace and boiler without modification with this level of ash content [58].

5.2.5 BIO-OIL COMPOSITION

5.2.5.1 SEWAGE SLUDGE PYROLYSIS OIL

The pyrolysis oil was analysed for composition using the GC-MS. The sewage sludge samples were found to contain various organic compounds. The composition of sewage sludge varies from site to site or batch to batch even if the same treatment processes is used. This is due to lack of common standards or procedure set from one site to the other [30]. Therefore the pyrolysis oil might vary in composition.

The spectra of the main compounds found in the pyrolysis oil are shown in Fig. 5.6 and displayed in Table 5.4. The main compounds in the sewage sludge pyrolysis oil are Aromatic hydrocarbons (Peaks 1, 2, 3) and phenols shown in Peak 7, 8, 9. The minor compounds are Alkene compounds (Peak 5), Indole compound (Peak 10), Alkane nitrile (Peak 11).

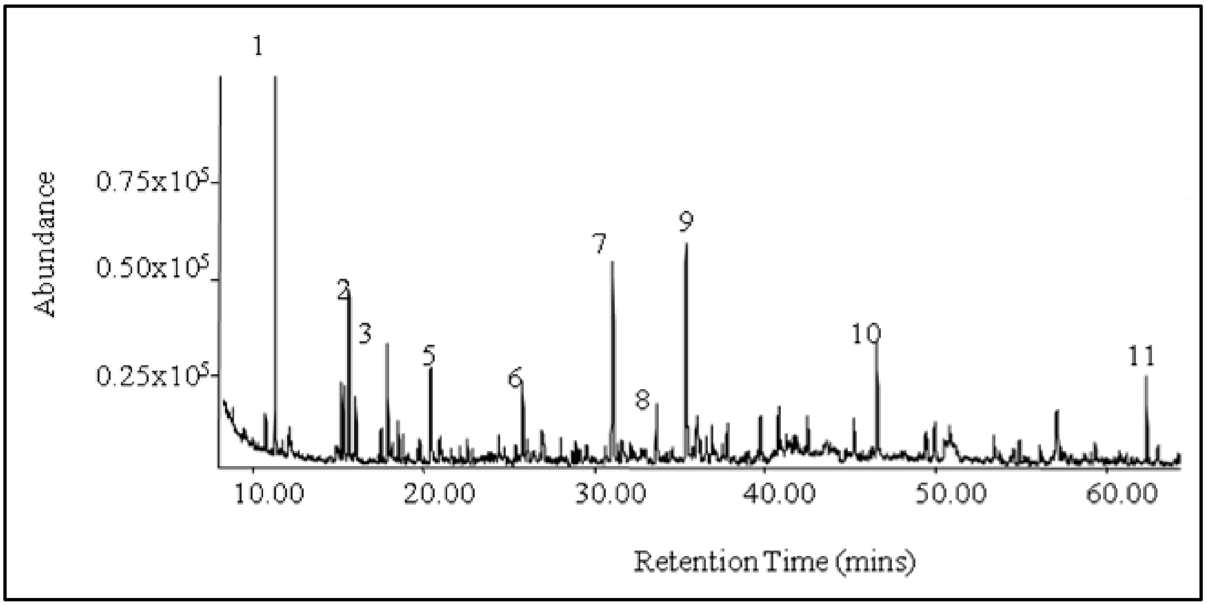


Figure 5.6: Chromatogram of the sewage sludge pyrolysis oil

Table 5.4: Chemical composition of sewage sludge pyrolysis oil

Peak no	Retention Time(min)	Compound	Formula	Molecular weight
1	11.07	Methyl benzene	C_7H_8	92
2	15.38	Ethyl benzene	C_8H_{10}	106
3	15.77	1,2-Dimethylbenzene	C_8H_{10}	106
4	17.62	Styrene	C_8H_8	104
5	20.15	1-Decene	$C_{10}H_{20}$	140
6	25.52	2-Ethyl-1-Decanol	$C_{12}H_{26}O$	186
7	30.8	Phenol	C_6H_6O	94
8	33.36	2-Methylphenol	C_7H_8O	108
9	35.09	4-Methylphenol	C_7H_8O	108
10	46.25	1H-indole	C_8H_7N	117
11	65.72	Hexadecanenitrile	$C_{16}H_{31}N$	237

Fonts et al [30], Park et al [36] all agree that sewage sludge pyrolysis oil contains mainly alkanes, alkenes, aromatics, aldehydes, fatty acids, carboxylic acids, ketones, nitrogen compounds and steroids. Stammbach et al [32], Shen and Zhang [34] found heavier fractions that had molecular weights greater than 150. The use of intermediate pyrolysis eliminates the heavier fraction by cycling char in the reactor that helps to break down the long chain fractions into smaller molecules that have molecular weight less than 150. The presence of shorter chain molecules helps improve the viscosity of the sewage sludge pyrolysis oil.

The pyrolysis oil has good chemical composition and due to its characteristics, it has the potential to be used as a fuel. The ideal combustion oil used for fuel applications should have straight chain hydrocarbons, as these possess a high heating value and lower viscosity. However, the presence of aromatic hydrocarbons within the pyrolysis oil gives it a high heating value although this is lower than biodiesel and diesel.

5.2.5.2 AQUEOUS PHASE

The aqueous phase obtained from the intermediate pyrolysis process would not be analysed using GC-MS due to high water content of 50 wt%. The aqueous phase was found to be insoluble in any of the solvents such as ethanol, chloroform, acetone, dichloromethane. However Fonts et al [5] and Kaminsky and Kummer [49] found the aqueous phase of sewage sludge from fast pyrolysis to contain nitrogen compounds such as propanenitrile and ammonia. The sample was analysed for the inorganic compounds as shown in Table 5.5. The dominant compound was found to be chloride with a 2300pm concentration while other elements had low concentration. These are reported in parts per million. The amount of sulphate in the solution was also higher than the other metals.

The aqueous phase is alkaline with a pH of 9. These authors [35] [49] also found this to range from 8 to 10. The alkalinity state is dominant in sewage sludge bio-oil as opposed to the acid state found in aqueous phase from lignocellulosic biomass. Acetic acid has been found to be a major contributor to the acidic state.

Azuara et al [59] suggested the use of the aqueous phase to be used as a fertilizer however this would not be possible with the solution from the sewage sludge intermediate pyrolysis. The mineral content is very low and this is coupled with a strong pungent smell that would not be ideal for crop growth. The best solution for the aqueous phase would therefore be treating it as normal waste that would undergo each stage in the wastewater treatment plants.

Table 5.5: Inorganic compounds found in the aqueous phase

Compound	(±0.3%) ppm
Cl	2300
SO_4	187
Br	72
Si	48.2
NO_3	29
Na	7.6
K	6.3
Ca	5.7
Fe	4.9
Mg	4.4
P	4.0
Al	3.0
Ni	1.0
Cr	0.6
Zn	0.6
B	0.3
Ba	0.2
Cu	0.1
Sr	0.1
Other metals	<0.1

5.2.6 PYROLYSIS BIOCHAR

Biochar/Char is a carbon rich solid material containing inorganic compounds. The biochar is very coarse and dry. Char is the largest product yield in the intermediate pyrolysis of sewage sludge. Many authors [24][30][34] in literature found this to be the case regardless of the type of pyrolysis carried out. The pyrolysis of sewage sludge at 450 ˚C yielded 49.1 wt% of biochar. These authors [6][24][25][30][34][37] found the biochar yield to range from 35 to 87 wt%. The properties of biochar will vary due to pyrolysis temperature and residence time.

Table 5.6 indicates that the biochar has a relatively lower carbon, hydrogen, oxygen and nitrogen content compared to the sewage sludge in Table 5.1. The greatest impact seems to be with the hydrogen and oxygen content. This is not surprising due to the fact that the decomposition behaviour yields condensable vapours that are found to be mostly hydrocarbons and oxygen containing compounds as shown section 5.2.5.1. Large quantities of carbon and nitrogen are retained in the biochar. The H/C ratio is also low and this was also found by Abrego et al [60]. This was attributed to presence of large quantities of aromatic structures such as methyl benzene [60].

The main draw back with sewage sludge biochar is the high ash content as shown in Table 5.6. Several authors [24][25][30][34][37] found this to be higher compared to lignocellulosic char. The high ash content of the biochar might inhibit its combustion characteristics. The biochar also has a lower higher heating value compared to digested sludge.

The sewage sludge biochar has a heating value of 11.2 MJ/kg. This is lower than the energy content obtained from lignocellulosic biochar. Other authors in literature such as [6][25][37] also found the higher heating value of the digested char to range from 5.2 to 16 MJ/kg.

Table 5.6: Analysis of sewage sludge biochar

	Sewage sludge biochar
Ultimate analysis(±0.03)(wt. %)[a]	
C	25.5
H	1.8
N	3.1
O	1.4
S	13.5
Ash (±1) (wt. %)	54.8
HHV(±0.001)((MJ/kg)	11.2

[a] Weight percentage on dry mass basis

There are different ways the char can be optimised, amongst these is using the char as a heat source for heating up the reactor or dryer on a large scale. Reusing the char in this form ensures sufficient energy can be gained from it although the ash from combustion process needs to be used utilised in an environmentally friendly way. Other uses of biochar have been identified as agricultural use, catalyst for the pyrolysis process, adsorbent [61]. Bagreev et al [61] found the sewage sludge biochar to be suitable as an adsorbent for the removal of pollutants such as H_2S. Beneficial properties of biochar for agricultural applications are explored in chapter 7.

5.2.7 PERMANENT GASES

A small percentage of 10.7 % permanent gases were produced with the intermediate pyrolysis of sewage sludge as shown in Table 5.7. These authors [31][32][37][49] also found the gas yield to range from 8 to 45 %. Piskorz et al [31], Stammbach et al [32], Park et al [36], and Sanchez et al [38] found that an increase in pyrolysis temperature increased the gas yield. The largest gas composition from sewage sludge was CO_2 with 8.5 %. The least quantity of gases was CH_4 with 1.0 %. Hydrogen gas was not detected by the gas chromatograph. This might be due to leakage of the gas from the sampling syringe to the detection device or due to lower volumes of hydrogen gas that cannot be detected by the system. Inguanzo et al [6], Karayildirim et al [24], Fonts et al [30], Piskorz et al [31], Shen and Zhang [34], Park et al [36] found the gas yield to contain varying composition and this included CO, CO_2, CH_4, H_2, N_2, H_2S and C_xH_y. The varying compositions of gas yield are mainly due to pyrolysis conditions and sludge type [35].

Table 5.7: Permanent gases from the intermediate pyrolysis of sewage sludge

	Permanent gases from sewage sludge pyrolysis
Gas percentage[a] (vol %)	10.7
Gas composition (vol %)	
CO_2	8.5
CO	1.2
CH_4	1.0

[a] Weight percentage on dry mass basis

5.3 SUMMARY

The pyrolysis oil has been identified as the most significant yield from the intermediate pyrolysis of sewage sludge. The pyrolysis oil has shown to have considerable advantages and some drawbacks. It has high energy content with a relatively low water content compared to other lignocellulosic biomass. The high flash point of the pyrolysis oil makes it safe to transport and store without significant hazards.

Among the disadvantages of the pyrolysis oil is the high ash content that may cause clogging of the injector nozzles if it is to be used in an engine. The high viscosity of the pyrolysis oil might also hinder some of its application especially during atomisation in the diesel engine. Although the pyrolysis oil is alkaline in nature, it has a high acid number that could cause corrosion to metals such as carbon steel. It is therefore advised that the pyrolysis oil should be stored in a stainless steel material.

The application of the pyrolysis oil for combustion purposes could be possible with modifications. The pyrolysis oil is immiscible with diesel but miscible with biodiesel. The miscibility with biodiesel would be explored in chapter 9 to investigate the characteristics and performance of the pyrolysis oil blend.

Biochar is the largest percentage of product yield from the sewage sludge intermediate pyrolysis process. It is essential to utilise it effectively in order to make the pyrolysis system efficient. Although combustion of char would be the primary factor for efficient utilisation of energy, its combustion would be hindered due to high ash content.

CHAPTER 6:CO - PYROLYSIS OF SEWAGE SLUDGE

This chapter explains the possible biomass that could be pyrolysised with sewage sludge to form bio-oil, biochar and non condensable gases. It explores the nature of pyrolysis yield obtained and characteristics of the products obtained from the co-pyrolysis of the selected biomass with sewage sludge. The implications of the products will also be discussed.

6.1 PREVIOUS WORK

Folgueras et al [62] carried out pyrolysis of bituminous coal with a blend of 10 and 50 wt% of sewage sludge. The sewage sludge was obtained from three Asturian urban wastewater treatment plant. The pyrolysis behaviour was studied using TGA. The sludges were found to be more reactive than coal. This is because the decomposition and devolatilisation occurred at lower temperatures than coal. The kinetic analysis using the thermogravimetric data showed a sequence of successive first order reactions with a logical experimental data.

Zhang et al [63] studied the behaviour of sewage sludge with rice straw using a thermal analyser. The percentages of 30%, 40% and 50% rice straw were mixed with sewage sludge. TGA was used to study the processes through the TG and DTG curves. They focused on the amount of volatile release during the co-pyrolysis experiments. The authors found that the use of rice straw affects the pyrolysis of sewage sludge. The release of volatile matter was enhanced with a very short time scale with the increase in rice straw fraction. There was also an increase in weight loss rate with the increase in the amount of rice straw. The results followed the trend of the first order reaction and Arrhenius law.

Park et al [64] studied the characteristics of co-pyrolysis of sawdust and coal blend using a fixed bed reactor and TGA. The authors found that using the fixed bed reactor, there was an increase of gas products up to 39% than that from the additive model which led to the reduction in tar and char yields. There was an increase in the energy content of the product gas especially CH_4 and CO. The co-pyrolysis enabled a 35% increase in product gas compared to pyrolysis of sawdust alone. The TGA experiments showed more volatile decomposition above 400 °C. The higher ash content from the saw dust showed a catalytic effect above 700 °C.

Ischia et al [65] studied the pyrolysis of sewage sludge with clay using TG-MS and Py-GC. The clay contained 39 wt% of kaolinite. The co-pyrolysis of sewage sludge with clay helped to reduce coke formation that could otherwise be generated from sludge. This was attributed to the acidity of solid surface that was enabled by water release from clay. The use of clay also produced a catalytic effect on the sludge pyrolysis. The co-pyrolysis also enabled a higher percentage of permanent gas production especially between 450 to 500 °C. The char from the co-pyrolysis was found to have good properties that would enable its disposal through vitrification. The char enabled entrapment of hazardous heavy metals that are found in sewage sludge.

6.2 METHODOLOGY

6.2.1 MATERIALS USED

The biomass used for ultimate and elemental analysis was ground into powder to pass through a sieve of 250 µm. However for the pyrolysis process, different forms of biomass were used (Fig.6.1). Mixed wood was chipped into small length ranging from 1 to 3 mm. Straw and sewage sludge were in form of pellets ranging from 3 to 5 mm. Rapeseed was in form of seeds. The biomass fractions used are; 60 wt% sewage sludge (SS) with 40 wt% mixed wood , 60 wt% sewage sludge with 40 wt% rapeseed, 60% sewage sludge with 40 % straw. Table 6.1 shows the properties of the biomass.

Figure 6.1: Samples of biomass used for co-pyrolysis process

Table 6.1: Properties of various biomass

	Sewage sludge	Mixed wood	Rapeseed	Straw
Proximate analysis (wt. %(±1))[a]				
Moisture	4.7	7.5	5.0	7.1
Volatiles	63.7	81.8	90.1	77.3
Ash	32.6	0.6	4.2	6.6
Ultimate analysis (wt. %) (±0.03)[b]				
C	35.6	50.6	60.25	44.19
H	5.20	5.86	9.03	5.68
N	4.33	1.85	4.19	0.10
O[c]	53	41.6	26.43	49.93
S	1.87	0.10	0.10	0.10
HHV(±0.001) (MJ/kg)	15.3	19.1	26.9	14.5

[a] Weight percentage based on dry basis

[b] Weight percentage based on dry ash free basis

[c] Obtained by difference

6.2.2 PYROLYSIS PROCESS

The pyrolysis process was carried out in a laboratory scale reactor. The experimental setup for the pyrolysis process is shown in Fig. 6.2. The reactor used is a cylindrical shaped quartz tube 40 cm in length with an internal diameter of 6 cm. The reactor was fitted with a glass cover that enabled the connection of the thermostat, nitrogen inlet and the outlet gases. The reactor outlet was connected to two cooling traps. The reactor was placed in the furnace for external heating. Liquid nitrogen was used as a cooling medium. The reactor was purged with nitrogen gas at a rate of 100 ml/min for the first ten minutes. It was heated at a rate of 25 ˚C/min to 450 ˚C and held at this temperature for 15 minutes. The vapour produced was cooled by the aid of the nitrogen traps and the non condensable gases were expelled through the electrostatic precipitator that was linked to the extractor.

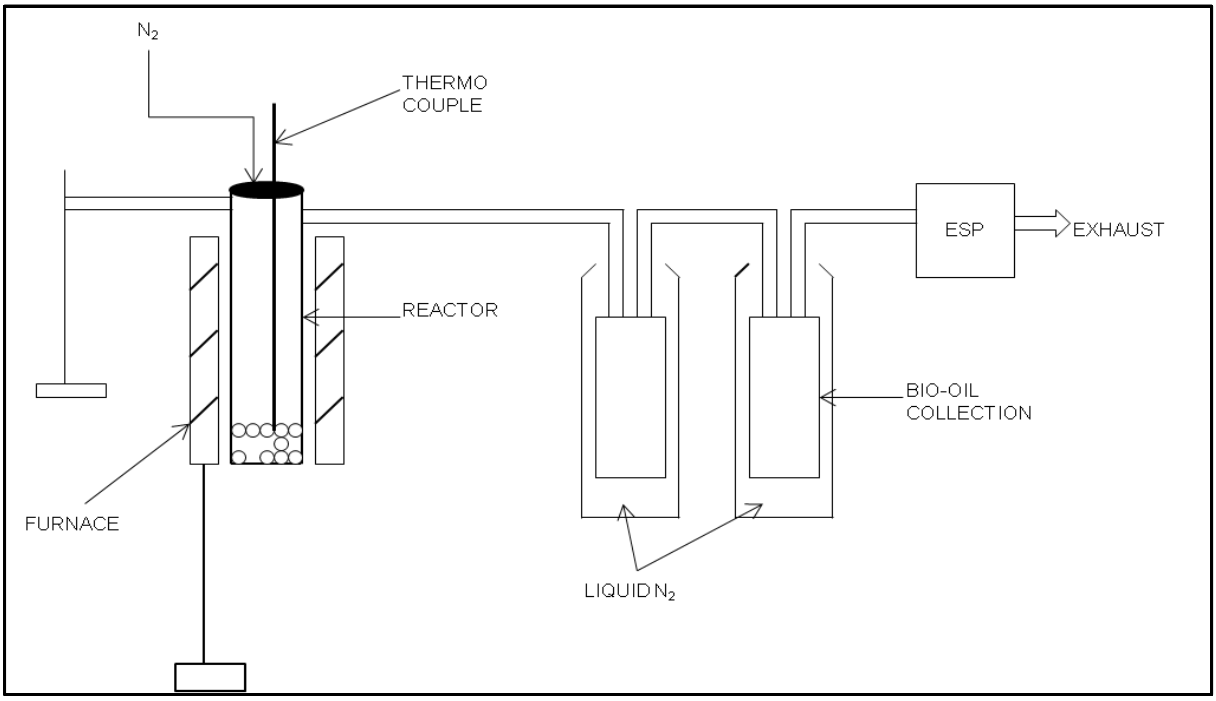


Figure 6.2: Laboratory scale pyrolysis experiment carried out at 450 °C

6.3 RESULTS AND DISCUSSION

6.3.1 PYROLYSIS YIELD

The co-pyrolysis of sewage sludge with other biomass produced a variation in product yield. Table 6.2 shows the amount of product yield obtained from the co-pyrolysis process. The product distribution from the co-pyrolysis yield will greatly vary due to the use of various biomass. The amount of gases produced was determined by difference from the mass balance. The rapeseed and sewage sludge fraction have the highest bio-oil content of 33.2 wt% with equal amount of the pyrolysis oil (organic/upper phase) and bottom phase as shown in Table 6.2. The increase in the percentage of the pyrolysis oil originates from the pyrolysis of rapeseed. This is because the pyrolysis of sewage sludge only yields 10 wt% of the pyrolysis oil (organic phase) compared to 30 wt% of the bottom phase. The increase in bio-oil yield is due to the synergistic effect from the co-pyrolysis with rapeseed. Cornelissen et al [66] found an increase in co-pyrolysis bio-oil yield of 28 % from polylactic acid and willow compared to willow bio-oil. Cao et al [67] found a significant increase in bio-oil obtained from co-pyrolysis of sawdust and tire compared to sawdust bio-oil. Brebu et al [68] also found an increase in bio-oil from co-pyrolysis of pine cone with synthetic polymers. Kar [69] found a 7.88 wt% increase in the co-pyrolysis bio-oil obtained from walnut shell and tar sand. Onal et al [70] found the greatest increase in bio-oil yield of 50.8 wt% from the co-pyrolysis of potato skin with high-density polyethylene compared to potato skin bio-oil.

On the other hand, straw and sewage sludge produced the least amount of bio-oil. The co-pyrolysis with rapeseed produced the highest percentage of char 53.3 wt% while sewage sludge and wood fraction had the lowest char content.

Fig. 6.3 shows the bio-oils obtained from the co-pyrolysis of sewage sludge with mixed wood, rapeseed and straw. The 40% mixed wood produced bio-oil that contains pyrolysis oil at the top and bottom layer (Fig. 6.3). The top layer contained lighter pyrolysis oil fractions while the bottom layer contained tar fractions originating from wood. The middle phase was removed and the two phases were mixed together for analysis. The pyrolysis oil has a mass percentage of 10.9 wt% compared to the bottom phase which is 21.8 wt%.

Table 6.2: Product yield from the co-pyrolysis of sewage sludge[a]

Biomass	Bio-oil (wt %)	Char (wt %)	Gases[b](wt %)
SS + 40% Wood	32.7	46.8	20.5
SS + 40% Rapeseed	33.2	53.3	13.5
SS + 40% Straw	27.8	48.7	23.5

[a]Pyrolysis yield percentage based on dry mass basis
[b]Obtained by difference

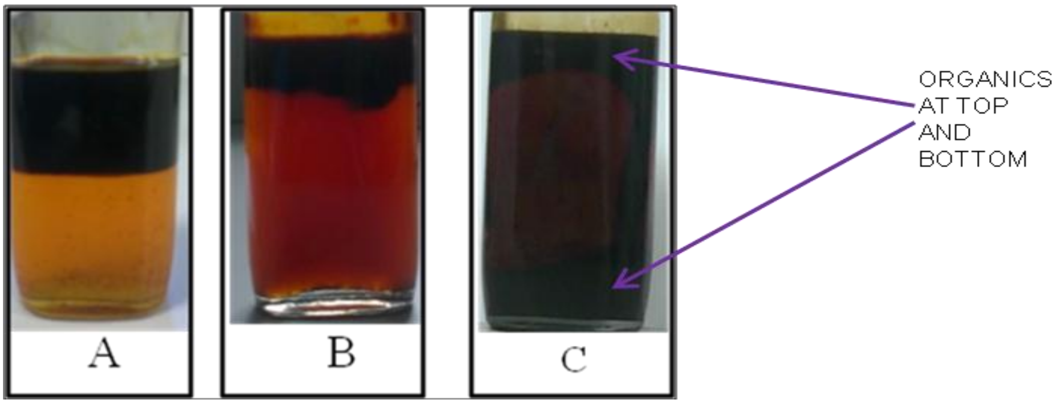


Figure 6.3: Bio-oils obtained from co-pyrolysis process: (A) SS + 40% Rapeseed, (B) SS + 40% Straw, (C) SS + 40% Wood

6.3.2 COMPOSITION

The bio-oil obtained from the co-pyrolysis process were analysed for composition using the gas chromatograph mass spectrometry. Fig. 6.4 shows the spectra obtained for bio-oil obtained from sewage sludge and straw. The main compounds detected were hydrocarbons and phenols as shown in Fig. 6.4 and Table 6.3. The compounds from sewage sludge bio-oil are Aromatic hydrocarbons (peaks 1, 2), Alkyl phenols (peaks 4, 7, 8) and Nitrogen compound (peak 9). The compounds originating from straw bio-oil are Phenols compounds (peaks 4, 5, 10) and Amino compound (peak 6). The Cycloalkene and Cycloalkane shown as peaks 3 and 11 are products from the reaction between sludge and straw bio-oil. The composition of the bio-oil is expected to differ significantly due to the nature of the biomass used. Varying authors [68][70][71] found diverse composition of the co-pyrolysis bio-oil depending on the biomass and conditions used for the pyrolysis process.

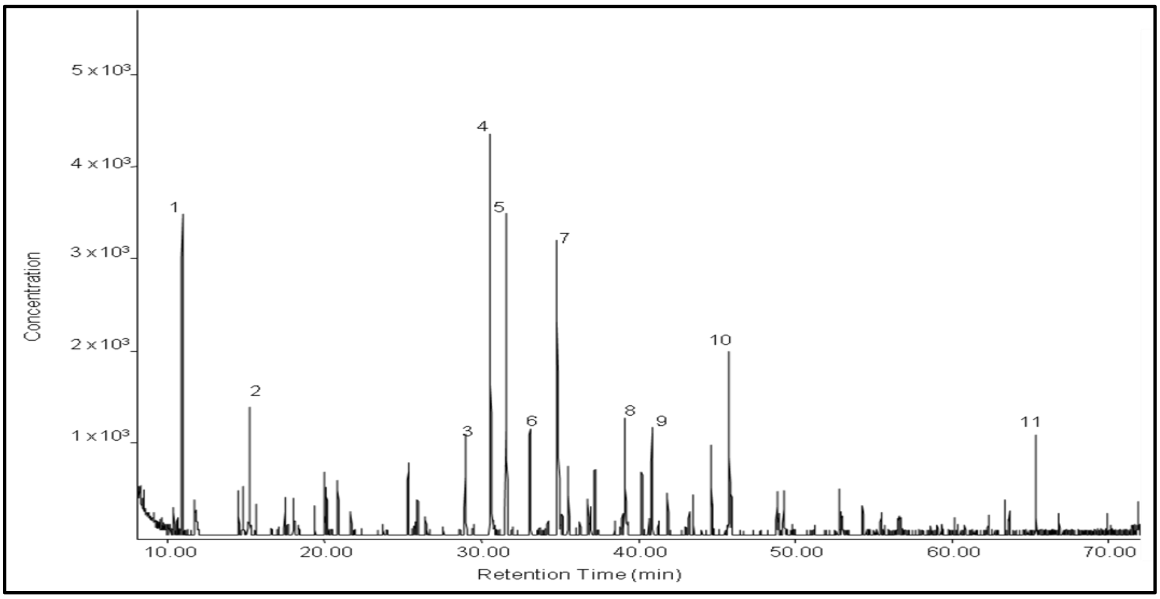


Figure 6.4: The chromatogram of co-pyrolysis bio-oil obtained from sewage sludge with 40% straw at 450 °C

Table 6.3: Composition of bio-oil from sewage sludge (SS) and straw (ST) pyrolysis

Peak no	Retention Time(min)	Compound name	Formula	Molecular weight	Source
1	10.9	Methylbenzene	C_7H_8	92	SS
2	15.2	Ethylbenzene	C_8H_{10}	106	SS
3	28.9	Cyclooctene	C_8H_{14}	110	SS+ST
4	30.5	Phenol	C_6H_5OH	94	SS, ST
5	31.5	2-Methoxy-phenol(Guaiacol)	$C_7H_8O_2$	124	ST
6	33.1	Dimethylamino-3-methyl-3,3-(E,E)	$C_{19}H_{23}ClN_2$	314	ST
7	34.8	4-Methylphenol	C_7H_8O	108	SS,ST
8	39.1	2-Ethylphenol	$C_8H_{10}O$	122	SS
9	40.8	2-Methoxy-3-(1-methylethyl) pyrazine	$C_8H_{12}N_2O$	152	SS
10	45.8	2,6-Dimethoxyphenol	$C_8H_{10}O_3$	154	ST
11	65.3	Cyclopropyl cyclohexane	C_9H_{16}	124	SS+ST

Fig. 6.5 shows the spectra for the bio-oil obtained from the co-pyrolysis of sewage sludge and mixed wood. Table 6.4 displays the compounds detected with the corresponding retention time. The highest percentage of the compounds detected are a result of decomposition of mixed wood amongst these are; Aromatic hydrocarbons (peak 1), Furan from cellulose (peak 3), Phenols (peak 5, 10) and derivatives of Methoxyphenols (peaks 6, 7, 8, 9, 12). The decomposition of lignin in wood causes the formation of methoxyphenols. A large number of these compounds are detected in wood bio-oil compared to the straw bio-oil fraction.

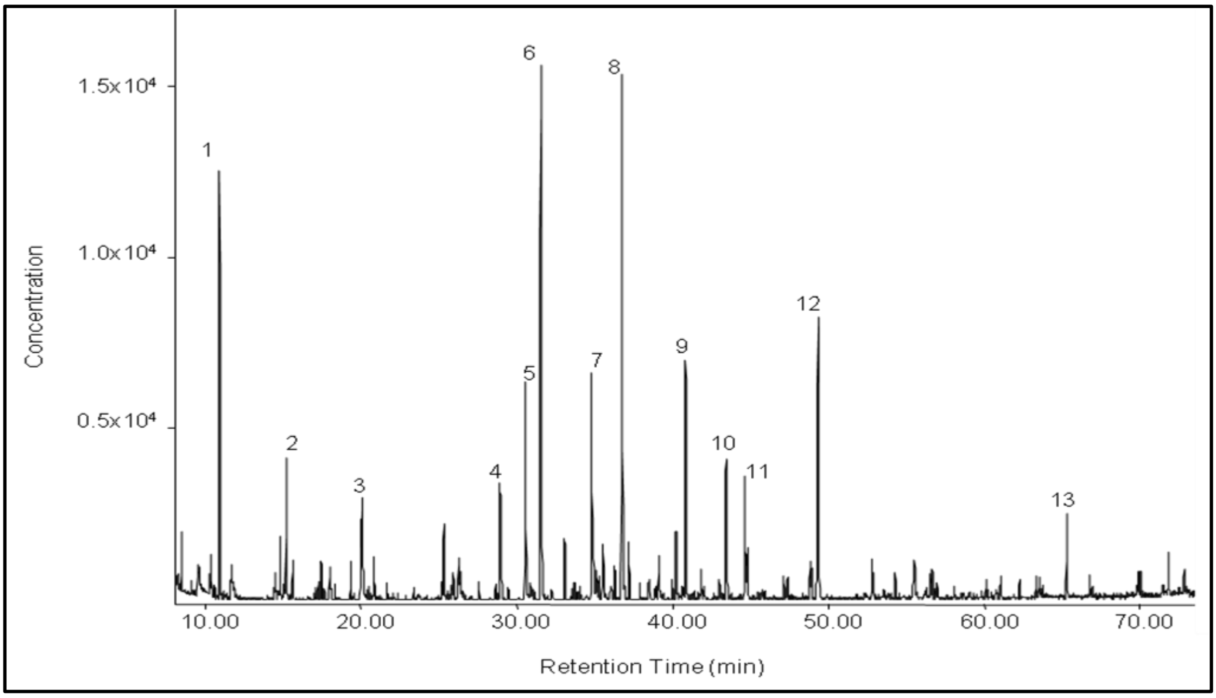


Figure 6.5: The chromatogram of co-pyrolysis bio-oil obtained from 40% mixed wood and sewage sludge at 450 °C

Table 6.4: Composition of bio-oil from sewage sludge (SS) and mixed wood (MW) pyrolysis

Peak no	Retention Time (min)	Compound name	Formula	Molecular weight	Source
1	10.8	Methylbenzene	C_7H_8	92	SS, MW
2	15.2	Ethylbenzene	C_8H_{10}	106	SS
3	20.0	2-Furanmethanol	$C_5H_6O_2$	98	MW
4	28.9	2,2-Dimethyl-3-hexene.	C_8H_{16}	112	SS + MW
5	30.5	Phenol	C_6H_5OH	94	SS, MW
6	31.5	2-Methoxyphenol	$C_6H_4(OH)(OCH_3)$	124	MW
7	34.8	4-Methylphenol	C_7H_8O	108	SS, MW
8	36.7	2-Methoxy-4-Methyl phenol/Creosol/4 Methyl guaiacol.	$C_8H_{10}O_2$	138	MW
9	40.8	4-Ethyl-2-methoxy-phenol/ 4Ethylguaiacol.	$C_9H_{12}O_2$	152	MW
10	43.4	5-Methyl-2-(1-methylethyl)-phenol.	$C_{10}H_{14}O$	150	MW
11	44.6	2,3,5-Trimethyl decane.	$C_{11}H_{24}$	156	SS+MW
12	49.3	2-Methoxy-4-(1-propenyl)-phenol.	$C_{10}H_{12}O_2$	164	MW
13	65.3	1,2-Dimethyl, cis-cyclohexane.	C_8H_{16}	112	SS+MW

Fig.6.6 shows the spectrum for the bio-oil obtained from the 40% rapeseed. The compounds are summarized in Table 6.5. The dominant compounds detected originate from the 40% rapeseed. The compounds from rapeseed bio-oil are Aromatic hydrocarbon (peak 1), Phenol (peak 3), Alkane hydrocarbon (peak 5, 9), Long chain alkenes (peaks 7, 8), Alkane nitriles (peaks 10, 12), fatty acid (peak 11), alcohol (peak 13) and an amide (peak 14). The compounds from sewage sludge bio-oil as shown in Table 6.5 are Aromatic hydrocarbon (peak 1), Silicon compound (peak 2), Phenols (peaks 3, 4) and Indole (peak 6). Peak 15 is unknown to belong to either rapeseed or sewage sludge bio-oil, so it might have been produced by the reaction between the two.

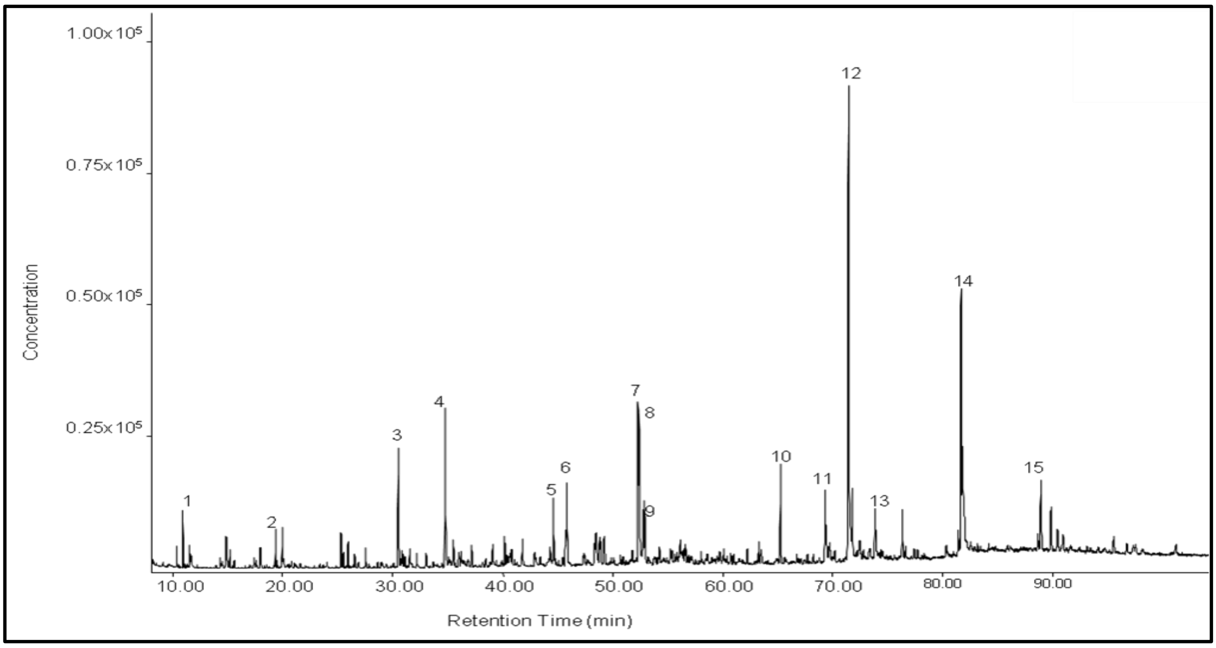


Figure 6.6: The chromatogram of co-pyrolysis bio-oil obtained from 40% rapeseed and sewage sludge at 450 °C

Table 6.5: Compounds detected from bio-oil obtained from co-pyrolysis of sewage sludge (SS) and rapeseed (RS)

Peak no	Retention Time (min)	Compound	Formula	Molecular weight	Source
1	10.8	Methylbenzene	C_7H_8	92	SS, RS
2	19.3	Octamethyl cyclotetrasiloxane	$C_8H_{24}O_4Si_4$	296	SS
3	30.5	Phenol	C_6H_5OH	94	SS, RS
4	34.8	4-Methyl phenol	C_7H_8O	108	SS
5	44.6	Hexadecane	$C_{16}H_{34}$	226	RS
6	45.8	1H-indole	C_8H_7N	117	SS
7	52.3	3-Hexadecene (Z)-	$C_{16}H_{32}$	224	RS
8	52.4	5-Octadecene, (E)-	$C_{18}H_{36}$	252	RS
9	52.8	Heptadecane	$C_{17}H_{36}$	240	RS
10	65.3	Tetradecanenitrile	$C_{14}H_{27}N$	209	RS
11	69.3	Methyl ester 9-octadecenoic acid	$C_{14}H_{36}O_2$	296	RS
12	71.8	Octadecanenitrile	$C_{18}H_{35}N$	265	RS
13	73.9	2-(9-Octadecenyloxyl)-, (Z)-ethanol	$C_{20}H_{40}O_2$	312	RS
14	81.7	4-Ethyl-5-methyl-Heptanamide	$C_{10}H_{23}NO$	173	RS
15	89	19S-Hydroxy-tecamine	$C_{20}H_{32}O_3$	320	SS+RS

6.3.3 ULTIMATE ANALYSIS OF THE PYROLYSIS OIL OBTAINED FROM CO-PYROLYSIS

6.3.3.1 CARBON AND HYDROGEN

Table 6.6 shows the ultimate analysis of the pyrolysis oil obtained from the co-pyrolysis process. The pyrolysis oil obtained from the 40% mixed wood has the highest carbon content of 68.9 wt% compared to other co-pyrolysis fractions. The carbon content of the 40% wood is also greater than that obtained from mixed wood alone. Onal et al [70] also found a remarkable increase in carbon content of 80 wt% in the co-pyrolysis bio-oil compared to biomass alone. On the other hand, the 40% straw pyrolysis oil has the lowest carbon content of only 53.4 wt%. This is lower than the carbon content obtained from just straw pyrolysis oil that is 61.9 wt%.

The pyrolysis oil obtained from 40% rapeseed has the highest hydrogen content of 11.7 wt%. The hydrogen content is greater than that obtained from the pyrolysis oil of rapeseed alone reported by Hornung et al [72] to be 10.6 wt%. The 40% rapeseed also increases the hydrogen content that is found in sewage sludge pyrolysis oil that is only 9.9 wt%. The results indicate that hydrogen content increase might be as a result of the reaction between the compounds found in rapeseed and sewage sludge such as 19S-Hydroxy-tecamine reported in Table 6.5. The hydrogen content from 40% mixed wood and 40% straw are very similar. A higher carbon and hydrogen, together with low oxygen content indicate a large amount of alkyl chain, which increase the HHV and the quality of the fuel. Cao et al [67] and Bhattacharya et al [71] also found an increase in the carbon and hydrogen content of the co-pyrolysis oil from completely different biomass which greatly improved the oil properties.

6.3.3.2 OXYGEN CONTENT

The 40% mixed wood contains the lowest oxygen content of 17.8 wt% compared to the other co-pyrolysis oil. It is also less than the oxygen content obtained from mixed wood alone that is 36.7 wt%. The co-pyrolysis with sewage sludge seems to have improved the oxygen content that is found in mixed wood. The reduction in oxygen content is among the advantages found with the co-pyrolysis process. Cornelissen et al [66] found lower oxygen content in the bio-oil obtained from willow and polylactic acid compared to willow alone. Cao et al [67] found a decrease in the oxygen content of bio-oil from co-pyrolysis of sawdust and tire. Bhattacharya et al [71] found lower oxygen content in the bio-oil from co-pyrolysis of wood and plastic. Onal et al [70] found a significant reduction in the oxygen content of co-pyrolysis oil from potato skin and high-density polyethylene.

In contrast, the pyrolysis oil from 40% straw has the highest percentage of oxygen that is 30.9 wt% compared to other fractions. The oxygen present in bio-oil is of various forms. As shown in Table 6.3, the oxygen present in 40% straw fraction takes the form of phenol and Methoxy groups such as 2-Methoxyphenol, 4-Methylphenol, 2-Ethylphenol and 2,6-Dimethoxyphenol. Some of these compounds are also present in other co-pyrolysis fractions however the percentage differs for each fraction.

Table 6.6: The ultimate analysis of the pyrolysis oil obtained from various biomass

Ultimate analysis[a] (±0.03) (wt. %)	Sewage sludge	SS + 40% Mixed Wood	Mixed wood	SS + 40% straw	Straw	SS + 40% Rapeseed	Rapeseed [55]
C	74.2	68.9	53.1	53.4	61.9	63.8	77.0
H	9.9	10.3	7.6	10.4	7.9	11.7	10.6
N	5.1	1.7	<0.1	4.2	1.1	4.6	1.4
O[b]	8.0	17.8[a]	36.7	30.9[a]	27.2	19.5	10.6
S	1.9	1.3	<0.1	1.1	<0.1	0.4	0.3

[a] Weight percentage based on dry ash free basis (results obtained externally)

[b] Obtained by difference

6.3.3.3 SULPHUR CONTENT

The 40% rapeseed has the lowest sulphur content of only 0.4 wt%. The co-pyrolysis of rapeseed with sewage sludge lowers the sulphur content found in sewage sludge pyrolysis oil alone that is 1.9 wt%. Brebu et al [68] also found lower sulphur content from bio-oil obtained from co-pyrolysis of pine cone with synthetic polymers. It is advantageous to have bio-oil will very little or no sulphur if the bio-oil is to be used in CHP systems since this can become a source of SOx. The presence of sulphur in bio-oils is due to contaminants being present in the biomass [25]. On the contrary, the 40% mixed wood pyrolysis oil has the highest sulphur content compared to 40% rapeseed and 40% straw fractions. However, the sulphur content from mixed wood alone is less than 0.1 wt%. In this case, the increase is due to the presence of sewage sludge.

6.3.3.4 NITROGEN CONTENT

The rapeseed with sewage sludge (SS) pyrolysis oil has the highest nitrogen content of 4.6 wt%. This value is still lower than the nitrogen content found in sewage sludge bio-oil that is 5.1 wt%. The bio-oil from 40% wood has the lowest nitrogen content of only 1.7 wt%. The amount of nitrogen present in the bio-oil is very crucial if the bio-oil is to be used as a fuel. High nitrogen contents in fuels give out nitrogen oxides that are hazardous to the environment.

6.3.4 PHYSICAL PROPERTIES OF THE CO-PYROLYSIS OIL

6.3.4.1 HIGHER HEATING VALUES

Table 6.7 shows the physical properties of the pyrolysis oil obtained from the co-pyrolysis of sewage sludge with other biomass. The 40% rapeseed has the highest energy content of 34.8 MJ/kg among the co-pyrolysis oils. However this value is lower than that obtained from the sewage sludge pyrolysis oil that ranges from 35.5 to 39 MJ/kg. The lowest energy content is found with the 40 % mixed wood which is 31.3 MJ/kg. Although this energy content appears to be low compared to those in Table 6.7, it is greater than that reported by Bridgwater [26] to be 17 MJ/kg obtained from pyrolysis of wood alone. According to these results, the co-pyrolysis with sewage sludge has a greater effect on wood. The authors who carried out co-pyrolysis of lignocellulosic biomass with other materials found similar results. Cao et al [67] found the co-pyrolysis oil from sawdust and tire to have greater energy content with increasing ratio of tire mass. Sawdust alone had an energy content of 28 MJ/kg and this increased to 42.4 MJ/kg with a 60 wt% tire mass. Bhattacharya et al [71] also found the co-pyrolysis oil from wood and plastic to have an increased energy content compared to pine wood alone. Onal et al [70] found an increase in the energy content of the co-pyrolysis oil from potato skin and high-density polyethylene compared to just potato skin. The increase was due to the hydrogen transfer from high-density polyethylene.

6.3.4.2 WATER CONTENT

The 40% mixed wood pyrolysis oil has the lowest water content of 5.1 wt%. This water content is higher than that from sewage sludge pyrolysis oil which is 4.12 wt%. However, the 5.1 wt% from 40% mixed wood is much lower than that reported by Bridgwater [29] obtained from fast pyrolysis of wood to be 25 wt%. According to the results, wood pyrolysis oil seems to benefit from the co-pyrolysis with sewage sludge since the water content is greatly reduced. Cornelissen et al [66] also found a significant reduction in the water content of the bio-oil obtained from the co-pyrolysis of willow and polylactic acid. Furthermore, Bhattacharya et al [71] also found a decrease in water content of bio-oil from co-pyrolysis of wood and plastic compared to wood alone.

The pyrolysis oil from 40% rapeseed has the highest water content of 8.1 wt% compared to other fractions. It is not clear why this fraction has the highest water content but it might be due to reactions occurring between the products producing water as a by-product. This is because the water content detected in this phase seemed to increase gradually compared to other fractions. Although a high water content aids with the reduction in viscosity, quantities greater than 0.5 wt% are not recommended for fuels.

6.3.4.3 VISCOSITY

The pyrolysis oil from 40% rapeseed has the lowest viscosity of 24.2 cSt compared to mixed wood and straw fractions. The co-pyrolysis of sewage sludge and rapeseed reduces the viscosity that is found with the sewage sludge pyrolysis oil that is 38-45 MJ/kg. This physical aspect of the pyrolysis oil enables handling, flow and pumping much easier compared to heavily viscous substances. On the other hand, the 40% mixed wood pyrolysis oil has the highest viscosity of 98.3 cSt. The increase in viscosity is caused by heavier tar compounds found in mixed wood such as those shown in Table 6.4 at peaks 7, 8, 9, 10, 12. The use of the pyrolysis oil from 40 % mixed wood without any pre-treatment in a CHP system would pose difficulties during pumping. The straw pyrolysis oil has a viscosity of 40.9 cSt. This viscosity can be reduced with blending of specially selected fuels or chemicals.

6.3.4.4 ACID NUMBER AND PH

The 40% straw pyrolysis oil has a very low acid number of 0.5 mgKOH/g. This value is much lower than that of sewage sludge pyrolysis oil which is 21.7 mgKOH/g. The co-pyrolysis of sewage sludge with straw improves the bio-oil properties by lowering the acid number found in sewage sludge pyrolysis oil. On the contrary, the 40% mixed wood pyrolysis oil has the highest acid number of 30.1 mgKOH/g with the lowest pH value of 4.9. Several authors [26][55][73][74] have reported the pH of varying types of wood to range from 2 to 3.7. Even though the 40% mixed wood has a high acid number, it is lower than those reported in literature [26][55][73][74]. According to these findings, the use of sewage sludge with wood greatly improves the acid number that is found in wood bio-oil. Bhattacharya et al [71] also reported lower acid values from the co-pyrolysis oil obtained from wood and plastic. The bio-oil acidity is very significant as this helps identify the corrosiveness of a substance in materials such as carbon steel and aluminium [55][58][74]. No acid number was detected for the 40 wt% rapeseed fraction. It is not clear why this occurred but the answer might lie within the composition of the co-pyrolysis bio-oil.

Table 6.7: Physical properties of the pyrolysis oil obtained from co-pyrolysis of biomass

Physical properties	Error (%)	SS + 40% Wood	SS + 40% Rapeseed	SS + 40% Straw
Viscosity @ 40°C (cSt)	(±1)	98	24.2	40.9
Acid number(mgKOH/g)	(±0.1)	30.1	0	0.5
pH	(± 0.1)	4.9	8.4	6.5
Water content (wt.%)	(±0.01)	5.1	8.2	6.8
HHV (MJ/kg)	(±0.001)	31.3	34.8	32.5

6.3.5 CHARACTERISTICS OF BIOCHAR FROM CO-PYROLYSIS PRODUCTS

The properties of biochar vary depending on the feedstock used for production, pyrolysis temperature and the residence time. Biochar obtained from co-pyrolysis of mixed wood, rapeseed and straw were analysed for proximate analysis, ultimate analysis, pH and the higher heating values. These results are displayed in Table 6.8.

6.3.5.1 ASH CONTENT

The lowest ash contents of the co-pyrolysis char is from 40% rapeseed and 40% wood with values of 32.6 wt% and 32.9 wt%. The co-pyrolysis of sewage sludge with 40% rapeseed and 40% wood facilitated the reduction of the ash content found in sewage sludge biochar as shown in Table 6.8. Brebu et al [68] also found the co-pyrolysis char from pine cone with synthetic polymers to have a very low ash content of less than 1 wt% compared to pine cone alone. On the other hand, biochar from 40% straw has the highest ash content among the co-pyrolysis char however this is still lower than the ash content from sewage sludge char.

6.3.5.2 CARBON AND HYDROGEN

Biochar is mainly composed of carbon link chains forming graphite like structure. The presence of carbon and hydrogen compounds enables the char to be combustible. Sewage sludge with 40% wood has the highest carbon content of 50.9 wt% with a relative hydrogen content of 4.18 wt%. On the contrary, the 40% rapeseed has the lowest carbon content of 47.15 wt% compared to the co-pyrolysis char yet this has the highest hydrogen content as shown in Table 6.8. The high hydrogen content is due to fatty acids from the 40% rapeseed; this is because this particular biochar was very oily compared to the rest of the co-pyrolysis char.

6.3.5.3 HIGHER HEATING VALUE

Biochar from 40% rapeseed has the highest energy content of 23.5 MJ/kg. The 40% mixed wood biochar also boosts the energy content of the sewage sludge biochar since this has 22.7 MJ/kg. The co-pyrolysis process improves the energy content which is found in the sewage sludge biochar since this is only 11 MJ/kg. The co-pyrolysis process of sewage sludge with 40% rapeseed and 40% mixed wood enables the biochar energy content to be doubled. Brebu et al [68] also found the co-pyrolysis char of pine corn with synthetic polymers to a higher energy content of 33.2 MJ/kg compared to that of pine corn alone that is 27.4 MJ/kg. The co-pyrolysis of sewage sludge with 40% mixed wood is low-cost compared to the use of rapeseed and very little difference exists between the energy contents obtained as shown in Table 6.8. The 40% straw biochar has the lowest energy content of 19.9 MJ/kg among the co-pyrolysis biochar however this is still higher than that obtained from sewage sludge.

Table 6.8: The characteristics of the co-pyrolysis biochar

	Sewage sludge char	SS + 40% Mixed Wood	SS + 40% Rapeseed	SS + 40% Straw
Proximate analysis(wt. %) %)(±1)[a]				
Moisture	5.37	2.31	2.11	4.4
Ash	54.8	32.9	32.6	40.2
Ultimate analysis (wt. %) (±0.03)[b]				
C	25.5	50.96	47.15	49.04
H	1.8	4.18	4.42	3.31
N	3.1	4.19	4.02	3.21
O	1.3	6.6	10.71	2.96
S	13.5	1.17	1.10	1.28
HHV(±0.001)(MJ/kg)[c]	11.2	22.7	23.5	19.9

[a] Weight percentage based on dry basis
[b]Obtained externally on dry ash free basis
[c]Higher heating values on dry basis

6.3.6 BIOCHAR FROM CO-PYROLYSIS PRODUCTS

The spectra for the co-pyrolysis char is shown in Fig. 6.7 and the corresponding peaks are displayed in Table 6.9. The spectra for the 40% mixed wood and 40% straw are very similar as shown in Fig. 6.7. The peaks identified for the 40% mixed wood and 40% straw biochar are typical of the sewage sludge biochar except the peak shown at 2949-2912 cm^{-1}. On the other hand, the spectrum for the 40% rapeseed biochar varies to that of 40% mixed wood and 40% straw. The main similarities found between the three biochar are mainly due to alkane compounds found between 2949-2912 cm^{-1} and 1473-1443 cm^{-1}. The third similarity was found to be with a peak in the range of 1075-1000 cm^{-1} that is due to secondary aliphatic compound.

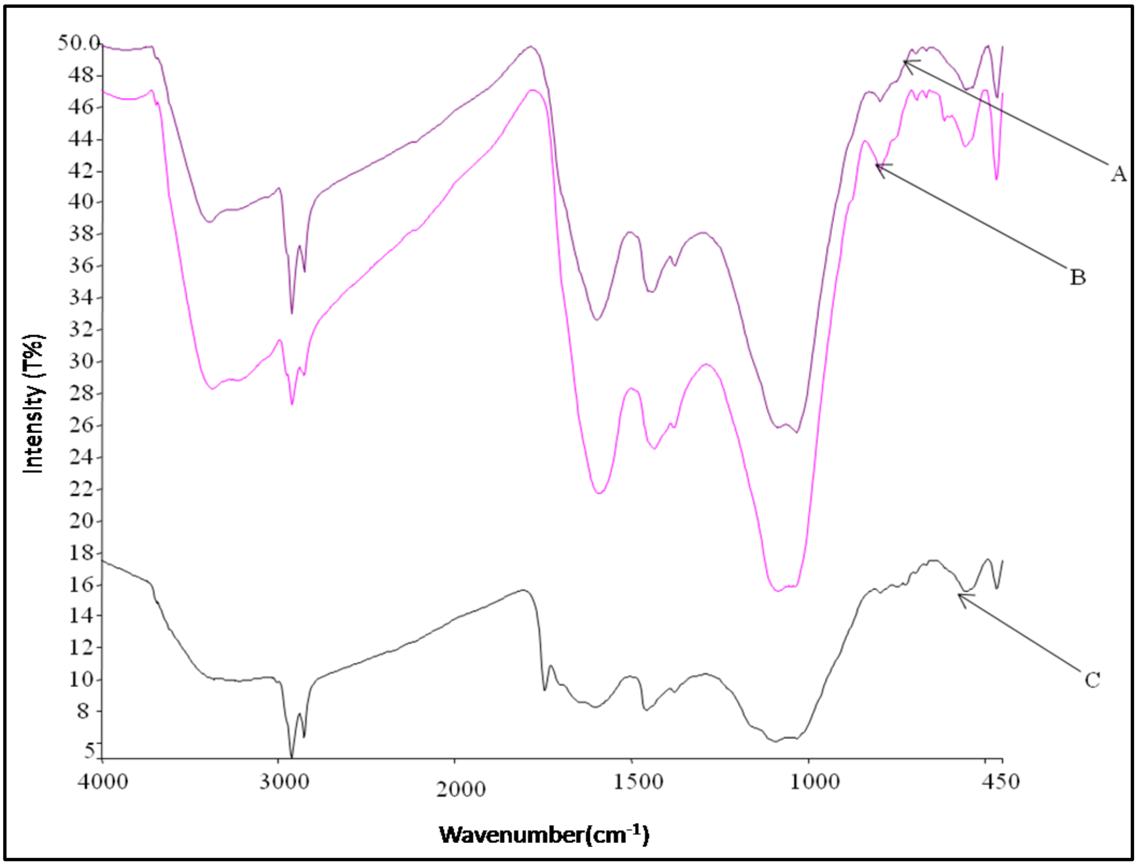


Figure 6.7: The spectra for co-pyrolysis biochar obtained from (A) 40% mixed wood, (B) 40% straw and (C) 40% rapeseed at 450 °C

Table 6.9: FT-IR analysis of the co-pyrolysis char

Wavenumber (cm^{-1})	Type of bond	SS + 40% Mixed Wood	SS + 40% Rapeseed	SS + 40 % Straw
3475-3350	C-C(=O)-NH_2	√	-	√
2949-2912	-CH_2-	√	√	√
1620-1585	Aromatic, 1,3,5-trisubstituted on benzene ring	√	-	√
1473-1443	-CH_2-	√	√	√
1075-1000	Secondary aliphatic, C-C-O	√	√	√
600-500	Amides, C(=O)-NH_2	√	-	√
500-460	-CH(CH_3)$_2$	√	-	√

6.3.7 CO-PYROLYSIS GASES

Table 6.10 shows the gas percentages of the non condensable gases obtained from the co-pyrolysis of sewage sludge with 40% mixed wood, 40% rapeseed and 40% straw. The 40% straw showed the highest percentage of permanent gases compared to other fractions. CO_2 was the largest percentage of gases detected in 40% straw. However, the 40% rapeseed has the lowest gas yield. The lowest composition CH_4 was detected in the 40% rapeseed. Ischia et al [65] also found that the co-pyrolysis of sewage sludge with clay increased biogas production. There is no literature regarding co-pyrolysis of sewage sludge with mixed wood, rapeseed and straw.

Table 6.10: Gas composition from co-pyrolysis products

	SS + 40% Mixed Wood	SS + 40% Rapeseed	SS + 40% Straw
Gas percentage (vol %) (dry mass basis)	20.5	13.5	23.5
Gas composition (vol %)			
CO_2	8.6	7.2	14.1
CO	8.8	6.1	7.3
CH_4	3.1	0.3	2.1

6.4 SUMMARY

The co-pyrolysis of sewage sludge with other biomass offers great improvements in some of the characteristics of the bio-oil, biochar and non condensable gases. The co-pyrolysis of sewage sludge with rapeseed showed the highest energy content compared to mixed wood and straw. However the energy content obtained is lower than that of sewage sludge pyrolysis oil. The use of 40% rapeseed increased the amount of bio-oil yield compared to sewage sludge pyrolysis alone. The highest viscosity and lowest pH of the pyrolysis oil was found to be with the 40% mixed wood.

The co-pyrolysis biochar illustrates varying characteristics. The 40% rapeseed has the highest energy content of 23.5 MJ/kg however it was found to be more costly compared to straw and mixed wood. The use of 40% mixed wood showed a great improvement with the sewage sludge biochar. The energy content of sewage sludge biochar was increased with the use of 40% mixed wood from 11.2 MJ/kg to 22.7 MJ/kg. The use of mixed wood with sewage sludge is the most cost effective way of improving the biochar characteristics found in the sludge.

The highest amount of non condensable gases was from the 40% straw. However CO_2 contributed significantly to the composition. On the other hand, the 40% mixed wood showed the highest CH_4 composition with relative amounts of CO_2 and CO.

The pyrolysis of sewage sludge produces a very strong pungent smell that is very undesirable. However the use of the 40% mixed wood with the sewage sludge masks the strong odour and results into a sweet smell that is neither offensive nor undesirable. The co-pyrolysis of sewage sludge and mixed wood is likely to be increased due to some of these advantages.

CHAPTER 7: POTENTIAL BENEFITS OF SEWAGE SLUDGE BIO-CHAR FOR AGRICULTURE

Sewage sludge has been applied to soil due to the potential benefits it delivers. However, biochar has been reported to have long term impact in agricultural use. This chapter discusses the potential benefits of sewage sludge biochar and that obtained from co-pyrolysis with mixed wood, straw and rapeseed. It forms a basis for further work that can be carried out in this area.

7.1 BIOCHAR

Since the discovery of the Terra Preta in Mexico that is referring to fertile soils enriched with char, the use of biochar for agriculture has been viewed as a great potential for carbon sequestration in the soil [75]. The use of biochar has been reported by several authors to have great benefits [75][76][77]. The use of biochar in the soil can increase water retention, enhance soil fertility, improve nutrients availability, and decrease emissions [75][76][77].

The porous structure of biochar allows micro-organisms long term habitation and better water retention capacity. Biochar differs depending on the feedstock and temperature used for its production [78]. Downie et al [79] states that the temperature used for the pyrolysis process greatly affect the structural changes of the biochar. The characteristic of a given biochar shows the potential benefits that could be derived from it. Amonette et al [78] identified biochar containing macronutrients such as N, P, Ca and Mg to be beneficial to plant growth. The presence of these minerals gives an indication of the potential benefits of biochar to soil.

Biochar has been reported to decrease nitrous oxide emission by up to 50 % [80]. The use of biochar with a fertilizer has been proven to enhance yield compared to chemical fertilizer alone [81].

The pyrolysis process is among the technologies used to produce biochar. However the properties of biochar differ depending on the biomass used, pyrolysis process, pyrolysis temperature, heating rate and the residence time [75][79][81][82][83].

This chapter investigates the basic properties needed for sewage sludge biochar soil application and it creates the basis for further work that could be carried out in this area.

7.2 SAMPLES

The samples used for this analysis are biochar obtained from intermediate pyrolysis of sewage sludge and co-pyrolysis biochar from 40 wt% mixed wood, 40 wt% straw and 40 wt% rapeseed. The co-pyrolysis biochar were obtained from laboratory scale experiments.

7.3 ANALYSIS METHODS

The pH of the biochar was determined by dissolving biochar in deionised water at a ratio of 1:5. The pH was measured after shaking the solution for 30 minutes. The volatile and ash content were measured at 550 °C for 30 minutes; this method was modified according to McLaughlin [84] because the biochar was deemed to be destined for the soil and not used as a fuel.

The earthworm avoidance tests were performed using the species Eisenia Andrei (red tiger). The earthworm avoidance test indicates the potential toxicity of test samples to soil organisms [85] [86]. This species has been employed by several researchers [85] [86] due to their sensitivity to environment and chemicals. They are also beneficial to the soil ecosystem. The test method was based on ISO (2005). The test chamber was a clear plastic box (20 cm length, 12 cm width and 5 cm height) with a perforated lid to allow aeration (Fig.7.1). A partition was placed in the middle of the box. The soil used for test was sieved to ≤ 2 mm. The control side was filled with 150 g of unconditioned soil while the test side was filled with 130 g of amended soil containing 20 g of biochar. The level of application corresponded to 2.56 dry kg per m^2 [87]. The partition was then removed and ten earth worms were placed in the middle. The container was sealed to prevent escape of the earth worms (Fig.7.1). The test was run at room temperature for a period of 48 hr. Three replicates of each sample were made for accuracy. The average net response of the worms to control and the amended soil was calculated using the statistical equation from Amorim [88] as shown below.

$$Response = \left(\frac{(Worms\ in\ control\ soil - Worms\ in\ the\ test\ soil)}{Number\ of\ worms}\right) x \quad 100 \qquad \textit{Equation 7.1}$$

A negative response indicated a preference to the soils while a positive response indicated an avoidance of the soil sample.

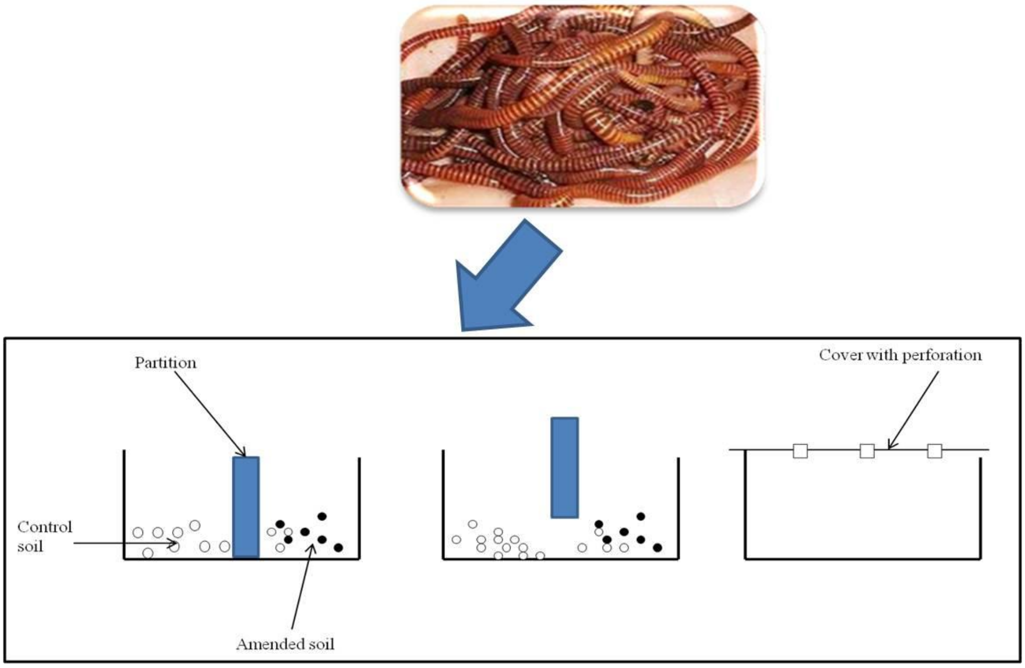


Figure 7.1: Experimental setup of the earthworm avoidance tests for the biochar samples

7.4 RESULTS AND DISCUSSION

7.4.1 BIOCHAR STRUCTURE

Biochar has a complex structure as shown in Fig.7.2. The graphite structure conceals both organic and inorganic molecules. Mineral deposits of biochar can be seen in Fig.7.2 for sewage sludge and 40% straw. These are not clearly visible using the scanning electron microscope for the 40% mixed wood and 40% rapeseed. The pores in the biochar structure give it a unique identity that distinguishes it from other types of fertilizers. The strong carbon atoms enable greater water retention capacity and slow decomposition [77] [78].

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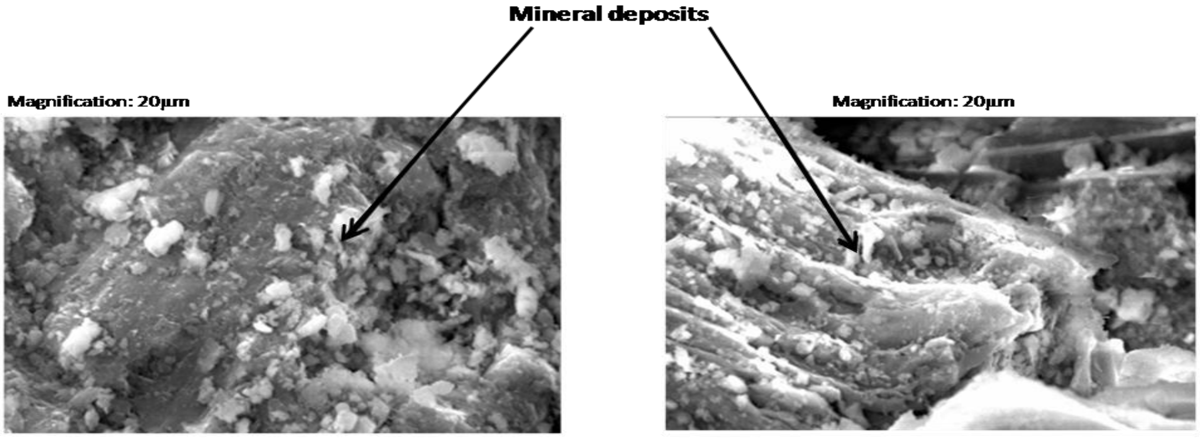
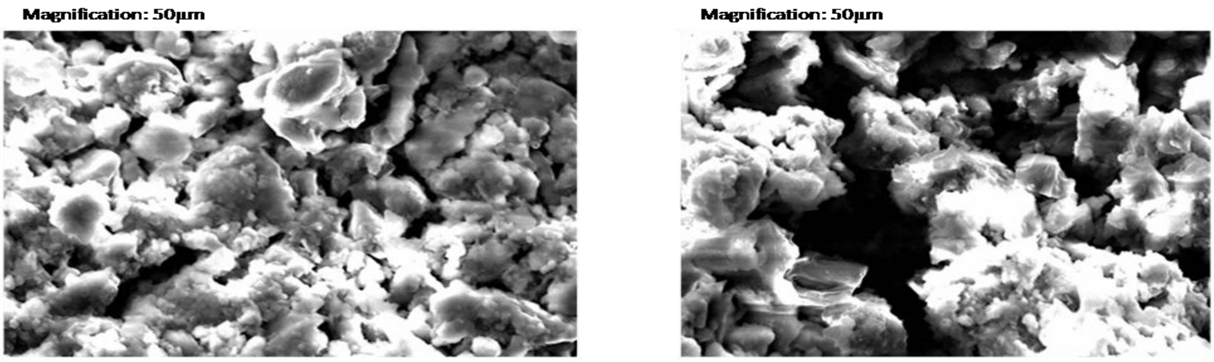


Sewage sludge biochar

Sewage sludge with 40% straw biochar



Sewage sludge with 40% rapeseed biochar

Sewage sludge with 40% mixed wood biochar

Figure 7.2: The scanned electron microscope images for sewage sludge biochar and co-pyrolysis biochar

7.4.2 CHARACTERISTICS OF SEWAGE SLUDGE AND CO-PYROLYSIS CHARS

Table 7.1 shows the proximate and ultimate analysis for the sewage sludge biochar and the co-pyrolysis biochar.

7.4.2.1 VOLATILE CONTENT

The volatile content of the biochar is shown in Table 7.1. The volatile content acts as a source of carbon and provides nutrients to soil microbes [84]. The 40% rapeseed char has the highest volatile content of the biochar. The 40% rapeseed retained some of the oil after the pyrolysis process that contributes to this amount. This implies that more nutrients will be found in the 40% rapeseed char. However, the sewage sludge biochar has the lowest volatile content due to having high amounts of ash.

7.4.2.2 ASH CONTENT

The ash content represents the percentage of inorganic compounds. The sewage sludge biochar contains the highest level of ash content and will therefore have higher percentage of inorganic compounds. The amount of ash contained in the biochar limits its agricultural application. Taylor [89] recommends 10 wt% ash content for application to the soil however if the value is greater, then metals contained in the biochar should be identified.

It is clear from Table 7.1, that sewage sludge biochar has the highest level of P, Ca, Mg and Si. The elements decrease the amount of fertilizer that could be added to the soil since these boost plant growth especially where high pH levels are required [75]. The inorganic in the soil may also help to reduce the effects of toxins present in the soil [75]. This is achieved by increasing the soil pH which weakens the effects of the toxins [75].

7.4.2.3 CARBON AND NITROGEN RATIO

The 40% straw biochar has the highest ratio of C:N being 15:1. The biochar containing 40% wood and 40% straw have the same C:N ratio of 12:1. On the other hand, sewage sludge biochar has the lowest amount of C:N. A low carbon to nitrogen ratio is favourable since this increases the population of decay organisms and allows more organic matter decomposition [90]. Although nitrogen is detected in biochar, this doesn't imply immediate availability to the soil or plant growth [76].

The ratio of carbon to nitrogen has been highlighted as a significant contribution a fertilizer would make to the soil. Having high ratios of C/N means that carbon will subsidise the benefits that could be obtained from nitrogen. It is clear from Table 7.1 that sewage sludge biochar has more carbon and nitrogen compared to sewage sludge and other biochar. It also has the lowest C:N ratio implying that the rate of mineralisation is predicted to be greater in the sewage sludge biochar compared to the rest shown in Table 7.1

The sewage sludge char the lowest C/P of 5.4 while the co-pyrolysis char have a C/P ratio ranging from 14.4 to 18.6. The sewage sludge char also has the lowest C/S of 1.9 while the co-pyrolysis char have a C/S ratio ranging from 38.3 to 43.5. Stevenson and Cole [91] recommended a ratio of C/N should be less than 20:1, phosphorus to be C/P less than 200:1 and sulphur to be C/S less than 200:1. All the samples shown in Table 7.1 are within the limits specified by Stevenson and Cole [91]. The biochar samples will therefore allow mineralisation that is the conversion of organic N, P and S into other forms by microorganisms [91]. This implies that the biochar will be beneficial to the soil.

7.4.2.4 PHOSPHORUS CONTENT

Sewage sludge biochar has the highest phosphorus content of 4.7 wt% and this is almost double that found in just sewage sludge to be 2.4 wt%. Phosphorus is a major nutrient found in a soil fertilizer. The sewage sludge char has an extra advantage over the other biochar. The 40% rapeseed biochar is the second highest to sewage sludge char with 3.28 wt%. The amount of N and P present in sewage sludge are influenced by the following; treatment process either aerobic or anaerobic digestion, amount of inorganic N or P, C: N ratio and pH [92][93][94]. Warman and Termeer [95] reported that the use of flocculants in wastewater treatment decreases the amount of phosphorus.

7.4.2.5 CALCIUM CONTENT

Sewage sludge biochar has the highest calcium content of 4.9 wt%. On the other hand, sewage sludge with 40% straw has the lowest calcium content of all the biochar found in the Table 7.1. Calcium helps to maintain chemical balance in the soil, improves water diffusion and neutralizes cell acids [76][91]. The availability of calcium is limited by the presence of other minerals in the soils such as potassium, iron and magnesium [77][78]. Excess amounts of calcium can only reduce the plants uptake of essential minerals [77][78].

7.4.2.6 pH

The acidity or alkalinity of biochar predicts its possible applications. Some soils require a boost with their pH while other need to lower this, depending on their location and activity being carried out. The sewage sludge biochar and the 40% straw show the highest pH values compared to those in Table 7.1. The sewage sludge biochar being alkaline could be beneficial to soils that are acidic. The high pH value of the sewage sludge biochar is attributed to the hydrolysis of alkali earth metals such as Ca and Mg as these are found to be in high amounts compared to other biochar. However, the

40% straw biochar might have other components that significantly contributed to the pH. This is because the Ca and Mg amounts in the 40% straw biochar are relatively low. Biochar with lower pH ranges have been reported by [78] [96] to inhibit the impact of heavy metals such as Cu and Mn to plant growth.

Table 7.1: The properties of sewage sludge char and co-pyrolysis char

	Sewage sludge (SS) char	SS + 40% Wood	SS + 40% Rapeseed	SS + 40 % Straw
Proximate analysis(wt. %)(±1)[a]				
Volatile content	35.4	55	61.7	53.8
Ash	58.5	31.7	29.8	42.7
Ultimate analysis (wt. %)(±0.03)[b]				
C	25.5	50.96	47.15	49.04
N	3.1	4.19	4.02	3.21
S	13.5	1.17	1.10	1.20
Ratios				
C:N	8:1	12:1	12:1	15:1
C:P	5.4	18.5	14.4	18.6
C:S	1.9	43.5	42.9	38.3
Ca	4.9	2.53	2.69	2.48
Mg	0.6	0.36	0.47	0.38
P	4.7	2.75	3.28	2.64
pH(±0.1)	8.3	7.80	7.18	9.82

[a] Weight percentage based on dry basis

[b] Weight percentage based on dry ash free basis

7.4.3 EARTH WORM AVOIDANCE TEST

Table 7.2 shows the results of the avoidance test with the Eisenia Fetida worm species. A higher negative response indicates a higher preference of the worms to the biochar soil mixtures. The results show a general tolerance of worms to the biochar soil mixtures. The worms showed a preference to the biochar soil mixtures compared to the control soil alone. This implies that the biochar soil samples were less toxic; this is because an average of 28 % of the worms was found in the control soil compared to an average of 67 % in test soil. Soil mixtures are considered to be toxic if > 80 % of worms prefers the control soil [86]. There was a greater preference for the sewage sludge with 40% straw biochar compared to other test samples while 40% rapeseed showed the least preference.

Table 7.2: Earthworm avoidance tests with biochar soil mixtures

Test sample	Average response (%)	Ranking of best response
SS+ 40 wt% Straw	-56.3	1
SS +40 wt% Wood	-43.8	2
Sewage sludge (SS) char	-37.5	3
SS + 40 wt% Rapeseed	-18.8	4

7.4.4 HEAVY METALS IN THE SEWAGE SLUDGE BIOCHAR

Sewage sludge has been used for agriculture for several years but there is concern over the presence of heavy metals [25]. The concentration of heavy metals into the environmental is of great concern due to the harmful effects they pose to humans and plants [22]. The metals that are toxic to humans when ingested through plants are copper, zinc and nickel [22]. The most toxic heavy metals are cadmium, mercury and lead [22][25]. The amount of heavy metals applied to the soil from sewage sludge is controlled by the EU directive 86/278/EEC. It limits the concentration of the soil being applied as well as the sludge being used. The concentration of metals in the soil must be known as well as the metals from the sludge [21]. The combined limits must comply with those shown in Table 7.3.

Table 7.3: European Council Directive 86/278/EEC Sewage Sludge Metal Level Standards [21]

The equation 7.2 recommended by Forster [21] is used to determine the application rate for each metal. The time period for the application is taken to be 30 years. The lowest application value of all the metals analysed is used to comply with the regulations.

$$Rate = \left[\frac{soil\ application\ limit - 2.2\ x\ (soil\ concentration)}{Sludge\ concentration}\right]\ x\ \left[\frac{1000}{Time\ period}\right] \qquad \textit{Equation 7.2}$$

The application of biochar to agriculture has been verified by several authors. However sewage sludge biochar has not undergone the same scrutiny as that of sewage sludge in term of legislations and restrictions [97]. It cannot be used in abundance without obtaining a permit from the Environmental Agency [97]. Shackley and Sohi [97] state that the current research in the UK has not yet established sufficient evidence to be submitted to the Environmental Agency about the potential benefits of biochar to the soil. It is recommended that an alternative legislation that would be used for biochar soil application to be the Water Resource Act 1991 or Waste framework directive [97]. The former identifies risks to surface or ground water while the latter prevents risks to air, water, soils, animals and plants [97].

Table 7.4 shows the comparison between the heavy metals found in the sewage sludge before pyrolysis and heavy metals contained in the pyrolysis biochar. On average the amount of heavy metals found in the pyrolysis biochar is double that in sewage sludge. Most of the heavy metals originally contained in sewage sludge remain in the char after pyrolysis, except the volatile elements mercury and cadmium were found to volatilize at temperature higher than 550 °C [49]. These authors [37][49][60] also found higher quantities metals in the char.

Table 7.4: Heavy metals in sewage sludge and pyrolysis char[1]

Heavy metals	Sewage sludge(ppm)	Pyrolysis biochar(ppm)
Chromium	44	79
Copper	346	571
Nickel	32	59
Lead	68	127
Zinc	585	0.11%
Cadmium	2	4

[1] Concentration and percentage on dry ash free basis (±0.3%)

7.5 SUMMARY

The biochar samples contain essential nutrients such as Ca, Mg and P that are beneficial to crop growth. The sewage sludge biochar contains more nutrients than the digested sludge and co-pyrolysis char. The earth worm avoidance test also proved that biochar can be tolerated in the soil however long term usage and its effects need to be investigated.

The study carried out about the biochar samples is limited as it is only a basis for further work that could be undertaken to investigate the impact of biochar for agricultural use. The results obtained can be expanded by carrying out field trials to determine long term impact of crop growth, micro-organisms growth or inhibition, limitations of biochar application and any other factor that might be of concern.

Further work undertaken would also enable government bodies such as the environmental agency to better understand its impact to the environment. This will then enable the environmental agency to permit the wider usage of biochar. However, clear benefits or disadvantages are needed to prove its feasibility for agricultural production.

CHAPTER 8: STABILITY OF SEWAGE SLUDGE PYROLYSIS OIL

This chapter investigates the thermal stability of sewage sludge pyrolysis oil obtained from the intermediate pyrolysis process. The main solvents used to test the thermal stability of sewage sludge pyrolysis oil are methanol and biodiesel. The samples are heated at 60 and 80 ˚C at varying times to determine the changes in characteristics of the bio-oil that are related to the ageing process.

8.1 NATURE OF BIO-OIL

Bio-oil is one of the major products obtained from the pyrolysis process. It has varying odour ranging from sweet smelling wood to pungent, originating from sewage sludge. It consists of a range of compounds depending on the feedstock used for pyrolysis. Bio-oils have been reported to have a high water content ranging from 15 to 30 wt% [55][74]. Bio-oils tend to contain a high water content compared to conventional fuels. The percentage of water has been observed to increase during storage. The tendency of water increase has been attributed to reactions occurring within the bio-oil that produce water as a by-product. The presence of water in the bio-oils affects its characteristics. It lowers the higher heating value and causes phase separation of the bio-oil [98].

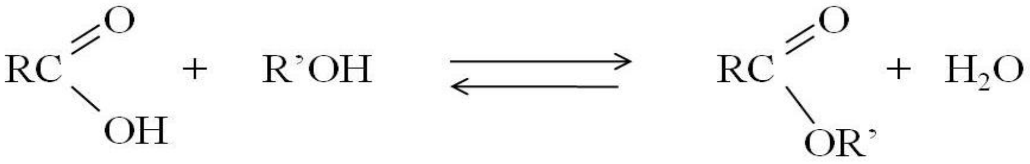
Bio-oils have also been reported to have high viscosities [74][98]. This has been observed to increase with storage time. The increase in viscosity is attributed to polymerisation reactions occurring within the bio-oil that form heavier fractions. The presence of char fines in unfiltered bio-oil has been reported by Agblevor et al [99] to accelerate the polymerisation reactions.

8.2 CAUSES OF INSTABILITY

Bio-oil contains varying compounds depending on the feedstock used for pyrolysis. Bio-oil contains a high concentration of oxygenated compounds [98]. Some of these are in form of phenols, methoxyphenols, aldehydes and ketones. Czernik and Bridgwater [74] state that the presence of high oxygen contents cause instability and variation in bio-oil properties. Instability of bio-oils also occurs when different compounds react with each other to form other compounds with diverse compositions producing water as a by-product [100]. The compounds formed are mainly attributed to some of following reactions [98][100];

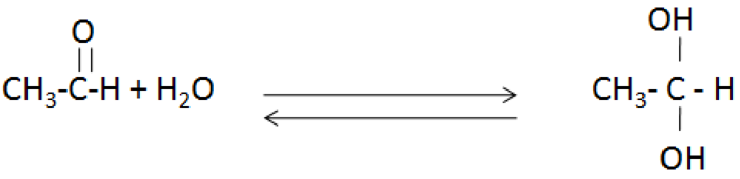
8.2.1 ESTERIFICATION REACTIONS

This involves the reaction of organic acids and alcohols to form esters and water



8.2.2 HYDRATION REACTIONS

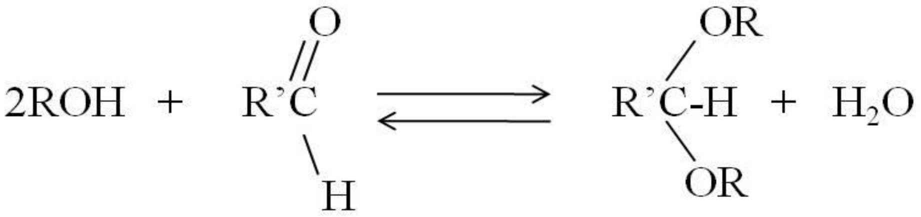
The hydration reaction entails the reaction of aldehydes and water to form hydrates.



$$CH_3\text{-}\overset{\overset{\displaystyle O}{||}}{C}\text{-}H + H_2O \rightleftarrows CH_3\text{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}\text{-}H$$

8.2.3 ACETALISATION REACTIONS

These involve the reaction of aldehydes and alcohols to forms two oxygen molecules attached to a carbon.



$$2\mathrm{ROH} + \mathrm{R'C(=O)H} \rightleftharpoons \mathrm{R'C(OR)_2\text{-}H} + \mathrm{H_2O}$$

These reactions form heavier compounds, increase the viscosity and solids content of the bio-oil. The increase in viscosity is also attributed to thermal degradation that causes loss of volatiles that causes the increase in viscosity [101]. Refrigeration is one of the methods used to delay polymerisation.

8.3 PREVIOUS WORK

Diebold and Czernik [102] studied six different solvents that included; 10 wt% methanol, 10 wt% ethanol, 10 wt% ethyl acetate, a mixture of 10 wt% acetone and methanol, and a mixture of 10 wt% methyl isobutyl ketone and methanol. They studied the stability at a range of temperatures from 7 to 90 ˚C. They found that the addition of 10 wt% of methanol proved to be the most effective amongst the solvents to increase the stability by reducing the molecular weight increase and viscosity. Diebold and Czernik [102] investigated the effects of ageing on biocrude oil with these additives ethyl acetate, methyl isobutyl ketone and methanol, acetone, methanol, acetone and methanol, and ethanol. Accelerated aging tests were run at 90 °C to screen the additives. The use of additives was found to dramatically decrease the rate of aging, as measured by the rate of increase of oil viscosity with time. However, the addition of methanol before ageing was found to be significant as this decreased the ageing rate by a factor of 20. It was also found to decrease the rate of ageing by diluting chemical reactions and formation of intermediate products. Methanol was also found to be the cheapest among the additive used.

Bouchera et al [103] investigated raw bio-oil (as-produced), raw bio-oil with aqueous phase and raw bio-oil with methanol mixtures were studied. The aqueous phase was added to the bio-oil at concentrations ranging from 5 to 25% and methanol from 5 to 15%, both with 5% stepwise increments. The authors used a varying time scales of 1, 6, 24, 72 and 168 hours and utilised temperatures of 40, 50 and 80 °C. The sample aged at room temperature was analysed at time zero, 65 and 260 days. The authors found significant changes in viscosity at 80 °C compared to 40 and 50 °C. The rise of the ageing rate with increasing temperature was attributed to the intensification of the condensation and polymerisation reactions that are responsible for the changes in the bio-oil that lead to an increase in viscosity. Ageing of the raw bio-oil at room temperature resulted in a dramatic viscosity increase during the first 65 days, after which a plateau was reached. The same tendency was observed when the viscosity was measured at 80 °C. It was found that the molecular weight increase after heating the bio-oil for one week at 80 °C was equivalent to keeping the sample for one year at room temperature. Bouchera et al [103] found the addition of methanol to the pyrolysis oil was found to improve stability in all fractions. Methanol also aided the reduction of viscosity by dissolving of molecules. The addition of the aqueous phase to pyrolysis oil was found to increase the thermal instability.

Hilten and Das [101] studied accelerated stability over 24 h at 80 ˚C for five samples; pure pine, pine stabilised with methanol, pine stabilised with ethanol, pure peanut hull, and peanut pine stabilised with methanol. They used thermal and oxidative tests to determine the stability of the bio-oils. The tests analysed changes in structure, viscosity, solids formation and oxidative onset temperature before and after ageing. An increase in viscosity indicated the presence of polymerisation reaction due to formation of longer chain molecules. GC-MS was used to determine the increase in concentration of compounds and the highest increase was regarded as most unstable. FT-IR was used to determine the formation and concentration of oxygenated functional groups such as alcohols, ethers, aldehydes and ketones. It was found that pine stabilised with methanol showed the most stability when viscosity and solids content were measured.

8.4 AIM OF THIS STUDY

The aim of this study is to determine the stability of sewage sludge pyrolysis oil derived from intermediate pyrolysis. The pyrolysis oil differs from all the other pyrolysis bio-oils as it is miscible with biodiesel without using any emulsification process. The study will investigate the thermal stability in 10 wt% methanol, 10 wt% biodiesel, 20 wt% biodiesel and pure pyrolysis oil without any solvent. The test temperatures used are 60 and 80 ˚C for a time period of 72 and 168 h. These time periods were used as they represent a variation in the tests.

8.5 METHODOLOGY

8.5.1 THERMAL STABILTY TESTS

The test mixtures were placed in sealed bottles to prevent loss of volatiles. Three replicates of each sample were made for consistency and accuracy of results. The mixtures were placed in the oven for 72 and 168 hours at 60 and 80 ˚C. Table 8.1 shows the heating temperature with the corresponding heating period and the proposed representation of the ageing time.

Table 8.1: Heating temperatures with the representative ageing period

Temperature (°C)	Heating period (h)	Representative period of ageing [102][103][104]
80	168	1 Year
60	168	6 months
80	72	5 months
60	72	3 weeks

8.6 RESULTS AND DISCUSSION

8.6.1 VISCOSITY

The measurement of viscosity is a major parameter to be studied for the investigation of the ageing properties of the pyrolysis oil. Table 8.2 shows an increase in viscosity from 72 h to 168 h at both temperatures of 60 and 80 °C. Fig. 8.1 shows the viscosity trend at 80 ˚C and Fig. 8.2 illustrates the changes at 60 ˚C. It can be observed that drastic changes in viscosity occurred at 80 ˚C (Fig.8.1) compared to those in Fig.8.2. Boucher et al [103] also found no significant changes in viscosity of bio-oil obtained from softwood bark aged at 50 °C; however significant changes were observed when the temperature was raised to 80 °C. Oasmaa and Kuoppala [104] found that the increase in viscosity for the bio-oil obtained from forestry residue aged at 80 °C for 24 h correlated to approximately one year of storage at room temperature. Hilten and Das [101] also found a significant increase in viscosity for bio-oil obtained from pine pellets and peanut hull samples aged at 80 °C for 24 h.

The raw pyrolysis oil with no additive has the greatest increase in viscosity at both temperatures of 60 and 80 °C. The pyrolysis oil has a 86.7 % increase in viscosity at 80 °C after 72 h of ageing while this is enhanced drastically with a 109.9 % increase in viscosity after 168 h. This trend is expected due to polymerisation reactions occurring within the bio-oil that cause heavier fractions to be formed leading to an increase in viscosity. The results are in agreement with similar trends observed from bio-oil with no additive by [74][102][103][104][105][106][107].

The 10% MeOH blend has a 5.0% increase in viscosity at 80 °C after 72 h while this is significantly increased after 168h at the same temperature. Diebold and Czernik [102] also found the use of 10% methanol with bio-oil to decrease the molecular weight increase and change in viscosity. Boucher et al [103] found the rate of viscosity increase of the methanol/oil mixtures to be less than the raw bio-oil from softwood bark. Hilten and Das [101] found the addition of methanol to have increased stability of bio-oil by reducing change in viscosity. It is clear that the addition of a small percentage of methanol to bio-oil aids the reduction in viscosity on the onset and improves the stability of the bio-oil.

The pyrolysis oil with 20% BD has a 4.7 % increase in viscosity at 60 °C after 72 h which then increases by 15.9 % after 168 h at the same temperature. At 80 °C, there is a 59.6 % increase in viscosity after 72 h of ageing which then increases by 98.8 % after 168 h. Overall the viscosity increase at 60 and 80 °C for 20% BD pyrolysis oil is less than that of the 10% MeOH blend. This implies that the use of the 20% BD is more effective in controlling the chemical changes the induce increase in viscosity. This is because the 20% BD pyrolysis oil samples have proved to be more stable compared to 10% MeOH when using viscosity as a criterion for determining stability.

Table 8.2: The kinematic viscosities for samples aged at 60 and 80 °C (±1), measured at a temperature of 40 °C

Sample Identification	Viscosity for unaged samples (cSt)	Viscosity for samples aged at 60˚C for 72 h (cSt)	Viscosity for samples aged at 60˚C for 168 h (cSt)	Viscosity for samples aged at 80˚C for 72 h (cSt)	Viscosity for samples aged at 80˚C for 168 h (cSt)
Pyrolysis oil(PO)	34.83	37.59	45.12	65.04	73.11
PO+ 10% Methanol	16.84	25.73	25.92	17.69	38.69
PO+ 10% Biodiesel	15.21	25.50	39.12	37.14	54.78
PO+ 20% Biodiesel	20.51	21.47	23.77	32.74	40.78

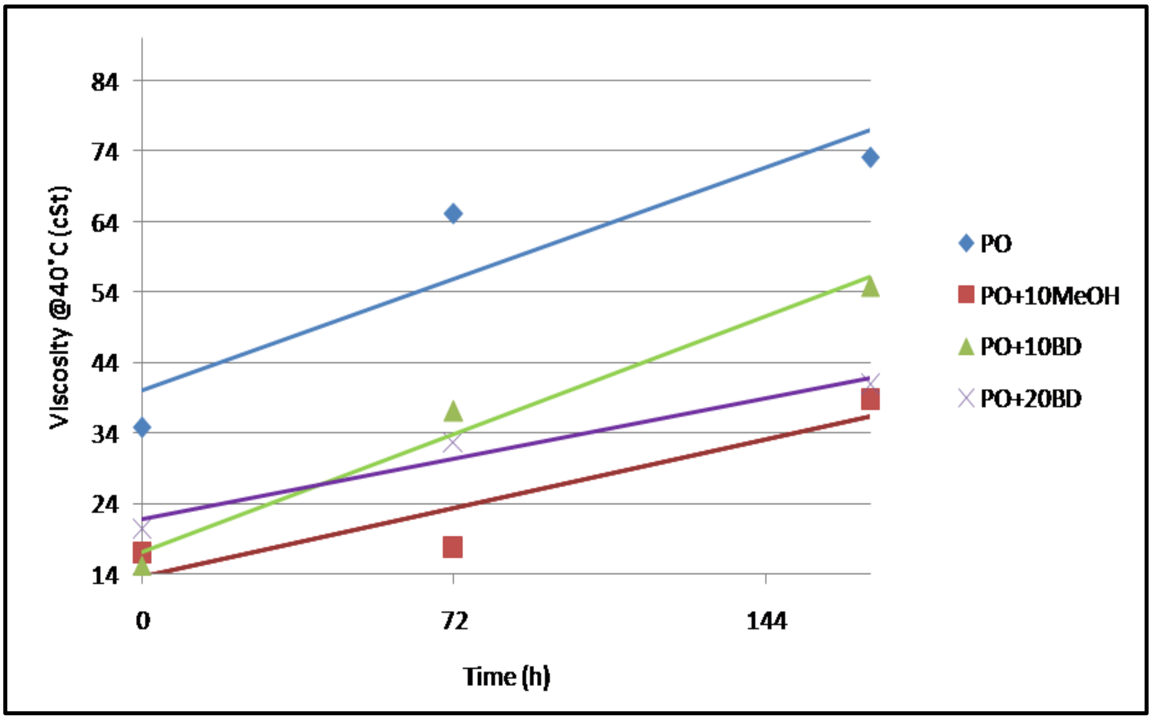


Figure 8.1: Viscosity against time for pyrolysis oil samples aged at 80 °C

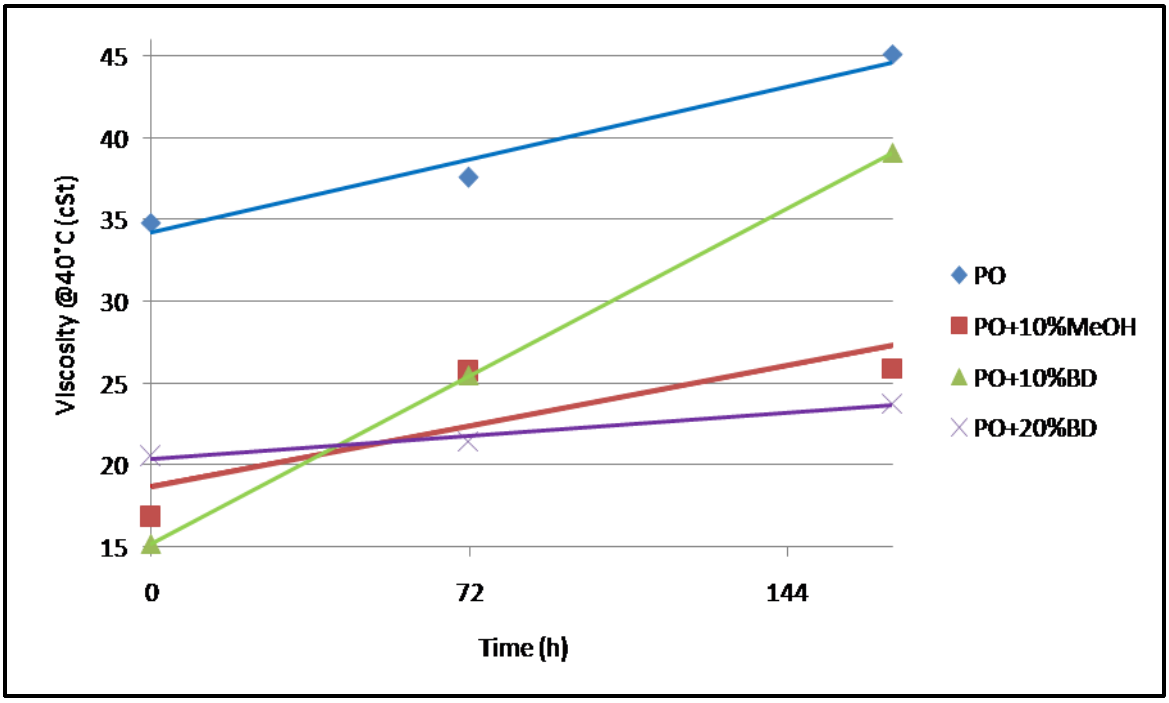


Figure 8.2: Viscosity against time for pyrolysis oil samples aged at 60 °C

These results indicate that it is sufficient to test for ageing properties of the bio-oil by carrying out tests at 80 °C for a minimum of 24 hours for lignocellulosic biomass and 168 h for other biomass. This is due to the fact that the change in viscosity is a major indicator for the bio-oil ageing process. The viscosity changes indicate that the 20% BD pyrolysis oil is more stable than the 10% MeOH. This might be due to the increase in concentration of biodiesel as the 10% biodiesel is less stable than the 10% MeOH. The addition of solvents to the pyrolysis oil shows an improvement in the stability.

8.6.2 COMPOSITIONAL ANALYSIS

GC-MS analysis was carried out for all samples for the raw and aged bio-oil for periods of 72 and 168 h. Fig. 8.3 shows the GC-MS spectra for the raw PO before ageing (A) and after ageing at 72 and 168 h (B). The retention times shown in Fig. 8.3 are displayed in Table 8.3. The raw pyrolysis oil (PO) shows an increase of compounds after 72 h at 80 °C. The new compounds detected after this time period are 2-Ethyl phenol; Methyl ester, hexadecanoic acid; Methyl ester, 9-Octadecenoic acid; and 9,17-Octadecadienal, and (z). The formation of these esters after ageing for 72 h confirms the presence of esterification reactions. There was also an increase in concentration of compounds after 168 h of ageing. Hilten and Das [101] also found an increase in concentration of compounds for bio-oil obtained from peanut hull. They also detected acetic acid after ageing which is a product of esterification reaction. Barreto et al [107] also found an increase in heavier fractions with increasing storage time which was attributed to polymerisation reactions. It is clear from the results obtained that chemical reactions occur during ageing of bio-oil. However due to the complex nature of bio-oil, only one chemical reaction can be confirmed from the products obtained but it is possible to have more than one chemical reaction. Hilten and Das [101] were also of the view that the GC-MS was not broad enough to confirm the nature of reactions that occur during ageing.

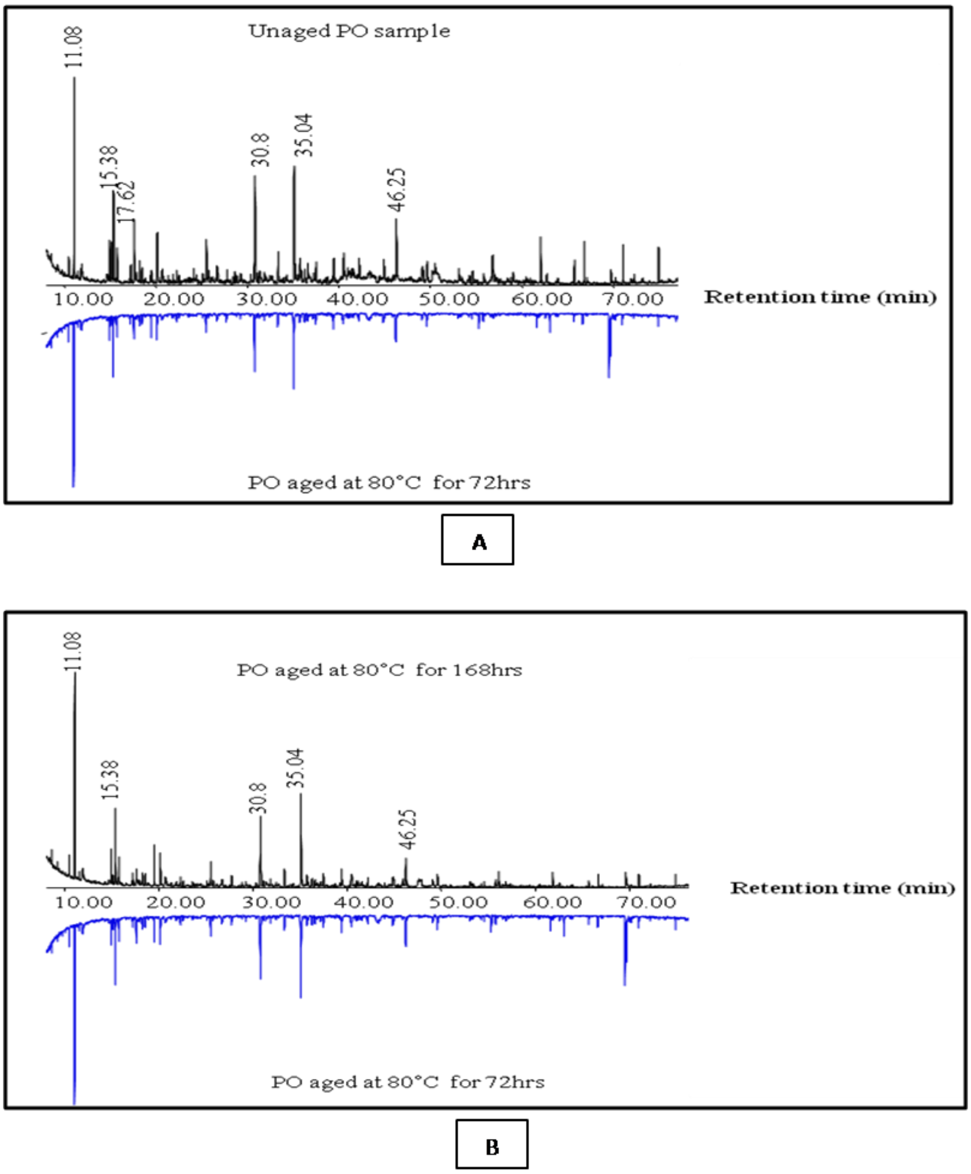


Figure 8.3: GC-MS spectra for pure pyrolysis oil (PO) from unaged (A) to aged at 80 °C after 168 h (B)

Table 8.3: Chemical composition for the unstabilised pyrolysis oil (PO)

Retention time (min)	Compounds	Unaged	Aged at 72 h at 80 °C	Aged at 168 h at 80 °C
11.08	Methyl benzene	√	√	√
15.38	Ethyl benzene	√	√	√
15.73	1,3 Dimethyl benzene	-	-	√
17.62	Styrene	√	√	√
30.8	Phenol	√	√	√
35.04	4 Methyl phenol	√	√	√
39.38	2-Ethyl phenol	-	√	-
46.25	1H-indole	√	√	√
63.04	Hexadecanoic acid	-	√	-
69.51	Methyl ester, 9-Octadecenoic acid	-	√	-
69.66	9,17-Octadecadienal,(z)	-	√	-

Fig. 8.4 shows the GC-MS spectra for 10 % MeOH, the major compounds detected are displayed in Table 8.4. The 10 % MeOH showed the greatest decrease in compounds after ageing at 72 h but then increased in composition after 168 h at 80 °C. The ageing of pyrolysis oil with methanol at 80 °C after 168 h yielded new compounds. These are; 1,4-Dimethyl benzene, 2-Methyl phenol and 2-Ethyl phenol as shown in Table 8.4. These compounds indicate the possibility that a methylation reaction could have occurred due to the presence of isomers. The use of methanol as an additive with the bio-oil has been found to delay polymerisation reaction [101][103][107]. Methanol causes dissolution of some compounds in the pyrolysis oil that alter some chemical composition. The results indicate that it is better to have an additive such as methanol in the bio-oil solution in order to delay ageing and also improve some of the physical properties such as viscosity.

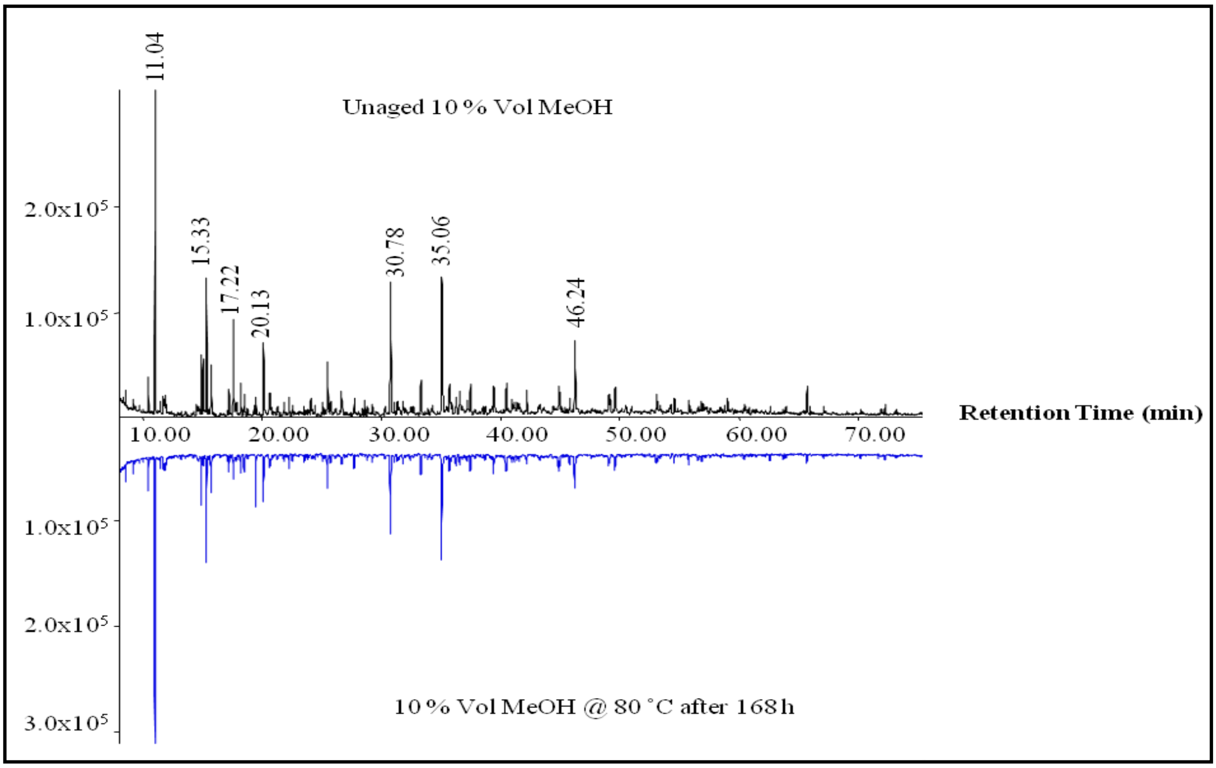


Figure 8.4: GC-MS spectra for 10 % MeOH from unaged to changes after thermal heating at 80 °C after 168 h

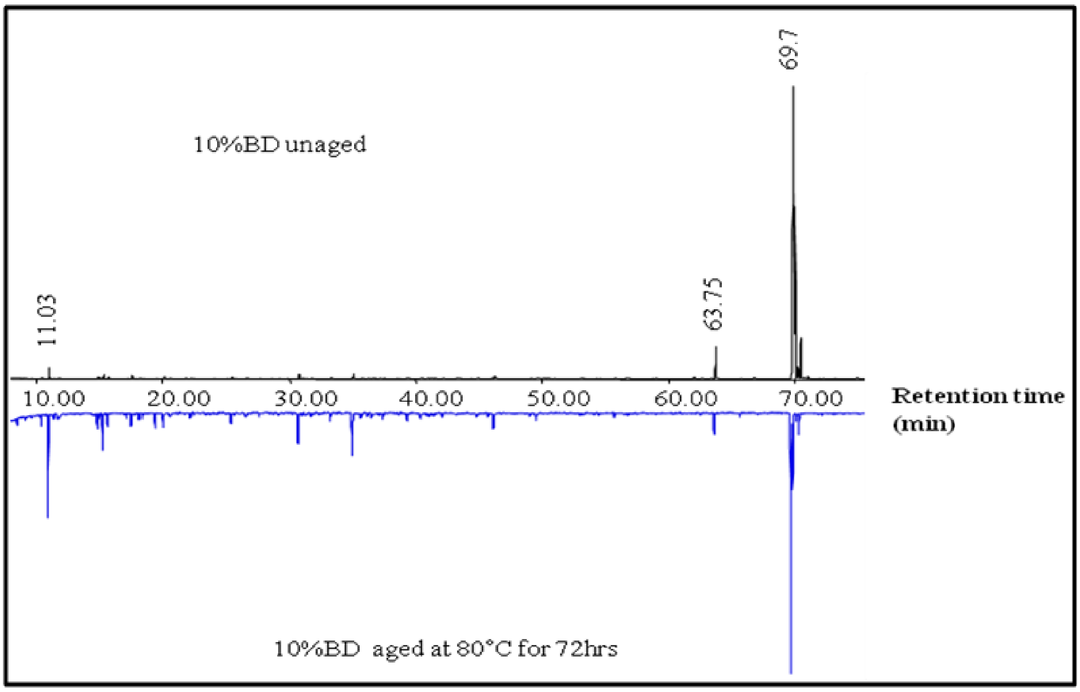
Table 8.4: Chemical composition for the pyrolysis oil (PO) + 10%MeOH

Retention time (min)	Compound	Unaged	Aged at 72 h at 80 °C	Aged at 168 h at 80 °C
11.04	Methyl benzene	√	√	√
15.35	Ethyl benzene	√	√	√
15.73	1,4-Dimethyl benzene	-	-	√
17.22	1,2 Dimethyl benzene	√	√	√
20.13	1-Decene	√	√	√
30.78	Phenol	√	√	√
33.31	2-Methyl phenol	-	-	√
35.06	4 Methyl phenol	√	√	√
39.39	2-Ethyl phenol	-	-	√
46.24	1H-indole	√	√	√

Fig. 8.5 shows the GC-MS spectra for the 10 % BD and the compounds of the spectra are displayed in Table 8.5. The pyrolysis oil with 10% BD aged at 80 ˚C after 168 h generated new compounds which are Ethyl benzene, Phenol, 4-Methyl phenol, and Methyl ester, 9-Octadecenoic acid as shown in Table 8.5. The compounds formed show the possibility of esterification reactions occurring with the 10% BD. However the extent of such reactions is more prominent with the raw pyrolysis oil. This additive has some benefit to the sewage sludge pyrolysis oil although it hasn't been used by any of the authors in literature.

Table 8.5: Chemical composition for the pyrolysis oil (PO) + 10%BD

Retention time (min)	Compounds	Unaged	Aged at 72 h at 80 °C	Aged at 168 h at 80 °C
11.08	Methyl benzene	√	√	√
15.34	Ethyl benzene	-	-	√
30.77	Phenol	-	-	√
35.05	4-Methyl phenol	-	-	√
63.75	Methyl ester, hexadecanoic acid	√	√	√
69.70	Methyl ester, 9-octadecenoic acid	-	-	√
69.91	Methyl ester, 10-octadecenoic acid	√	√	√
70.03	Methyl ester, 10,13-octadecadienoic acid	√	√	√
70.24	Methyl ester, octadecanoic acid	√	√	√



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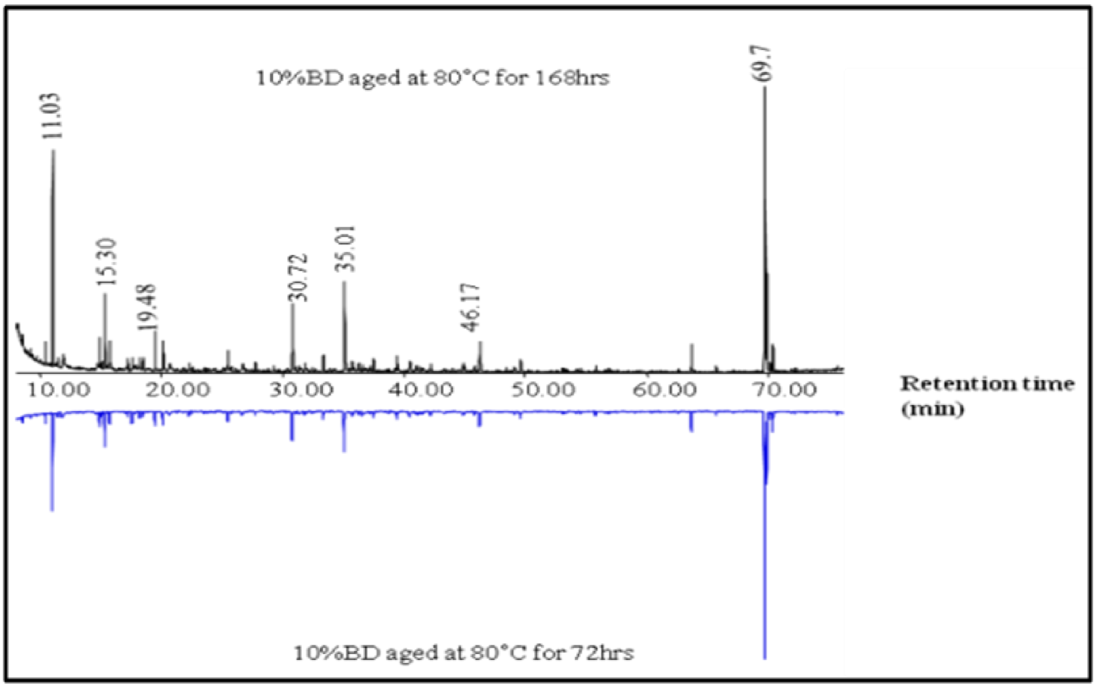

B

Figure 8.5: GC-MS spectra for 10% BD from unaged shown in [A], to changes after thermal heating after 168 h in [B]

The spectrum for the pyrolysis oil containing the 20% BD is shown in Fig. 8.6 and the compounds detected are displayed in Table 8.6. The pyrolysis oil containing 20% BD confirms new compounds at 80 °C after 168 h of ageing. These are Ethyl benzene, Phenol and 4-Methyl phenol shown in Table 8.6. According to these results, esterification reactions might be occurring within the pyrolysis oil. However, the reaction seems to be shifting to the left not the right since these reactions are reversible (section 8.2.1). The results also indicate fewer compounds compared to 10% MeOH pyrolysis oil which confirms that the 20% BD additive is more effective at controlling stability of the sewage sludge pyrolysis oil.

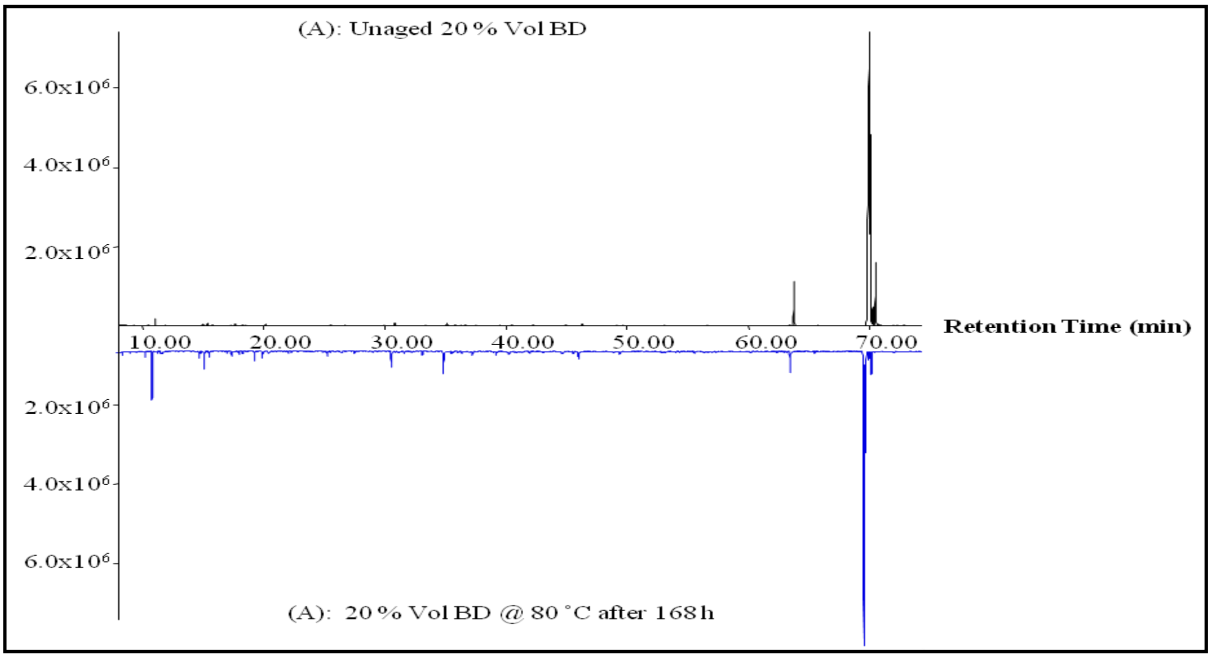

Figure 8.6: GC-MS spectra for 20% BD from unaged to changes after thermal heating at 80 °C after 168 h

Table 8.6: Chemical composition for the pyrolysis oil (PO) + 20%BD

Retention time (min)	Compounds	Unaged	Aged at 72 h at 80 °C	Aged at 168 h at 80 °C
11.08	Methyl benzene	√	√	√
15.33	Ethyl benzene	-	-	√
30.75	Phenol	-	-	√
35.03	4-Methyl phenol	-	-	√
63.76	Methyl ester, hexadecenoic acid	√	√	√
69.70	Methyl ester, 9-octadecenoic acid	√	√	√
70.08	Methyl ester, 9, 12-octadecadienoic acid	√	√	√
70.24	Methyl ester, Octadecanoic acid	√	√	√

8.6.3 FUNCTIONAL GROUP CHANGES

The changes in functional groups of the pyrolysis oil were studied using the FT-IR analysis. The FT-IR spectra in Fig.8.7 show the results of raw sewage sludge pyrolysis oil (PO), 10% methanol mixture (10 % MeOH), 10% biodiesel mixture (10 % BD) and 20% biodiesel mixture (20 % BD) at 80 ˚C with a range of 4000 to 400 cm^{-1}. A summary of the overall functional groups present in the pyrolysis oil fractions are shown in Table 8.7, Table 8.8, Table 8.9 and Table 8.10.

Table 8.7 shows a summary of functional groups detected from the ageing of the sewage sludge pyrolysis oil at 80 °C. Fig 8.7 displays a similar finger print for the pyrolysis oil aged at 72 and 168 h and Table 8.7 confirms the same changes in structure of the pyrolysis oil. The main structural change is peak formation between 1700-1500 cm^{-1} that correlates to C=C bond, this was detected at 72 and 168 h. The C=C bond corresponds to an alkene such as 1-Decene shown in Table 8.4 however this doesn't give any indication about the ageing process of the pyrolysis oil. The other change in the structure of the pyrolysis oil after ageing arouse with the disappearance of a peak between 1490-1440 cm^{-1} that corresponds to an amide with C-N-H bend. It is possible that an amide with a C-N-H bond reacted with a another compound to form a different structure but there is no evidence to support this idea.

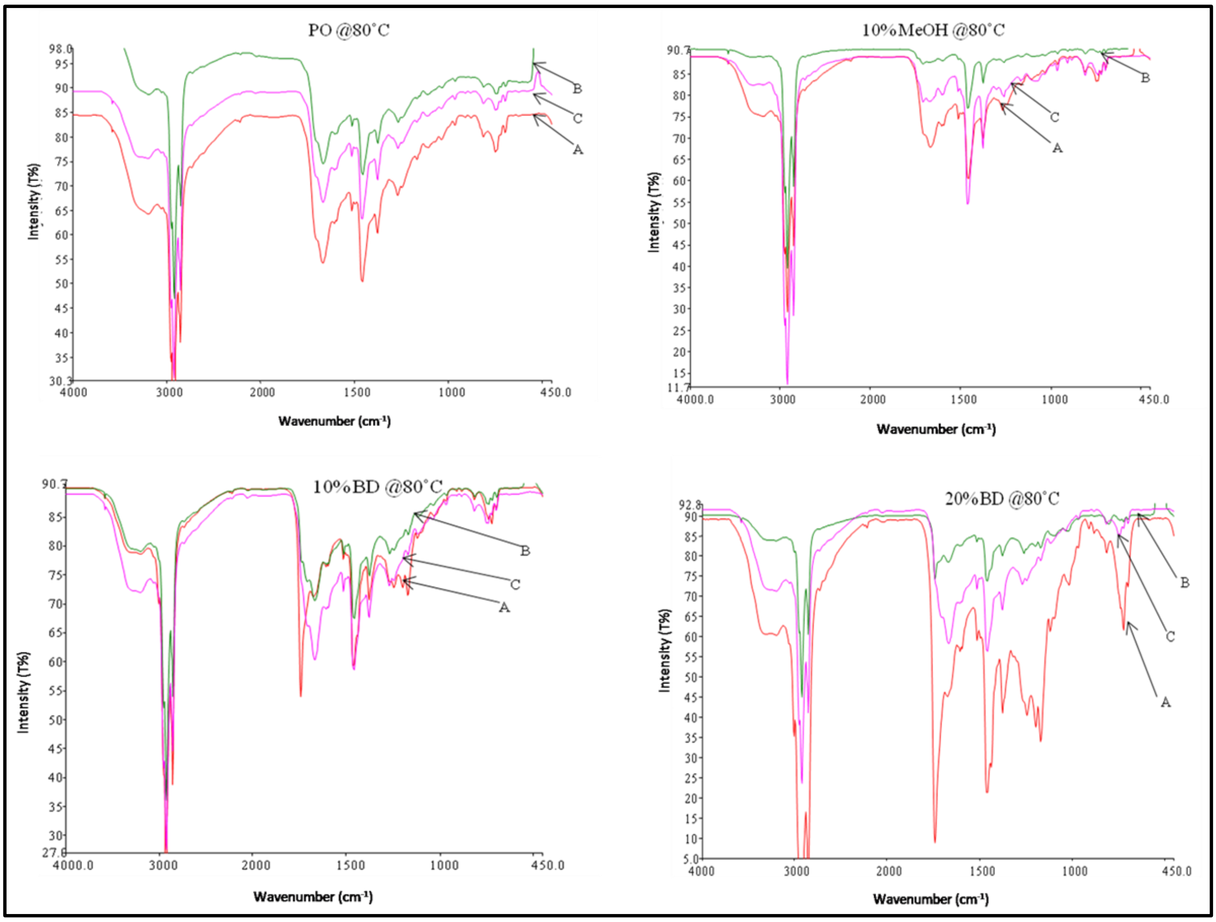

Figure 8.7: FT-IR spectra of pyrolysis oil fractions aged at 80 °C, **[A]** for unaged sample, [**B**] for aged sample after 72 h, [**C**] for aged sample after 168 h

Table 8.7: Summary of major functional groups in the pyrolysis oil (PO)

Wavenumber (cm^{-1})	Type of bond	Unaged(PO)	Aged at 72 h at 80˚C	Aged at 168 h at 80˚C
2950-2850	Alkyl, C-H stretch	√	√	√
1700-1500	C=C bond	-	√	√
1690-1630	Amide, C=O	√	√	√
1490-1440	Amide, C-N-H bend	√	-	-
1430-1200	Secondary, C-O-H	√	√	√
1410-1310	Tertiary, C-O-H	√	√	√
800-750	Tertiary, C-C-O	√	√	√

Table 8.8 shows a summary of compounds detected in the 10% MeOH pyrolysis oil. The peak at 1710 cm^{-1} after 72 h indicates the presence of a C=O stretch that corresponds to a carboxylic acid. After ageing the pyrolysis oil for 168 h with 10% MeOH, new peaks are detected. The peak formed between 1410-1310 cm^{-1} correspond to a secondary alcohol with a C-O-H stretch. However, there was no secondary alcohol detected with the GC-MS spectrum but this could be related to the additive used with the pyrolysis oil. The peak at 1708 cm^{-1} correlates to C=O stretch that is be attributed to a ketone. A ketone is a product of an oxidation reaction with a secondary alcohol. This reaction is a possibility since the functional groups in Table 8.8 already reveal the presence of a secondary alcohol. The peak at 811 cm^{-1} is a representative of a primary alcohol and in this case it is the presence of methanol. The peak at 741 cm^{-1} corresponds to an amide with NH_2 wag. Amides are formed from the reaction between a carboxylic acid and an amine. The carboxylic acid detected at 1710 cm^{-1} after 72 h of ageing and an unknown amine could be responsible for the formation of the amide. This is because the peak at 1710 cm^{-1} disappears after 168 h of ageing meaning that it is transformed into a different structure.

Table 8.8: Summary of the major functional groups contained in 10%MeOH

Wavenumber (cm^{-1})	Type of bond	Unaged(10% MeOH)	Aged at 72 h at 80˚C	Aged at 168 h at 80˚C
2950-2850	C-H stretch	√	√	√
1690-1630	Amide, C=O stretch	√	-	-
1780-1710	COOH bond	-	√	-
1750-1680	Ketone, C=O stretch	-	-	√
1490-1440	C-N-H bend	√	√	√
1430-1200	Tertiary, C-O-H bend	√	√	-
1410-1310	Secondary, C-O-H	-	-	√
900-800	Primary, C-O-H bend	-	-	√
800-750	C-C-O stretch	√	-	-
720-600	Amide, NH_2	-	-	√

The spectrum for the 10 % BD is shown in Fig. 8.7 and the functional groups are displayed in Table 8.9. The ageing of the pyrolysis oil with 10% BD after 168 h shows a peak at 3200 cm^{-1} that corresponds to a hydroxyl group with (-OH) as a functional group. In this case, it could be a hydroxyl group attached to aryl ring to form a phenol. This is because a phenol was detected in the composition analysis shown in Table 8.5. After 72 and 168 h of aging, there is formation of a peak at 1668 cm^{-1} that indicates an amide with C=O stretch. Another peak at 1515 cm^{-1} that may be attributed to the presence of an amide with C-N-H bend is observed. The formations of amides are due to the reactions occurring between carboxylic acid and an amine. The amide formation is possible due to the presence of a carboxylic acid and the amide (C-N-H) shown in Table 8.9. The peak at 1457 cm^{-1} is a result of methylene group which could be attached to any of the esters named in Table 8.5. The peak at 752 cm^{-1} that is formed after 72 and 168 h corresponds to a phenyl substitution that corresponds to one of the phenol compounds observed in Table 8.5.

Table 8.9: Summary of major functional groups contained in 10% biodiesel (BD).

Wavenumber (cm^{-1})	Type of bond	Unaged(10% BD)	Aged at 72 h at 80˚C	Aged at 168 h at 80˚C
3400-3000	O-H stretch	-	-	√
2950-2850	Alkyl, C-H stretch	√	√	-
1780-1710	COOH bond	√	-	-
1690-1630	Amide, C=O	-	√	√
1550-1510	Amide, C-N-H bend	-	-	√
1485-1445	Methylene C-H bend	√	√	√
1430-1200	Secondary, C-C-O	-	√	-
770-730	Monosubstitution (phenyl)	-	√	√

Fig. 8.7 shows the FT-IR spectra for 20 % BD. Table 8.10 shows a summary of the spectra from the raw pyrolysis oil to the aged samples for the 20% BD. The peak at 3200 cm^{-1} formed after 168 h of ageing corresponds to a hydroxyl group with (-OH) stretch that is normally found in alcohols. The peak at 1670 cm^{-1} formed after 168 h of ageing corresponds to an alkenyl with C=C stretch. The composition analysis shown in Table 8.6 contains long chain alkene which could be representative of this peak. The peak between 1210-1110 cm^{-1} detected in the raw and aged pyrolysis oil after 168 h corresponds to a tertiary alcohol with C-O stretch. There is no clear indication of this peak to the composition results obtained in Table 8.6. There is also a new peak formed after 72 and 168 h at 802 cm^{-1}, this corresponds to a para substitution. According to the composition analysis obtained earlier, there is no detected compound that fits this description however due to the complexity of the pyrolysis oil there could be undetected compounds.

Table 8.10: Summary of major functional groups contained in 20% biodiesel (BD)

Wavenumber (cm^{-1})	Type of bond	Unaged(20% BD)	Aged at 72 h at 80˚C	Aged at 168 h at 80˚C
3400-2500	O-H stretch	√	-	√
2950-2850	Alkyl, C-H stretch	√	√	√
1680-1620	Alkenyl C=C stretch	-	-	√
1550-1510	Amide, C-N-H bend	√	-	√
1485-1445	Methylene C-H bend	√	√	√
1210-1110	Tertiary,C-O stretch	√	-	√
860-800	1,4-Disubstitution (para)	-	√	√
750-700	Amide, C-N	√	-	-

8.6.4 FUNCTIONAL GROUP CHANGES AT 60 ˚C

FT-IR analysis was used to observe the changes in functional groups at 60 ˚C as shown in Fig.8.8. The PO at 60 ˚C displays the same peaks as those observed at 80 ˚C after 72 h except for the formation of a single peak at 1515 cm^{-1}. This peak corresponds to an amide with C-N-H bend, however the composition data of the raw pyrolysis oil didn't confirm any amide. The finger prints obtained at 60 and 80 °C are identical. This implies that detecting the changes in functional group using the FT-IR analysis is not very reliable compared to viscosity or composition changes.

The structural changes for the pyrolysis oil containing the 10 % MeOH at 60 and 80 ˚C appear to be different. This is because various peaks are observed at 60 ˚C compared to 80 ˚C. After 72 h at 60 ˚C, peaks at 1261, 966, 909, 812 and 741 cm^{-1} are observed. The peak at 1261 cm^{-1} is due to the presence of a secondary aliphatic alcohol with C-O-H bend. The peaks at 966 and 909 cm^{-1} are due to alkenes compounds with a CH_2 wag. The peak at 812 cm^{-1} corresponds to primary alcohols with C-O-H bend, which is this case is the presence of methanol. The peak at 741 cm^{-1} is assigned to a phenyl group that was detected in the composition analysis at 80 °C. The 10 % MeOH also displays two additional peaks after 168 h compared to the peaks after the same time at 80 ˚C. These are 1261 and 811 cm^{-1} that have already been identified after ageing for 72 h at 60 ˚C.

The pyrolysis oil containing the 10 % BD exhibits a different structure at 60 ˚C to that obtained at 80 ˚C. Two additional peaks are identified after 72 and 168 h at 60 ˚C. These peaks are 1740 and 1170 cm^{-1}. The peak at 1740 cm^{-1} corresponds to carboxylic acid with C=O stretch. According to the GC-MS analysis reported in Table A2.3 these compounds are methyl ester, hexacanoic acid and methyl ester, 8-octadecenoic acid. The peak at 1170 cm^{-1} corresponds to tertiary aliphatic alcohols with C-C-O stretch. There is no clear information to identify this particular compound. The peak at 3200 cm^{-1}

that appears at 80 ˚C after 168 h is not detected at 60 ˚C after the same time. This might be due a certain reaction occurring at higher temperature.

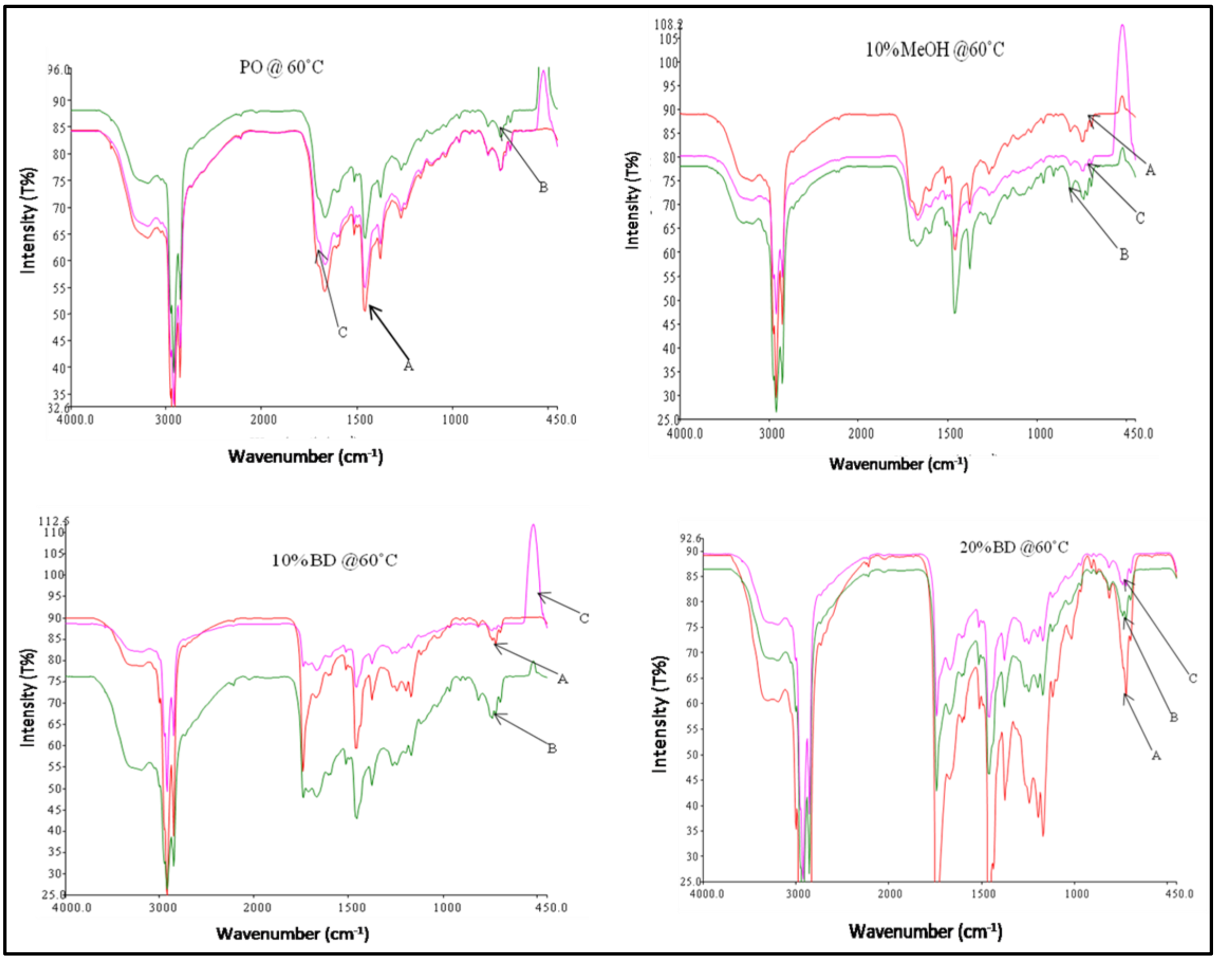

Figure 8.8: FT-IR spectra of the pyrolysis oil fractions aged at 60 °C, [**A**] for unaged sample, [**B**] for aged samples after 72 h, [**C**] for aged samples after 168 h

The 20 % BD at 60 ˚C shows a similar finger print to the one displayed at 80 ˚C. However there are additional peaks displayed at 60 ˚C after 72 h. These peaks have been identified to be 3194 cm^{-1} that corresponds to carboxylic acid with O-H stretch. The carboxylic acid compounds in this case are 9,12-Octadecadienoic acid (Z,Z)- and Methyl, 9,12,15-Octadecatrienoic acid same as those found in Table A2.4.The peak at 1673 cm^{-1} corresponds to alkenyl with C=C stretch. The peak at 1515 cm^{-1} corresponds to amide with C-N-H bend. The peaks at 1197 and 1170 cm^{-1} corresponds to tertiary alcohols with C-C-O stretch. The peak at 724 cm^{-1} corresponds to amide with C-N stretch. The ageing of the pyrolysis oil with 20% BD at 60 °C after 168 h doesn't show any changes similar to the ones observed after the same time period at 80 °C. This might be due to the temperature differences used for the ageing of the pyrolysis oil.

8.6.5 WATER CONTENT

The determination of the water content in pyrolysis oil enables to detect changes that might be occurring during ageing. Fig. 8.9 shows the water content measurements of the pyrolysis oil aged at 80 °C. The pyrolysis oil with no additive showed the greatest increase in water content with a 53 % rise. This increase arouse due to esterification reactions occurring that produce water as a by-product. This is supported by the compounds found in the spectrum that confirmed an increase of compounds after 72 h of ageing at 80 ˚C shown in Table 8.3. A phase separation of the sewage sludge pyrolysis oil with no additive was observed due to high water content. Czernik et al [108] also found an increase in water content after ageing bio-oil obtained from wood. Oasmaa and Kuoppala [104] found an increase in water content after 3 months of storage and this was thought to be a result of condensation reactions of aldehydes and ketones. On the other hand, Kim et al [109] did not notice any change in the water content of the bio-oil after ageing at room temperature for 10 weeks.

The pyrolysis oil containing 10% MeOH did not show any increase in the amount of water content after 72 h of ageing. However, after ageing the pyrolysis oil for 168 h there was a 22 % increase in water content. The low water content is caused by the presence of 10% MeOH that cause dissolution of some compounds that induce delay in the polymerisation reactions.

The water content obtained for the 10% BD doesn't show a clear trend since this seems to decrease after ageing for 72 h and then slightly increases after 168 h. The compounds formed in Table 8.5 after 168 h of thermal ageing indicate the possibility of having esterification reaction that aids the formation of water.

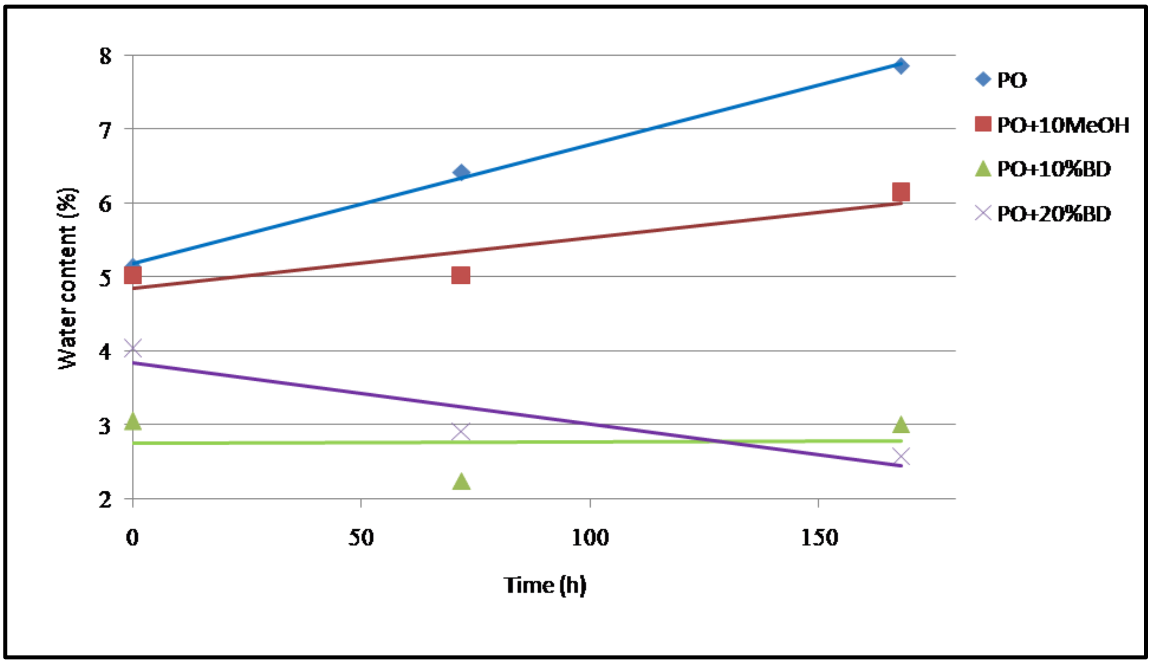

Figure 8.9: Water content measurement against ageing time for pyrolysis oil samples aged at 80 °C

The pyrolysis oil containing the 20% BD exhibited a different trend compared to other samples. There was a gradual decrease in the water content with increasing ageing time. The clue to this phenomenon lies with the results shown in Table 8.6. The table indicates compounds that are produced after 168 h of ageing and these are a result of esterification reactions. This is because esters are detected before ageing that end up consuming water as the ageing time increases. This implies that the esterification reactions are being shifted to the left rather than the right causing the water content to decrease since these types of reactions are reversible.

8.6.7 pH

The change in state of the pyrolysis oil is determined by pH measurements. The pH of the pyrolysis oil was found to range from 9 to 10 as shown in Fig. 8.10. This indicates that all the pyrolysis oil fractions are alkaline although the 10% MeOH is slightly more alkaline than the rest of the samples. The changes in pH are not significant as pyrolysis oil retain their alkalinity state with an overall pH of 9. Oasmaa and Kuoppala [104] also found no change in the pH of the pyrolysis oil after ageing for 6 months. Kim et al [109] found no change in the pH of the pyrolysis oil after ageing for 10 weeks. However, Ortega et al [106] found pyrolysis oil obtained from hard and soft wood aged between 65 and 85 °C to have a lower pH compared to the raw pyrolysis oil. The reason for lowering of pH that Ortega et al [106] found was due to the production of acetic acid that causes a lower pH. The state of the pyrolysis oil is mainly determined by the composition and It is clear from Table 8.3, 8.4, 8.5 and 8.6 that all the compounds formed were not in abundance in order to cause a change in the overall state of the pyrolysis oil.

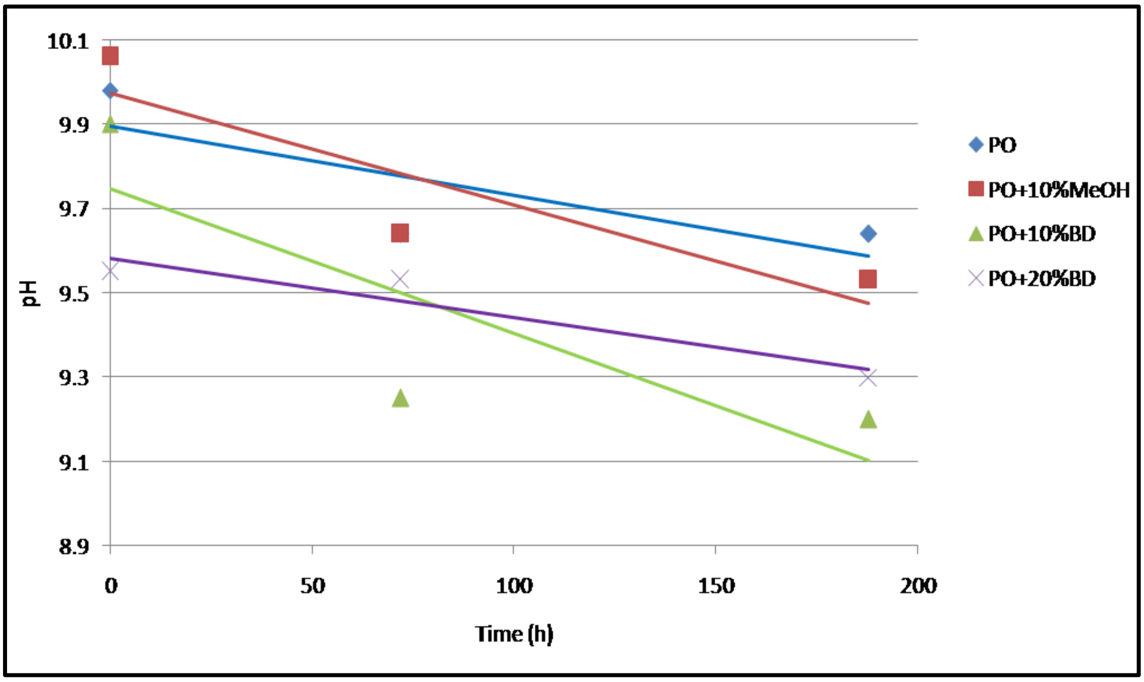

Figure 8.10: pH measurements of pyrolysis oil samples aged at 80 °C

8.7 SUMMARY

The most effective temperature for testing thermal stability is at 80 ˚C as this showed the most drastic changes compared to 60 ˚C. The other authors in literature such as Hilten and Das [101] and Bouchera et al [103] found similar results. The most reliable measurement of testing thermal stability seems to be observing the change in viscosity and composition compared to water content and pH. The 20% biodiesel blend showed the least change in viscosity compared to other pyrolysis oil fractions. The 20% biodiesel pyrolysis oil proved to be more thermally stable compared to the 10% MeOH when using viscosity as the parameter for determining stability. The increase in concentration of the biodiesel from 10 % to 20 % greatly increased the stability of the pyrolysis oil fractions.

The results from the GC-MS show that the unstabilised pyrolysis oil (PO) showed the highest change in compounds and concentration after aging. This was expected as the PO contained no solvent, therefore it was prone to polymerisation reactions. The increase in water concentration of the unstabilised pyrolysis oil confirms the existence of esterification reactions. The 20% biodiesel blend showed the least change in concentration and compounds after aging compared to other pyrolysis oil fractions.

The composition analysis of the pyrolysis oil showed an overall increase in concentration of aromatic hydrocarbons like Methyl benzene and Ethyl benzene in PO, 10% MeOH and 10% Biodiesel. According to the change in composition of compounds esterification and methylation reactions might have occurred.

The changes in functional groups analysed by the FT-IR was unexpected. The unstabilised pyrolysis oil only showed a single change at 1514 cm^{-1} that corresponded to C-N-H bend compound that could be a methyl amine. More functional groups were expected for the unstabilised pyrolysis oil.

The 20% BD on the other hand showed the greatest increase in functional groups. The peak at 3194 cm^{-1} corresponded to carboxylic acid with O-H stretch. This peak could represent hexadecanoic acid or Octadecanoic acid that originates from biodiesel. The peak at 1673 cm^{-1} corresponded to amides with C=O stretch. The amide formation is a result of the reaction between the carboxylic acid like Octadecanoic acid and an amine that could be present in the pyrolysis oil. The peaks at 1197 cm^{-1} and 1170 cm^{-1} corresponds to tertiary aliphatic alcohols with C-C-O stretch. The aliphatic would have resulted from the reaction between an alkyl and hydroxyl compound found in the biodiesel to form these peaks.

The use of FT-IR to detect change in functional groups is not a reliable method of assessing the stability of the pyrolysis oil as the information obtained is limited.

CHAPTER 9:ENGINE TESTS WITH SEWAGE SLUDGE PYROLYSIS OIL BLENDS

This chapter describes the engine tests carried out using the intermediate pyrolysis oil obtained from sewage sludge. It details the impact of the pyrolysis oil in a diesel engine in terms of performance and emissions. The results are compared to the performance of biodiesel and diesel fuels.

9.1 PREVIOUS WORK

The use of pyrolysis oil in the diesel engine has been widely researched by several companies and universities. The main concerns of using pyrolysis oils in engines is mainly due to corrosiveness from acids, high water content, high viscosity, ignition and instability. The quest for renewable energy for production of heat and power has accelerated research for use of pyrolysis oils in engines.

Various researchers have investigated the application of various fuels in diesel engines. Solantausta et al [110] tested bio-oils obtained from wood fast pyrolysis with additives of 5-9 vol % in a direct injection petter diesel engine with one cylinder, 80 mm bore, 110 mm stroke and a compression ratio of 15.3:1. It was found that the emissions from CO_2, NO_x and hydrocarbons were similar to those obtained from diesel fuels. Nevertheless, they encountered the problem of coke formation that caused clogging of injection nozzles.

Shihadeh [111] studied wood pyrolysis oil from two different processes; ENSYN and NREL pyrolysis oils. The pyrolysis oils were preheated to 55 ˚C to initiate ignition. The pyrolysis oils were tested in a single cylinder diesel engine with 80.26 mm bore, 88.9 mm stroke, 2400 rpm and compression ratio of 19.8:1. It was found that the thermal efficiency of the pyrolysis oils was similar to that of diesel fuel although the latter had greater heat release. However, in order to perform the tests there was rigorous cleaning of cylinder walls, removal and cleaning of piston, head and valve before each run in an attempt to avoid technical hitches. This could be impractical to apply on a daily basis.

Chiaramontia et al [112] tested three emulsions of bio crude oil (BCO) and diesel. These were BCO/diesel ratios of 27/75, 50/50 and 75/25. The studied found that there was severe damage to injector and fuel pump which were due to the corrosiveness of bio crude oil. They recommended the use of stainless stress in engines to avoid corrosiveness of bio-oils.

Mani et al [113] used waste plastic oil obtained from pyrolysis process for testing in a DI diesel engine. They used a single cylinder, four strokes with 110 mm stroke and compression ratio 17.5:1. The tests were successful as it was found that the brake thermal efficiency was similar to that of diesel. However, there was an increase in smoke and emissions especially the NO_x, CO and unburnt hydrocarbons compared to diesel fuel.

In Germany, a successful operation of using pyrolysis oil in diesel engine has been achieved. Scholl et al [114] used a twelve cylinder engine that was designed with selective material to run a mixture of 96 vol% of pyrolysis oil with only 4 vol% of diesel. A power generation of 300 kW/h was achieved successfully with no damage to the diesel engine.

9.1.1 USE OF BIODIESEL

As the worlds fuel demand increases, there is need to find alternative renewable fuels that would be used to complement the existing demand. Biodiesel is one of the renewable fuels that have proved to have great potential as a biofuel. It can be used directly in a diesel engine without requiring any modification of the fuel or the engine. It has a high energy content, low viscosity and good combustion properties due to high oxygen content. It has also proved to be more biodegradable than diesel [115]. It is non flammable due to having a higher flash point and it is non toxic compared to fossil diesel [116]. In addition to this, it mixes well with the pyrolysis oils without any form of emulsion being used. These factors increase the application of this biofuel.

The use of biodiesel has some draw backs that need to be recognised. Biodiesel has no anti freezing properties so its use might be problematic during cold weather conditions. It also degrades after prolonged periods so care should be taken after long term storage [116]. It has also been reported by Demirbas [116] that the use of biodiesel in diesel engines that regularly run on diesel fuel causes blockage of the fuel filters. This happens when the diesel fuel form deposits inside fuel tanks and hoses that are then loosen by the use of biodiesel resulting into a blockage [116].

9.1.2 USE OF SEWAGE SLUDGE PYROLYSIS OIL

The pyrolysis oil obtained from the intermediate pyrolysis of sewage sludge has shown great potential to be used as a fuel. It has a high energy and oxygen content that are desirable for fuel applications. It is alkaline in nature. However it has some drawbacks such as having a strong pungent smell, high viscosity, high sulphur and nitrogen content. These factors might thwart some of its applications. Due to the draw backs from the sewage sludge pyrolysis oil, it was necessary to blend it with biodiesel in order to improve some of its characteristics. The pyrolysis oil mixed well with biodiesel without agitation or using any emulsifier. Among the benefits of blending with biodiesel is that the pungent smell is masked making the sewage sludge pyrolysis oil more desirable for applications.

9.2 METHODOLOGY

9.2.1 ENGINE DESCRIPTION

The engine used is a Lister diesel engine that is water cooled with 2 cylinders. The engine is very robust and able to combust low grade fuels. The major characteristics of the engine are shown in Table 9.1.

Table 9.1: Characteristics of the Lister diesel engine [117]

9.2.2 SETUP OF THE TEST ENGINE

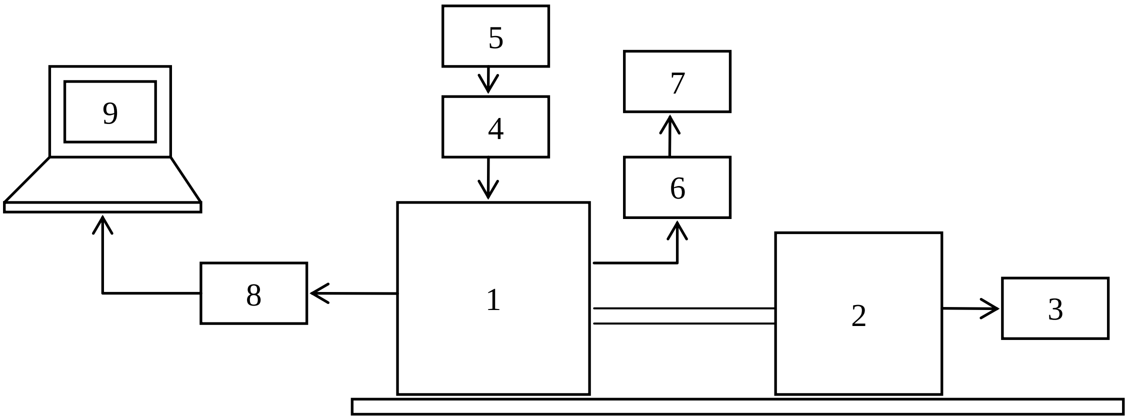

Figure 9.1: The setup of the Lister diesel engine

1. Diesel engine
2. Generator
3. Power
4. Fuel measurement
5. Fuel Tank
6. Exhaust gas analyzer
7. Smoke meter
8. Radiator
9. Flow rate and temperature measurement

9.2.3 OPERATION

The engine tests were carried out in collaboration with a fellow PhD student whose background is based in mechanical engineering and his research work is focused on testing of pyrolysis oils in the Lister diesel engine. He was in full charge of the engine operation due to his knowledge however measurements of various aspects during the engine tests were taken together. The sewage sludge pyrolysis oil used for testing was produced solely by the author of this thesis.

The fuel mixtures used in the internal combustion (IC) Lister diesel engine are diesel, biodiesel, mixture of 30% sewage sludge pyrolysis oil with 70 % biodiesel (30%SS, 70%BD) and mixture of 50% sewage sludge pyrolysis oil with 50% biodiesel (50%SS, 50%BD). There was no pre-heating of the pyrolysis oils before injection into engine. The engine was warned up with diesel fuel combustions for 30 minutes to ensure good operation and stabilise the water flow. The test samples were then analysed and repeated four times to ensure constancy and reliability of results. Each load of the test sample lasted approximately 20 minutes. After testing the samples, biodiesel was used in the engine and allowed to run for 30 minutes to clear up any clogging of fuel lines and residues left behind by the mixture. The engine was then run with diesel fuel for 30 minutes before shutdown. No modifications were made to the engine.

9.2.4 ANALYSIS METHODS

The fuel consumption was calculated by the time taken for the fuel to flow in the graduated cylinder for every 100 ml into the engine. The exhaust gas emissions and smoke measurements were analysed using the Bosch BEA 850 analyser and a smoke opacity meter. Readings were taken at several intervals after the engine had reached steady state. The exhaust gas temperature was measured using a K type thermocouple.

Table 9.2: Measurement tools used for engine operations

Equipment	Measurement	Error
Bosch BEA 850	CO	± 0.001 vol.%
	NOx	± 1 ppm
	HC	± 1 ppm
	Smoke opacity	± 0.1%
Graduated cylindrical burette	Flow rate	± 5 ml
Stop watch	Flow rate	± 2 s
Thermocouple	Exhaust gas temperature	± 2.2 °C

9.2.5 PROPERTIES OF THE FUELS USED FOR ENGINE TEST

The fuels used for testing in the IC Lister diesel engine were analysed for variation that might affect their overall performance. Table 9.2 shows the physiochemical properties of the test fuels. Most of the fuel properties have been discussed in chapter 5. The sewage sludge pyrolysis oil blends have a higher viscosity and water content that might affect the combustion properties. The energy content of the pyrolysis oil blends is lower compared to diesel and biodiesel therefore the thermal efficiency will be greatly affected by this. The pyrolysis oil blends have a higher oxygen and nitrogen content that will greatly affect the emission rates.

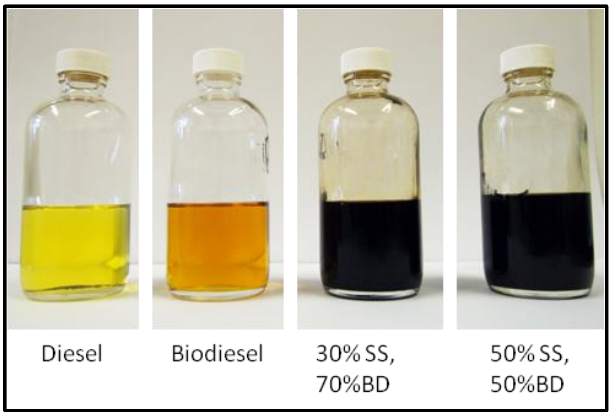

Figure 9.2: Test samples used in the Lister diesel engine

Table 9.3: Properties of the fuels used for the engine tests

	Units	Sewage sludge pyrolysis oil (SS)	Diesel	Biodiesel	30 %SS, 70 %BD	50 %SS, 50 %BD
Ultimate analysis	wt.% (±0.03)[b]					
C		74.2	85.6	78.86	75.49	75.86
H		9.9	13.37	12.63	11.78	10.62
N		5.1	0.10	<0.10	1.74	1.07
O		8.0	0.83	7.67a	10.36	11.72
S		1.9	0.10	0.74	0.63	0.73
Density @ 20 °C	g/ml	0.990	0.825	0.890	0.920	0.920
Water content	wt.%	4.12	0.05	0.35	2.12	0.45
Ash content	wt.%	0.23	0.01	0.1	0.08	0.14
pH	(±0.1)	9	7.0	7.8	8.7	8.31
Viscosity @ 40 °C	cSt	38	3.0	6.0	9.31	7.76
HHV	(±0.001)(MJ/kg	39	45	39	37.4	38.4

[a] Measured on dry ash free basis
[b] Obtained externally

9.3 RESULTS AND DISCUSSION

The performance of the engine was evaluated based on the thermal efficiency, exhaust gas temperature, fuel consumption and the emissions in the exhaust gases. The results obtained in this section were collaboration with a PhD student. The results obtained are a shared right with the student.

9.3.1 PERFORMANCE

9.3.1.1 BRAKE SPECIFIC FUEL CONSUMPTION

It is a ratio of fuel consumption divided by the rate of power production [118]. It measures the efficiency of the engine. Fig. 9.3 shows the specific fuel consumption of the fuel blends against brake power. There is an overall decrease in specific fuel consumption as the brake power increases. The 50% SS blend has the highest brake specific fuel consumptions compared to all the test fuels. This might be due to the reduced energy content of the 50% SS that requires more fuel to be combusted compared to other test fuels. Diesel has the lowest overall fuel consumption due to having a high energy content of 45 MJ/kg and would therefore need less fuel to be combusted.

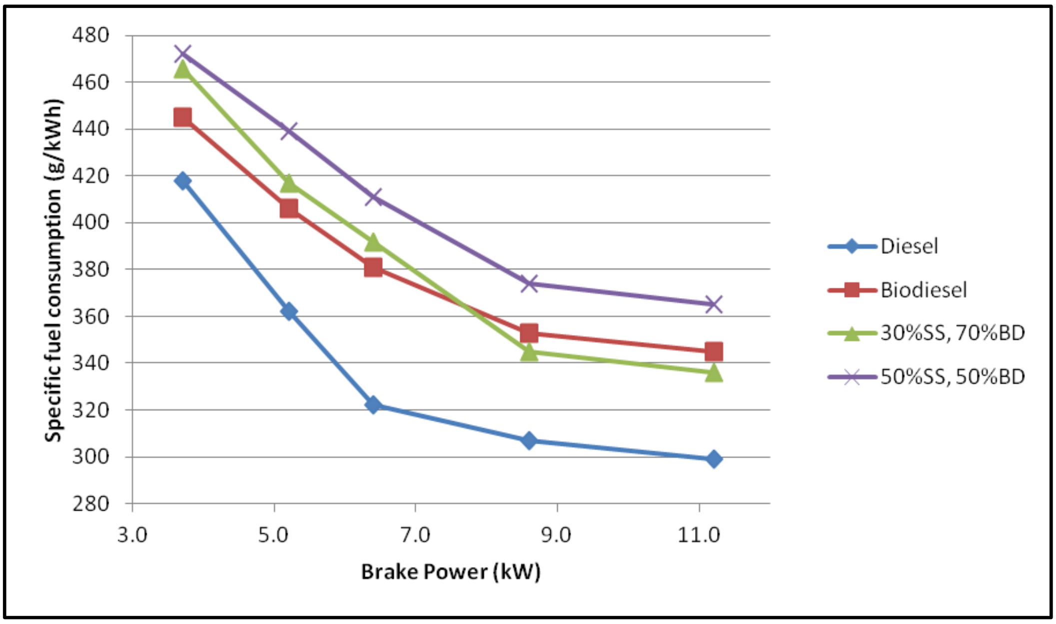

Figure 9.3: The graph showing specific fuel consumption versus brake power for the test samples [119]

9.3.1.2 BRAKE THERMAL EFFICIENCY

The brake thermal efficiency is a measure of the how efficient the energy in the fuel is converted to mechanical output [120]. The brake thermal efficiency of the fuels increases with increase in brake power (Fig.9.4). The increase is due to the reduction in heat losses and increase in power. Diesel fuel has the highest thermal efficiency compared to biodiesel and the pyrolysis oil blends. However, the 50% SS showed the lowest thermal efficiency compared to other test fuels. This might be due to the decrease in the energy content and increase in the fuel consumption of the 50% SS as it contains a higher percentage of pyrolysis oil compared to the 30% SS blend.

Figure 9.4: The brake thermal efficiency of the test samples against brake power [119]

9.3.1.3 EXHAUST GAS TEMPERATURE

There is an overall increase in the exhaust gas temperature of the fuels with increase in the brake power (Fig. 9.5). Biodiesel has the highest exhaust gas temperature among all test fuels. The increase in power demands a higher fuel consumption which in turn increases the in cylinder temperature that increases the exhaust gas temperature. On the other hand, the 50% SS has the lowest exhaust gas temperature.

Figure 9.5: The exhaust gas temperature attained by the test samples against brake power [119]

9.3.2 EMISSIONS

The measure of emissions obtained from the combustion of fuels gives a great insight into the long term environment impact of their application.

9.3.2.1 NO_x EMISSIONS

NO_2 is more harmful to humans than nitrogen oxide [121]. NO_x emissions can cause damage to the human body by causing internal bleeding, respiratory diseases and cancer [121]. The emission of the NO_x in the engine depends on the O_2 concentration, reaction time and in-cylinder temperature [122][123][124]. There is an overall increase in the NO_x emissions with the increase in power (Fig. 9.6). The increase in power promotes a high in-cylinder temperature that leads to the NO_x formation [125]. Biodiesel showed the highest NO_x emissions compared to other fuels. The high NO_x might be due to the fact that, biodiesel attained the highest exhaust gas temperature that enabled the high release of the emissions. In contrast, the 50% SS showed the lowest NO_x emission due to having lowest exhaust gas temperature as shown in Fig.9.5.

Figure 9.6: The NOx concentrations obtained for the test samples against brake power [119]

9.3.2.2 CO EMISSIONS

The production of CO is mainly due to the incomplete combustion of fuels. CO exposure can cause headaches, damage to the central nervous systems and even death [121]. Fig 9.7 shows the CO emissions of the test fuels. There is an overall increase in the CO production with the increase in power (Fig. 9.7). As the engine power increases, time available for complete combustion is reduced leading to the formation of CO [126]. Furthermore as the volume of fuel increases with the higher power, the shortened time for combustion reduces the air intake that contributes further to the CO production [126]. Biodiesel shows the greatest increase in CO production compared to the test samples. The high O_2 content found in biodiesel enhances more CO production. On the other hand, diesel shows the least amount of CO production with increase in power. This is one of the major reasons diesel is commercially available and biodiesel isn't.

Figure 9.7: The CO concentration obtained for test samples against brake power [119]

9.3.2.3 HYDROCARBON (HC) EMISSIONS

The hydrocarbon emissions are mainly due to incomplete combustion of the fuels. The release of HC in the air causes further reactions that are accelerated by sunlight leading to the formation of peroxy acetyl nitrates (PAN) [121]. These are potential causes of cancer to human [121]. Fig.9.8 shows the HC emissions of the test fuels. There is a variation of the HC emissions in the test fuels. On average, diesel shows the least amount of hydrocarbon emissions. On the other hand, on average the 30% SS blend shows the greatest increase in the hydrocarbon emissions. This might be due to a higher biodiesel concentration since biodiesel is the only test fuel that shows a gradual increase in HC emission as power increases. The high power might also not permit sufficient time for air to fuel mixtures for the hydrocarbons found in biodiesel leading to more HC emissions.

Figure 9.8: The hydrocarbon emissions versus brake power [119]

9.3.2.4 OPACITY

The exhaust opacity is the measure of the amount of smoke produced by a fuel. Soot is a dark substance that is a major composition of smoke opacity [124][126]. Fig. 9.9 shows the amount of smoke opacity produced by the test samples. There is an overall increase of smoke as the engine power increases. As the engine power increases, more fuel is consumed leading to an increase in smoke. The increase in fuel consumption as power increases, leads to lower air to fuel ratio that causes incomplete combustion causing more smoke. Diesel showed the highest increase in smoke compared to the other test samples. This might be due to a lower oxygen content of the fuel that promotes soot formation. On the contrary, the 50% SS blend has a higher smoke increase with engine power compared to biodiesel and 30% SS blend. The 50% SS blend has the highest oxygen content of all the fuel blends yet more smoke was observed compared to biodiesel and 30% SS. There is no clear explanation to this but the composition of blend might highlight some clues to this. The 30% SS has the lowest smoke measurement among the test fuels.

Figure 9.9: The smoke opacity measurements versus brake power [119]

9.4 SUMMARY

The brake specific fuel consumption for diesel is lower than that of the pyrolysis oil blends. The 50% SS has the highest specific fuel consumption among the test fuels. This shows that the pyrolysis oil is inferior in performance compared to conventional fuels. Greater improvements will be needed for the pyrolysis oil to attain the performance of the conventional fuels.

Diesel has the highest brake thermal efficiency among the test fuels. On the other hand, the higher percentage of the pyrolysis oil showed the lowest brake thermal efficiency. This confirms that the sewage sludge pyrolysis oil if used on its own in a diesel engine will have a lower brake thermal efficiency.

In terms of emissions, the biodiesel fuel has more NOx and CO emissions compared to the pyrolysis oil blends. Diesel has the lowest CO and hydrocarbon emissions among the test fuels.

CHAPTER 10: ECONOMIC EVALUATION OF ELECTRICITY PRODUCTION FROM SEWAGE SLUDGE PYROLYSIS OIL

This chapter describes the techno-economic evaluation of using the intermediate pyrolysis process for the production of sewage sludge bio-oil for engine application. It examines the investment costs that could be needed to implement such a process. It highlights the operating costs and cost per kilowatt of electricity that would be required in order to break even. It also analyses the profitability of the process.

10.1 COMBINED HEAT AND POWER SYSTEMS

These systems are able to convert energy of the fuel into electricity and heat that can be utilised in several ways. Approximately 40-80 % of the energy burnt is wasted as heat [127]. Efficient utilisation of the heat produced is the key to successful operation of these types of systems. The internal combustion engine used in CHP systems is of particular interest in this study. The internal combustion(IC) engine is of two types spark ignition and compression or diesel engine. The diesel engine is preferred for use in this study. The diesel engines have been reported to have better performance compared to spark ignition engines [127]. The diesel engine has no spark plug to initiate combustion. Air is compressed in a cylinder by a piston with a high pressure that its temperature rises above its flash point causing ignition [127]. The efficiency of this type of engines ranges from 30 to 50 % [127]. The energy distribution of the fuel energy is mainly to the shaft power, engine exhaust (30 to 50%) and engine cooling system. The heat can be utilised to provide hot water for district heating schemes, domestic use, space heating and generating steam. The draw back with this type of engine is the increased emissions of the nitrogen oxides [127]. The increased emissions are due to the intensified temperature rise inside the engine cylinder [127].

10.2 PREVIOUS WORK

Fonts et al [47] carried out a review on sewage sludge pyrolysis for liquid production. The authors reported the first pyrolysis oil from sludge technology (Enersludge) that was carried out in Perth, by the Western Australian Water Corporation. The year of operating the plant the Subiaco plant was 1996. Sewage sludge was fed in form of pellets and the pyrolysis reaction was carried out at 450 °C at 1.5kPa. The main operations of the plant reported by the Fonts et al [47] were dewatering, drying of the sludge, pyrolysis of sludge, heat recovery, gas cleaning and refining of products. The average pyrolysis yields of the plant were 45 % pyrolysis oil (excluding the aqueous phase) and 40 % char. The plant was able to produce over 300 tonnes of pyrolysis oil over its lifetime that was effectively combusted by industrial users. The reactor performed well and the plant was able to prove the environmental benefits of sludge to oil production. However, the plant ceased operation due to complications that arouse with controlling of odour emissions and maintenance issues that were extremely pricey than estimates made [47].

At the University of Waterloo, Cottam and Bridgwater [128] conducted an economic evaluation based on a flash pyrolysis process. The study focused on dry wood with 7 wt% moisture content. The feed rate of the reactor was estimated to be 1000 tonnes/day of wood. The study was limited as no assumptions or capital costs were detailed. The feedstock costs were identified as the main variable that affected the cost of bio-oil.

Islam and Ani [129] carried out a technological and economic study on the conversion of rice husks into bio-oil using fast pyrolysis. The economic analysis was based on a fluidised bed reactor that operated at 0.3 kg/h. The actual economic assessment was determined for the feed throughput of 100 and 1000 kg/h. The plant life was taken to be 10 years with operation of 10 hours per day. The process was assumed to operate at 3120 h/yr with a feedstock cost of $20/tonne. The labour cost was rated at $1 per hour in Malaysia. The cost of bio-oil was found to be $0.38/kg for 100kg/h and $0.18/kg for 1000 kg/h with a total capital investment of $97,000 and $389,000. It was found that the 1000 kg/h was more economical to run based on the lowest production cost for the bio-oil. The main variables for study were identified to be equipment costs, feedstock and labour costs.

An economic evaluation based on fast pyrolysis reactor design was carried out at the University of New Hampshire [130]. The analysis was based on using wood chips as a feedstock for the production of bio-oil at three feed rates. The feed rates analysed were 100, 200 and 400 metric tonnes per day of wood chips. The feed had 45% moisture and could cost \$18 per wet tonne. The plant was to be operated for 24 hours/day for 330 days per year. The cost of bio-oil including capital costs was found to be \$1.21 per gallon, \$0.99 per gallon, \$0.89 per gallon for 100, 200 and 400 wet tonne per day. The total capital investments were estimated to be \$6.6, \$8.8 and \$14 million.

Ringer et al [131] carried out an economic evaluation based on 550 dry ton/day wood chips with 50 % moisture content. The feedstock was \$30/dry ton and the projected sale price of the bio-oil was estimated to be \$7.62/GJ, LHV. However the study determined that an increase in facility and bio-oil production would decrease the projected sale price to \$4.75/GJ, LHV. The total capital investments approximated to be \$48 million.

Kim and parker [25] carried out a technical and economic evaluation of pyrolysis of sewage sludge for the production of bio-oil based on a laboratory scale experiment. The evaluation focused upon the primary, waste activated and the digested sludge. The economic value of the bio-oil was evaluated based upon 70 % of the price for crude oil. The prices of the bio-oil for primary, waste activated and digested sludge were estimated to be 9.9, 6.9 and 5.6¢/kg-ds.

10.2 DESIGN BASIS

The process design for the plant layout is based on the intermediate pyrolysis process. The full optimisation of this process involves pre-drying of feed stock to minimise water content, the intermediate pyrolysis reaction, collection of pyrolysis products, combustion of char and electricity generation from the pyrolysis oil. Fig. 10.1 shows a flow diagram for the process.

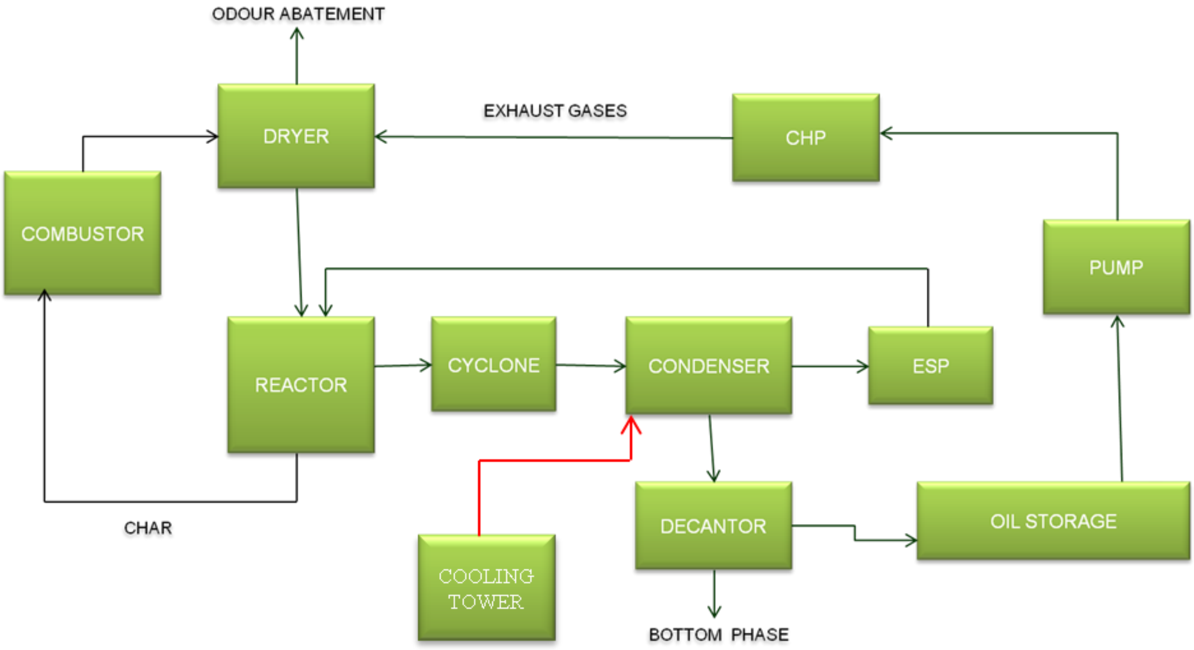

Figure 10.1: Plant layout of the proposed process for electricity production from sewage sludge pyrolysis oil

10.3 PROCESS DESCRIPTION

The process involves drying of biomass to a moisture content of 10 to 20 wt%. The reactor is purged with nitrogen for approximately 10 minutes to remove any presence of oxygen in the system. The biomass is then feed to the pyrolysis unit at approximately 450 ˚C to yield biochar, bio-oil and non condensable gases. The gas stream is condensed with the aid of cooling water to form bio-oil while the non condensable gases are expelled through the electrostatic precipitator. Char is removed with the aid of a conveyor belt leading to the combustion chamber. The char is combusted to provide heat to the dryer. The non condensable gases are combusted to provide heat to the reactor. The bio-oil from the condenser is separated into pyrolysis oil and aqueous phase. The pyrolysis oil is used in a CHP system for electricity production.

10.3.1 SEWAGE SLUDGE PREPARATION

The feedstock is dried to approximately 10% moisture content to minimise the amount of water present in the bio-oil. It also reduces waste of heat energy that could otherwise be transferred to the water phase. The feedstock can be made into pellets that could involve grinding the sewage sludge into powder then pelletizing it using suitable equipment. A cheaper alternative to this could be to feed the material in selected chunks that would be feed through the chute of the reactor. The feedstock is then fed via a hopper with the aid of a screw feeder into the reactor. The feedstock preparation for intermediate pyrolysis process is different to that of fast pyrolysis process.

10.3.2 DRYING

The rotary dryer is assumed to be used for sewage sludge. A rotary dryer is used due to its agility, various mode of heating and the capacity. The dryer is sought to be heated using steam generated from the recycled flue gas originating from the engine and extra heat supplied from the combustions of biochar. The sewage sludge fed to the dryer is estimated to have a moisture content of 75 wt%. The dry mass content of the sewage sludge after drying assumed to be 25 wt%.

10.3.3 SLUDGE CONVEYING AND FEEDING

The design used for conveying the material from the dryer to the reactor is assumed to be a closed system with no air inlet. The material is assumed to be fed to the reactor using a compression screw that drives the material into the reactor without letting any air in. The feed to the reactor does not undergo any further treatment after drying. This is in accordance to the intermediate pyrolysis process feed stock preparation. The design of the compression screw would enable larger particle sizes to be broken down and fed to the reactor.

10.3.4 PYROLYSIS REACTION

The reactor used for the pyrolysis process is assumed to contain two screws, the inner and outer screws. These move in opposite direction, the inner screw takes material in while the other screw transports material out. Nitrogen gas is purged through the reactor system before the commencement of the reaction to remove any presence of air in the system. Nitrogen is also used as a standby gas to increase the safety of the process system and for complete emptying in case of an emergency situation.

The reactor converts biomass into biochar, bio-oil and non condensable gases. The operating temperature of the reactor ranges from 450 to 500 ˚C.

10.3.5 GAS CLEANING

The cyclone is used to separate the char particulates from the gas stream escaping from the reactor. It employs the centrifugal force to discharge solid particles downwards to the bottom while the gases escape at the top. The cyclone is used for gas cleaning as it can separate particles down to 0.5 µm. The filtration unit is necessary in order to remove any aerosol in form of char particles that are carried within the gas vapours escaping from the reactor. The cyclone should be operated between 400 to 450 ˚C to avoid condensation of the vapours. The cyclone has been chosen to be used for char particulate removal due to its robustness and ease of maintenance. Char particulates in bio-oil causes impurities and limits the application. The char particulates also escalate the ageing process of the bio-oil.

10.3.6 BIO-OIL COLLECTION

The condenser used for the bio-oil collection is assumed to be a shell and tube heat exchanger. This is because the shell and tube heat exchanger has a large surface area that allows cooling and collection of the condensate. It also allows the escape of non condensable gases that are then recycled for use. The sewage sludge bio-oil contains two layers; pyrolysis oil (organic/upper phase) and the bottom (aqueous) phase. The pyrolysis oil shown in Fig.10.2 is of most interest for this economic study. The two phases are separated with the aid of a decanter. The aqueous phase is recycled to the waste treatment process. The pyrolysis oil is collected in a storage vessel made of stainless steel to avoid corrosion. A centrifugal pump is used to transport the organic phase to the engine. It has been assumed that the pump is preferably made of copper and designed to cope with low viscosities.

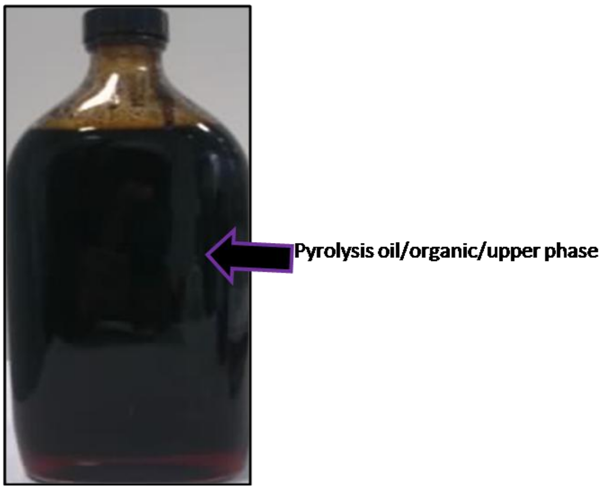

Figure 10.2: The pyrolysis oil (organic phase) of the sewage sludge bio-oil

10.3.7 EXTRA GAS CLEANING

The non condensable gases and residues are sent through the electrostatic precipitator. This allows entrapment of any particulates or residues that are contained in the gas phase and also allows cleaner gases such as methane, hydrogen and carbon monoxide to be reused without any particulates. The recycled gases can then be combusted in the burner to provide extra heat to the reactor. The gases can also be used in specially designed engines.

10.3.8 CHAR COMBUSTION

Biochar is the largest product obtained from sewage sludge intermediate pyrolysis. It has an ash content of 54.8 wt% so the available combustible matter is 45.2 wt%. The char obtained from sewage sludge is to be burnt in the combustor. The hot gases from the combustor can then be transferred to the dryer. Due to high ash content in the sewage sludge char, a fixed bed combustor with grates is recommended for use.

10.3.9 GAS COMBUSTION

Natural gas is used as the main fuel for combustion to provide the heat needed for the reactor and the dryer. Natural gas is cheaper compared to electricity costs. The burner used for natural gas combustion is assumed to employ convection and radiation sections that are necessary to ensure a high efficiency. The burner efficiency has been taken to be 85 % with a potential of combusting of the recycled gases.

10.3.10 POWER PRODUCTION

The pyrolysis oil produced from sewage sludge is to be used in a specially designed CHP system. The electricity produced is assumed to meet the plant demand and the surplus can be sold to the national grid. The engine used is assumed to be specially selected materials of construction that are able to handle the corrosiveness of the sewage sludge pyrolysis oil. This eliminates any operational problems that could otherwise arise from such a process.

10.3.11 EXHAUST GASES

The gases produced from the combustion of the pyrolysis oil in the engine contain sufficient heat that can be reused. The exhaust gases are assumed to be at a temperature of 550 °C. The exhaust gases can be used to provide extra heat for the dryer.

10.4 MASS AND ENERGY BALANCE

The overall mass and energy balance was carried out for the feed rate of 0.2 t/h, 1.0 t/h and 2.0 t/h. The conversion of the pyrolysis system is assumed to be 100 %. The details for the mass and energy balance are detailed in Table 10.1. A detailed mass balance for the proposed flow sheet is given in Appendix A3.1.

Table 10.1: Mass balance for the pyrolysis products

Feed (kg/h)	Char (kg/h)	Bio-oil (kg/h)		Permanent gases(kg/h)(By difference)
		Pyrolysis oil (kg/h)	Bottom (Aqueous) phase (kg/h)	
2000	1000	266.7	533.3	200
1000	500	133.3	266.7	100
200	100	26.7	53.3	20

10.5 BIO-OIL YIELD FROM INDUSTRIAL PROCESS

The total bio-oil yield was determined from the mass and energy balance of the intermediate pyrolysis process of sewage sludge. The intermediate pyrolysis yields shown in Table 10.2 are used for the economic evaluation.

Table 10.2: Intermediate pyrolysis yields for the digested sewage sludge

Plant capacity (dry sewage sludge processed per hour)				
		0.2 t/h	**1 t/h**	**2 t/h**
Dewatered sludge per year (75% moisture)	[kg/yr]	6,336,000	31,680,000	63,360,000
Dried sludge per year	[kg/yr]	1,584,000	7,920,000	15,840,000
Char yield per year	[kg/yr]	792,000	3,960,000	7,920,000
Non condensable gases per year	[kg/yr]	158,400	792,000	1,584,000
Bio-oil yield per year	[kg/yr]	633,600	3,168,000	6,336,000
Pyrolysis oil yield per year	[kg/yr]	211,200	1,056,000	2,112,000
Pyrolysis oil yield	[L/yr]	213,333	1,066,667	2,133,333

It should be noted that sewage sludge varies from place to place and from region to region. The data given above will therefore vary. The bio-oil quality is also affected by the type of sludge used. Fonts et al [47] agreed with this point.

10.6 ECONOMIC EVALUATION METHODOLOGY

The estimated total capital investment is adapted from Peters et al [132], no models were used for the estimations. Equipment purchase costs were estimated using the method described by [133]. The assumptions undertaken in the economic evaluation are shown in Table 10.3. The profitability analysis sheet of the project investment was taken from Sinnott and Towler [134].

Table 10.3: Basis of the economic evaluation

	Assumptions of the economic evaluation
1	No interest payments as capital costs are paid in full (100% equity financed)
2	Dewatered sludge has a moisture content of 75% [7]
3	Royalties are included in the capital costs
4	No costs of land as this is assumed to be available
5	Plant operation is assumed to be 24 h with 330 days (7920 hours)
6	The product yield is 50% char, 40% bio-oil (pyrolysis oil and aqueous phase), 10% non condensable gases.
7	Heat capacity of dried sewage sludge is 1.83 kJ/kg °C [25]
8	Char combustion assumed to be 100% efficient
9	Plant life is 20 years
10	Maintenance at 2% capital investment

The operating cost includes the costs of drying, utilities, maintenance, labour costs and non-production labour. The cost per litre of the pyrolysis oil is calculated by dividing the sum of annual operating costs by the annual oil yield production.

10.6.1 EQUIPMENT COSTS

The equipment costs also known as plant costs is the purchase price of the equipment in a specific country including insurance and maintenance. The capital costs were determined by obtaining direct quotes from companies and using the Equation 10.1 given by [134] to be;

$$Ce = a + \ bS^n \qquad \textit{Equation 10.1}$$

Where Ce is the purchased equipment costs on US dollars based on Jan. 2007, (a) and (b) are constants), (S) is the size of the equipment and (n) is the exponent for equipment.

Direct quotes from companies were scaled up using Equation 10.2. The base capital cost of the plant (C_1) with capacity (S_1). The unknown capital costs (C_2) is given by capacity (S_2). The superscript n is the scaling factor for the equipment from [132].

$$C_2 = C_1 * \left(\frac{S_2}{S_1}\right)^n \qquad \textit{Equation 10.2}$$

The equipment costs are updated using the Chemical Engineering Plant Cost Index (CEPCI) for 2007 and 2011.

$$C_2 = C_1 * \left(\frac{S_2}{S_1}\right)^n * \left(\frac{CEPCI}{CEPCI_1}\right) * installed\ capital\ cost \qquad \textit{Equation 10.3}$$

The total installed equipment costs are adjusted using the Hand factor shown in Equation 10.4 that included material adjustment factor (F_m), instrumentation factor (F_i), building factor (F_b) and place factor (F_p) published by Brown [135].

$$Installed\ capital\ cost = \ \sum[Equipment\ purchase\ costs * (Hand\ factor * \ F_m)] * F_i * F_b * F_p:$$

Equation 10.4

The total purchase equipment costs were obtained by adding taxes, insurance, service and repair of the individual equipments costs. This accounted for 4 % of the total installed equipment purchase costs.

10.6.2 TOTAL CAPITAL INVESTMENT

Table 10.4 shows the assumptions taken for the estimation of the investment costs. Capital costs are a major part of the total investments costs. Capital costs involve both direct and indirect costs. The direct costs are the total purchased equipment costs, building, process and auxiliary. The indirect costs include engineering and supervision, legal expenses, construction and contractor fee and contingency. A contingency factor of 10 % of the total equipment purchase costs is the minimum advised limit set by [134][135][136].

Table 10.4: The assumptions undertaken for estimation of total capital investment

	Basis
Building, process and auxiliary	10% of Total purchase equipment costs
Engineering and supervision	15% of Total purchase equipment costs
Legal expenses	5% of Total purchase equipment costs
Construction expense and constructor fee	10% of Total purchase equipment costs
Contingency	10% of Total purchase equipment costs
Fixed capital investment	Sum of above
Working capital	10% of Total purchase equipment costs
Total capital investment	Sum of above

10.6.3 OPERATING COSTS

The operating costs envelop every costs needed to achieve the final product. These are utility costs, labour costs, consumables, waste disposal, maintenance, overheads etc.

10.6.3.1 UTILITY COSTS

The electricity consumed by the plant to operate the feeding system of sewage sludge, pumps and all other controls such as the reactor, dryer, electrostatic precipitator, combustor, cyclone and engine were estimated calculated and estimated as shown in Table 10.5. The estimated power consumption could be taken from the generator before connection to the national grid.

Table 10.5: Assumptions for electricity usage for the plants

	Plant capacity (dry t/h)		
	0.2 t/h	**1.0 t/h**	**2.0 t/h**
		Values (kW)	
Sewage sludge conveying, metering and feeding [137]	18.8	68.1	118.6
Bio-oil liquid pump	1.3	4.6	7.9
Cooling water pump	1.0	3.4	6.0
Electricity powered controls (20% of above)	4.2	15.2	26.5

The other utility costs for the plants were taken as shown in Table 10.6. The natural gas costs were obtained from the U.S energy administration prices quoted for the United Kingdom 2010. The natural gas prices were estimated to be £0.0052/MJ [138].

Table 10.6: Utility costs used for estimation of the process requirements

Utilities	Unit	Value	Reference
Natural gas costs	[£/MJ]	0.0052	[138]
Nitrogen costs	[£/L]	0.09	[139]
Cooling water	[£/m^3]	0.50	[7]
Lubrication oil	[£/kWh]	0.0112	[137]

10.6.3.2 LABOUR COSTS

The numbers of personnel required by the process system were estimated using Ulrich's counting method described by [135] and by comparison to similar plant capacities. Appendix A3.5 shows an example of Ulrich's method. The operating plants are assumed to be a continuous process, operating 24 h a day for 7 days a week with 3 shifts per day. The operating days per year is taken to be 330 days with 7920 h. Contractor fees working due to overall maintenance of the plant and equipments during down time has not been considered. The cost per hr for each employee is assumed to be £18 per hour.

Table 10.7: Labour costs requirements for the plant

	Plant capacity		
	0.2 t/h	1.0 t/h	2.0 t/h
No of personnel per shift	1.5	2.5	2.5
Total cost per year (£/a)	213,840	356,400	356,400

10.6.3.3 DRYING COSTS

Sewage sludge from Severn Trent Water is dewatered by centrifuge and no further drying is carried out. For this economic evaluation it will be assumed that the biochar obtained from sewage sludge is combusted to provide the heat required for the dryer. Sewage sludge char has an average of 50 % ash content so the combustible material is approximately 50 %. Table 10.8 shows the parameters used for calculating the heat required for drying. A detailed calculation for drying heat requirements is given in Appendix A3.2.

Table 10.8: Assumptions taken for drying requirements [25]

Parameter	Units	Value
Specific heat capacity for water	[kJ/kg °C]	4.18
Heat of evaporation for water at 1 atm	[kJ/kg]	2257
Specific heat capacity for the sludge	[kJ/kg °C]	1.83
Dewatered sludge temperature	[°C]	15
Sludge is dried to a final temperature	[°C]	100

$$Q_{drying} = M_{ds} * W * \left[(Cp_{water} * \quad \Delta T) + H_{vap}\right] + [M_{ds} * (1 - W)] * Cp_{sludge} * \Delta T \ [25] :$$

Equation 10.5

Where M_{ds} refers to unit mass of dewatered sludge (kg), W is water content in the sludge, Cp_{water} as heat capacity of water, H_{vap} as latent heat of vaporisation of water, Cp_{sludge} as the heat capacity of solids in dewatered sludge and ΔT as the temperature difference between the initial and final (105°C).

It was assumed that the dewatered sludge is at 15˚C and dried to 100 ˚C, ΔT = 85 ˚C, $H_{vap\,=}$ 2090 kJ/kg, Cp_{water} = 4.18 kJ/kg ˚C, Cp_{sludge} = 1.83 kJ/kg ˚C [25].

10.6.3.4 MAINTENANCE AND OVERHEAD

The servicing of the equipments is essential to their performance and reliability. The cost of service and repair of the individual equipments has been accounted for in the sum of the total purchase equipment costs. This was taken to be 2 % of the total individual equipment costs. The taxes and insurance cost of plant was taken to be 2 % of the total individual equipment costs. Maintenance and overheads were estimated to be 4 % of the investment costs. This allows for any problems encountered to be addressed quickly and effectively.

10.6.4 INTERNAL COMBUSTION ENGINE

The internal combustion (IC) engine is assumed to be the drive for the CHP system. The IC engine is assumed to be specially designed to deal with the inferiority of sewage sludge pyrolysis oil. The IC engine comprises of combustion chamber, electrical generator, heat recovery system, exhaust and control system [140,141]. The CHP capacity of the plant is assumed to be as shown in Table 10.9. A 20% design capacity was taken in count as advised by [142]. The CHP system has been reported by Beggs [141] to have the efficiency ranging from 30 to 37 %. However modern engine are being manufactured by companies such as Schneil and Clarke energy that are able to attain greater efficiencies than those reported in literature. The overall heat and power from the engine is assumed to be as shown in Table 10.10.

Table 10.9: Calculated CHP size for the plant capacities

Plant capacity (t/h)	CHP size
2.0	1 MW
1.0	500 kW
0.2	200 kW

The estimated efficiencies in Table 10.10 are used for the calculation of the electricity demand for the plants. The sewage sludge pyrolysis oil is an inferior fuel compared to diesel and biodiesel and therefore it is assumed that the efficiency of the fuel to be much less compared to conventional fuels. The sewage sludge pyrolysis oil is to be the only fuel used for the CHP system. It should be noted that actual performance of the pyrolysis oil in a specially designed engine would be less or more but until this is justified, the above assumptions have been implemented to enable the evaluation to be undertaken.

Table 10.10: Estimates for the energy distribution in the engine

Energy dispersion	Efficiencies reported in literature [140,143]	Estimated efficiencies (± 5)
Shaft power	38 to 35 %	30 %
Exhaust gases	40 to 30 %	35 %
Cooling water	30 to 12 %	30 %
Radiation	12 to 5 %	5 %

10.6.5 RENEWABLE INCENTIVES

The profitability of the CHP systems is mainly dependant on the government incentives that are currently in operation. The sewage sludge pyrolysis oil used in a CHP system qualifies for the renewable obligation certificate (ROC). The pyrolysis oil having a higher heating value greater than 10 MJ/kg qualifies for two ROCS. Each ROC is equivalent to £0.04p/kWh produced [144]. Electricity is sold to the national grid at 0.065p/kWh excluding the renewable obligation certificate awards [7].

The renewable heat incentives (RHI) for CHP systems have a number of criteria that have to be met. The CHP should be certified by Ofgem, metering should be implemented, a medium such as hot water/ steam should be involved [144]. The most critical item of such a system is the way the hot water or steam is utilised. Some of the eligible heat uses described by [144] are domestic heating schemes such as space heating, heating of water for direct use in large premises, heat for domestic premises that also provides heat elsewhere and carrying out a process. However, heat used for generation of electricity doesn't qualify for the RHI [7,144].

10.7 ECONOMIC EVALUATION RESULTS

The economic evaluation of project was assessed using a cash flow sheet in excel sheet depicted from [134] shown in Appendix A3.6.2, A3.6.3 and A3.6.4. The project is assumed to be 100 % equity financed. The plant life was estimated to be 20 years with a straight line depression of 10 years taken after a 3 year period. The working capital is estimated to be 20 % of the total equipment purchase costs. The start-up period is taken to be within 6 months. Land for the plant operation is assumed to be available to the company. A 12% discount rate has been used according to the department of trade and industry [137][140]. Loyalties are assumed to be negligible.

10.7.1 TOTAL CAPITAL INVESTMENT

The intermediate pyrolysis process has not yet been fully commercialised. The equipment purchase costs have been estimated to have an error of ± 30 %. The equipments costs are shown in Table 10.11. The total capital investments for the projects are calculated to be as shown in Table 10.12.

The cost of the pyrolysis reactor was estimated by the manufacture of the intermediate pyrolysis systems [145]. The reactor is assumed to be specially designed to utilise other source of heating like natural gas instead of electricity input.

The cost of cooling tower is significantly high. This is due to standard sizes available for the cooling tower. Costs for the customary made towers are not known. So actually costs might be less than those estimated in Table 10.11.

The cost of the CHP is based on natural gas priced systems [146]. However customisation of the CHP is available and depends on the type of fuel to be utilised. The CHP system designed for the sewage sludge pyrolysis oil should have specially designed items such as fuel line, injector, combustion chamber in order to deal with the complexity of the oil properties.

Table 10.11: Estimated equipment purchase costs

		Plant capacity (dry t/h)		
	Units	**0.2**	**1.0**	**2.0**
			Installed capital costs (£) ± 30%	
Drying	Dryer, odour abatement	87,549	184,188	240,211
Char combustion	Combustor	88,585	222,221	381,671
Pyrolysis process	Reactor, Feeding and conveyor, char collection, natural gas burner	108,970	296,438	516,859
Filter units	Cyclone, ESP	58,818	346,246	477,988
Cooling water tower	Cooling tower	273,625	273,789	273,975
Product recovery and storage	Condenser, Decantor, Storage tank, oil pump, water pump	261,204	454,606	528,747
CHP	CHP [135]	142,857	357,142	714,285

The total capital investments are estimated as shown in Table 10.12. The total capital investment costs are assumed to be £1.7million$_{2011}$ for 0.2 t/h, £3.5 million$_{2011}$ for 1.0 t/h and £5.3 million$_{2011}$ for 2.0 t/h plants. It should be noted that these prices are only an estimate based on the assumptions taken, actual prices might vary greatly. This is because Severn Trent Water [7] undertook an economic evaluation for the use of sewage sludge pyrolysis oil for electricity production based on a 0.2 t/h and they found the investment costs to be £ 4.0 million$_{2011}$. The analysis was carried out by a team of professionals in the field which makes their estimates more realistic since the process is assumed to be a continuous automated process that is more expensive than the values shown in Table 10.12.

Table 10.12: Total capital investments for the projects

	Plant capacity (dry t/h)		
	0.2	**1.0**	**2.0**
		Costs (£) ± 30%	
Total purchased equipment costs	1,062,473	2,220,014	3,259,085
Building, process & auxiliary	106,247	222,001	325,909
Engineering and supervision	175,308	366,302	537,749
Legal expenses	53,124	111,001	162,954
Construction expense and constructor fee	106,247	222,001	325,909
Contingency	106,247	222,001	325,909
Fixed capital investment	1,609,646	3,363,322	4,937,514
Working capital	106,247	222,001	325,909
Total capital investment	1,715,893	3,585,323	5,263,422

10.7.2 TOTAL OPERATING COSTS FOR ELECTRICITY PRODUCTION

The operating cost to produce each kWh of electricity was obtained from the costs of producing bio-oil to injection of the pyrolysis oil into the engine. The lower heating value of the pyrolysis oil was taken to be 37 MJ/kg. The engine output power was estimated to be 30 % of the overall energy input, 35 % as exhaust gases, 30 % cooling water and 5 % taken as heat losses.

10.7.3 ELECTRICITY UNIT PRICE WITHOUT DOMESTIC HEATING SCHEME

Table 10.13 shows the production costs involved in producing electricity from sewage sludge pyrolysis oil without using the domestic heating schemes. The electricity unit sell price was based on the sum of the total operating and annualised capital costs divided by the total electricity output excluding plant parasitic load as shown in equation 10.6. Table 10.13, the calculated electricity costs for 0.2 t/h, 1.0 t/h and 2.0 t/h are £1.07 per kWh, £0.34 per kWh and £0.20 per kWh. The results obtained are very high for cost of electricity in the UK. A study by Peacocke et al [137] for the production of electricity from wood pyrolysis oil also found similar results. Peacocke et al [137] reported results by Wellman and BTG process for electricity production from wood pyrolysis oil to have an average price per kWh to be; 46.7 kWh for 0.25 t/h, 22.9 kWh for 1.0 t/h and 17.9 kWh for 2.0 t/h.

$$Electricity\ unit\ costs = \frac{Annual\ production\ costs + Annualised\ capital\ costs}{Total\ electricity\ yield - Total\ electricity\ demand\ of\ the\ plant}$$

Equation 10.6

The electricity price shown in Table 10.13 reflects the minimum amount that the electricity could be sold in order to break even. The companies participating in the renewable obligation certificate current sell their electricity to the national grid excluding the renewable payments at a rate of £0.065 per kWh [7]. This amount is much less than that of the estimated electricity price for the three plant capacities. It could be more economical if the electricity generation cost including capital costs were below or equal to the UK's feed in tariff.

If the company's sole objective for installation of the proposed pyrolysis process is to sell the electricity produced for a profit, then this would be unachievable. However, if the company installs the proposed system in order to meet its own electricity demand where the outgoings are much greater than the proposed capital investment over a certain period then such a process will be ideal. The sewage sludge pyrolysis oil use in a CHP would perhaps be more economical for a much larger plant operation than that discussed.

Table 10.13: Capital and production costs of electricity without domestic heating scheme

Bio-oil production costs		Plant capacity (dry t/h)		
		0.2	**1.0**	**2.0**
	Units	Costs (£/yr) ± 30%		
Drying process	[£/yr]	7421	37104	74207
Reactor costs		22327	111284	222394
Nitrogen costs		5940	29700	59400
Miscellaneous		10625	22200	32591
Cooling water		300	1500	3000
Labour costs		213840	356400	356400
Maintenance		21249	44400	65182
Overheads		21249	44400	65182
Total		302951	646988	878355
Engine				
Pyrolysis oil	[kg/yr]	211200	1056000	2112000
Overall	[MJ/yr]	7814400	39072000	78144000
30% engine conversion	[MJ/yr]	2344320	11721600	23443200
kW of oil	[kWh/yr]	651200	3256000	6512000
Electricity production per year	[kWh/yr]	651200	3256000	6512000
Estimated electricity demand from the plant	[kWh/yr]	199687	723644	1259937
Total output excluding plant demand	[kWh/yr]	451513	2532356	5252063
Lubrication oil per kWh	[£/yr]	1302	6512	13024
Capital costs				
Total capital investment with pyrolysis process	[£]	1715894	3585325	5263423
Annualised capital charge at 12% over 20 yrs	[£/yr]	229930	480433	705299
Renewable credits				
Co-product credits (2 rocs for electricity @0.04p/kwh)		52096	260480	520960
Total operating costs(excluding capital)	[£/yr]	252157	393020	370419
Total operating costs including capital	[£/yr]	482087	873454	1075718
Electricity production costs	[£/kWh]	0.39	0.12	0.06
Electricity costs including capital investment	[£/kWh]	1.07	0.34	0.20

10.7.4 ELECTRICITY UNIT PRICE WITH DOMESTIC HEATING SCHEME

The calculated electricity price while obtaining the renewable heat incentive as shown in Table 10.14 is estimated to be £1.09, £0.36, £0.22 per kWh for 0.2 t/h, 1.0 t/h and 2.0 t/h. It should be noted that the domestic heating scheme installation costs have not been taken into account for this calculation. Therefore the calculated electricity price would be much higher than those presented due to increased capital costs. It should also be noted that the income from the selling of heat through the district heating scheme is not reflected in the price of electricity. The renewable heat incentive amount used for estimation of payments is £0.026 per kWh [144].

10.7.5 PROFITABILITY ANALYSIS

The financial analysis was carried out using the excel sheet outlined in Appendix A3.6.2, A3.6.3, A3.6.4. The income shown in the Appendices are based on the sale prices shown in Table 10.14. The main income for the project originates from the sale of the electricity generated that is boosted by the renewable incentives. The estimated electricity prices without domestic heating schemes are 1.07 per kWh, 0.34 per kWh, 0.20 per kWh for 0.2 t/h, 1.0 t/h and 2.0 t/h. The estimated electricity prices are very high even if the electricity was sold directly to the consumers without feeding into the national grid. According to the Europe's energy portal publication [147], the average electricity price in the UK ranges from £0.11 to £0.126 per kWh.

The sale of electricity produced from sewage sludge pyrolysis oil is not cost-effective due to the high prices. However the process can be made economical or profitable if the company's sole intention for investment is to use the generated electricity to meet its own demand where the outgoings over a certain period are more than the estimated investment costs for the period of the project. Profitability of the pyrolysis process can be achieved with alternations to the system that would enable lower production costs.

Table 10.14: Capital and production costs of electricity with domestic heating scheme

		Plant capacity (dry t/h)		
		0.2	**1.0**	**2.0**
	Units	Costs (£/yr) ± 30%		
Bio-oil production				
Natural gas costs	[£/yr]	55,900	279,150	558,125
Cooling water	[£/yr]	1,200	6,000	12,000
Nitrogen costs	[£/yr]	5,940	29,700	59,400
Labour costs	[£/yr]	213,840	356,400	356,400
Maintenance	[£/yr]	21,249	44,400	65,182
Overheads	[£/yr]	21,249	44,400	65,182
Miscellaneous costs	[£/yr]	10,625	22,200	32,591
Electricity production				
Oil produced	[kg/yr]	211,200	1,056,000	2,112,000
Electricity production per yr	[kWh/yr]	7,814,400	39,072,000	78,144,000
30% Engine conversion	[MJ/yr]	2,344,320	11,721,600	23,443,200
Estimated electricity demand from the plant	[MJ/yr]	199,687	723,644	1,259,937
Total electricity output excluding demand	[MJ/yr]	451,513	2,532,356	5,252,063
Engine Lubrication oil	[£/yr]	1,302	6,512	13,024
Renewable credits				
Electricity production credits	[£]	52,096	260,480	520,960
Renewable heat incentives	[£]	16,931	84,656	169,312
Capital investment and operating costs				
Capital costs	[£]	1,715,893	3,585,323	5,263,422
Annualised capital charge at 12% over 20 yrs	[£]	229,930	480433	705,299
Total operating costs(excluding capital)	[£/yr]	262,279	443,627	471,632
Total operating costs including capital	[£/yr]	492,208	924,060	1,176,930
Electricity production costs	[£/kWh]	0.40	0.14	0.07
Electricity costs including capital investment	[£/kWh]	1.09	0.36	0.22

10.7.6 SENSITIVITY ANALYSIS

Sensitivity analysis was undertaken to determine the variables that affected the electricity unit price. The results of the sensitivity analysis for the three plant capacities are shown in Fig.10.3, Fig.10.4, and Fig. 10.5. The analysis identified capital costs and labour costs as the major variables that affected the electricity unit price. The greatest increase with variation factor occurs with the capital costs. An increase in capital costs increases the electricity unit price significantly.

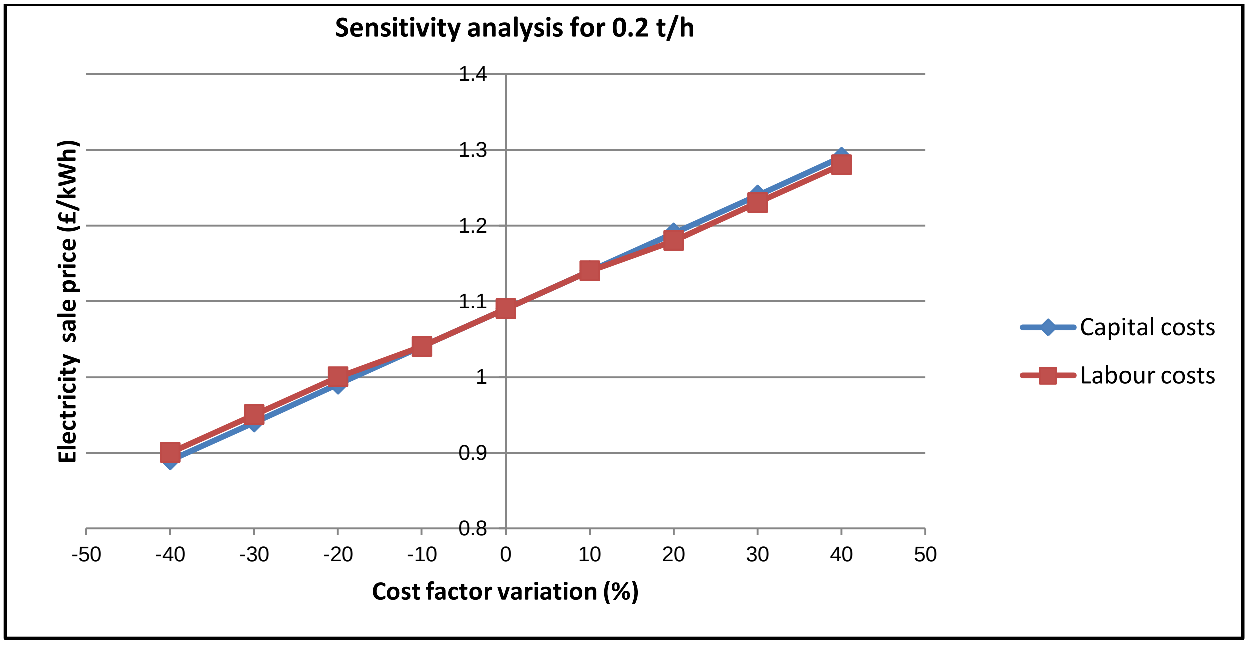

Figure 10.3: Cost variation factors for 0.2 t/h plant

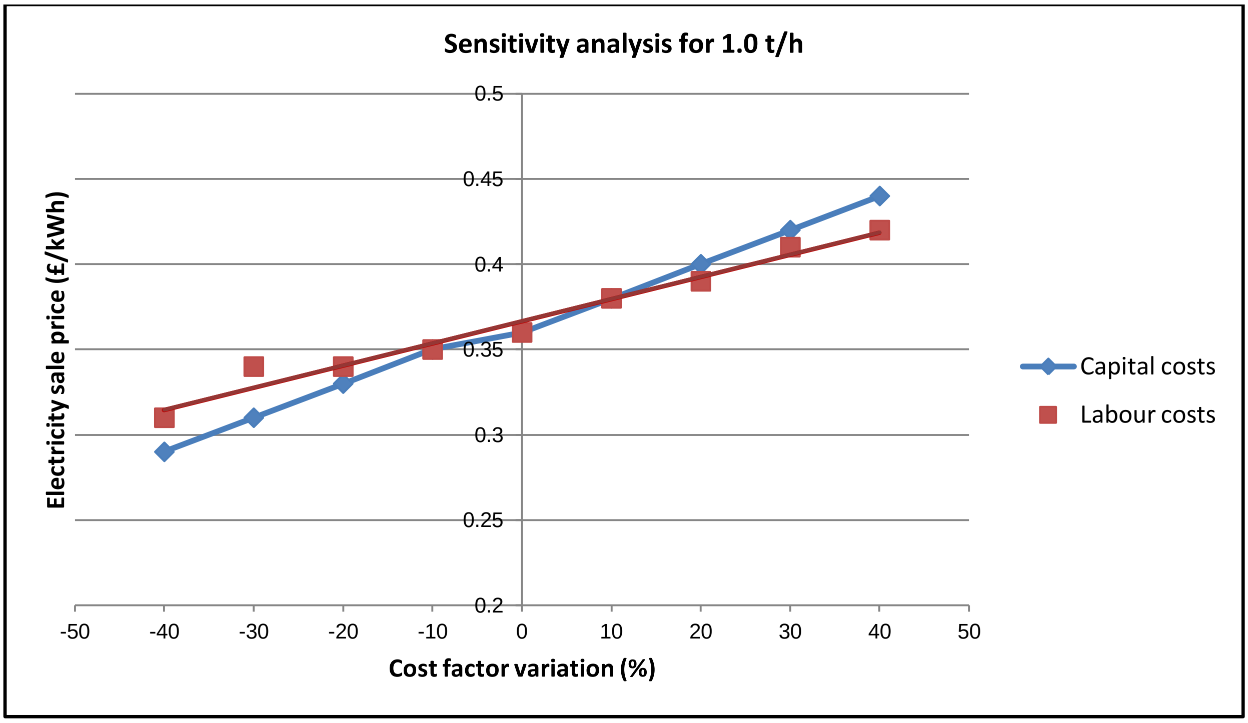

Figure 10.4: Cost variation factors for the 1.0 t/h plant

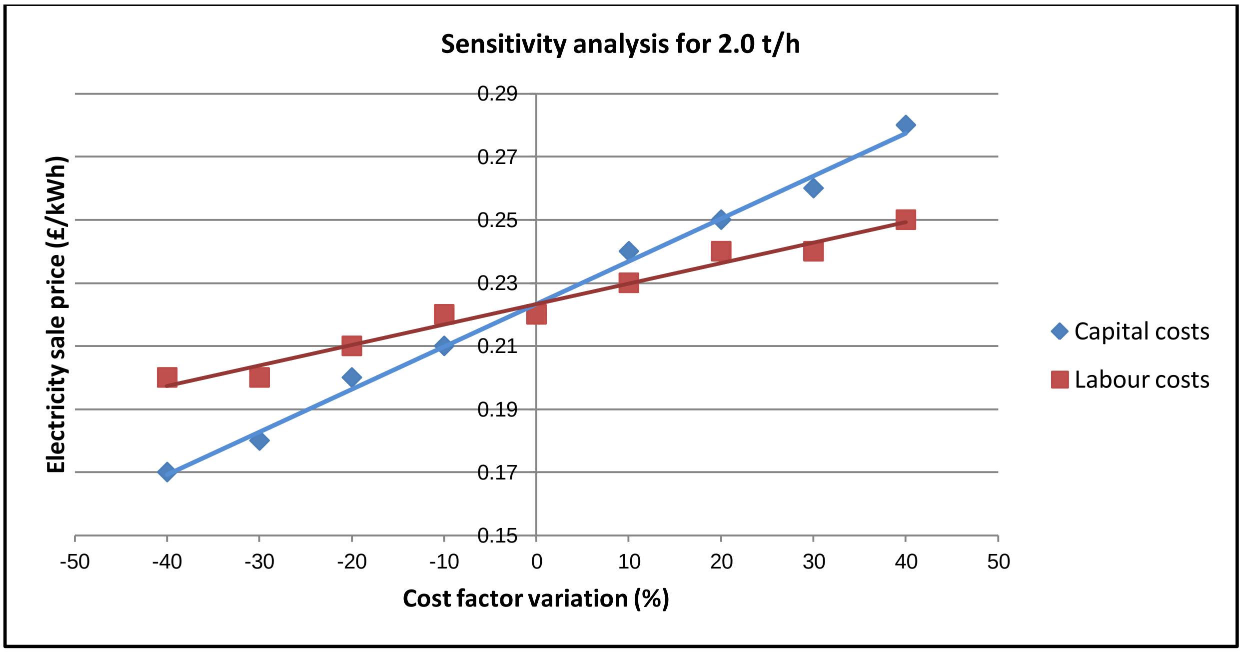

Figure 10.5: Cost variation factors for the 2.0 t/h plant

10.8 LIMITATION OF THE ECONOMIC EVALUATION

The economic evaluations carried out for the production of electricity from sewage sludge pyrolysis oil has several limitations among these are;

- Information about the large scale intermediate pyrolysis processes is limited as there is no commercialised plant as yet in operation as compared to fast pyrolysis process.

- There is lack of information regarding actual costs of power production from a CHP system using pyrolysis oil. There might be an underestimation of the actual costs.

- The profitability of the power production from pyrolysis oil depends on renewable incentives set up by the regulatory authorities; however without the incentives it is not worth undertaking such a project. Any decrease or termination of the incentives would greatly affect the profitability of the process.

- Although the plant has been assumed to be fully automatic, actual costs of implementing such an operating mode will be much higher than the estimated values.

- There is uncertainty over the proposed system design on a large scale due to the infancy of the intermediate pyrolysis process.

- There is lack of commercially available intermediate pyrolysis reactors compared to slow and fast pyrolysis systems.

10.10 SUMMARY

Among the advantages of using sewage sludge as a feedstock for power production is that it is free for wastewater treatment companies. It is one of the biomass that will always be available as long as humanity exists. Although there are no commercially available intermediate pyrolysis plants, small differences exist between fast and intermediate pyrolysis. According to the literature and the economic analysis carried out, it is clear that larger operating plants are more commercial viable than small scale operations.

The use of sewage sludge pyrolysis oil for electricity production is achievable. The process can also be made profitable if some of these measures are implemented or made possible; process system alterations that enables lower operating costs, electricity generated is cheaper than that bought from the national grid, electricity generated is only intended for company sole use where capital investments are much lower than those incurred by the company in the long term, if electricity produced by a company can be sold directly to consumers, combustion of pyrolysis oil with an additive to increase efficiency of the fuel.

The amount of electricity produced by CHP has the largest impact on the unit price of electricity. This is also affected by the efficiency of the CHP. Lower efficiency will greatly increase the electricity unit price.

The full utilisation of heat and power from the CHP would make the process more economical, however not every heat produced would qualify for the renewable heat incentives.

The sewage sludge pyrolysis oil has a high energy content that is comparable to biodiesel. However the smell from the pyrolysis oil should be combated with the addition of a solvent. The addition of biodiesel to sewage sludge bio-oil has proved to be beneficial in this respect. It is essential to utilise the pyrolysis bio-oil once it is produced and not to store this longer than 6 month as the viscosity of the bio-oil increases with time.

The type of sewage sludge used for the pyrolysis process will have great effect on the pyrolysis oil yield. Care should be taken to ensure that a particular sludge is used in order to maintain the characteristics of the pyrolysis oil expected.

Capital costs of the plant are the most sensitive factor to the electricity unit price. A slight increase in capital costs would greatly affect the unit price of electricity.

Apart from the feedstock preparation steps and reaction process, there is little difference between fast and intermediate pyrolysis process. The feasibility of a commercially operating intermediate pyrolysis is a reality although the reactor design and specification need a specialist team to ensure its success.

Further investigations are also needed with regards to the long term performance of the sewage sludge pyrolysis oil in engines.

CHAPTER 11: CONCLUSIONS AND RECOMMENDATIONS

11.1 CONCLUSION

The average pyrolysis yields obtained from the intermediate pyrolysis of sewage sludge are 50 % biochar, 40 % bio-oil (organic and aqueous phase) and 10 % non condensable gases. The main achievement of the intermediate pyrolysis process has been the use of a large reactor that has not been utilised by other authors to attain large quantities of the pyrolysis yields. This has enabled the pyrolysis oil (organic phase) to be blended and tested in the Lister diesel engine. This has not been achieved by any of the authors in literature.

The main pyrolysis product of interest has been the organic phase of the sewage sludge bio-oil. An average of 33 wt% of the organic phase of sewage sludge bio-oil has been achieved. Larger quantities of the organic phases of sewage sludge have been achieved on a small scale by fast pyrolysis process. Inguanzo et al [6] found the organic yield to be 60 wt% , Park et al [36] found this to range from 52 to 57 wt% and Pokorna et al [37] found this to be 44 wt%.

The major impact of the intermediate pyrolysis process has been to the nature of pyrolysis oil (organic phase) produced. There was reduction of tar fractions that are cracked to form shorter chain molecules. The cracking occurs during the pyrolysis process with the aid of char cycling in the reactor. This improved the properties of the pyrolysis oil such as viscosity. Authors like [32][34] found tar compounds in the organic phases using the fast pyrolysis.

The intermediate pyrolysis of sewage sludge has been able to achieve organic phases that have an energy content ranging from 35 to 39 MJ/kg. The fast pyrolysis process of sewage sludge achieved varying energy content of the organic phases; Pokorna et al [37] found this to be 24.7 MJ/kg while Fonts et al [5] found this to be 41 MJ/kg. The slow pyrolysis of sewage sludge found the energy contents of the organic phase to be in the same range. Shen and Zhang [34] found the organic phase to have an energy content of 38 MJ/kg while Kim and Parker [25] found this to range from 36 to 39 MJ/kg. The reasons for the differences are due to; different reactors, operating conditions, and varying sludge types used for the pyrolysis process. These conditions greatly affect the product type and yield, Fonts et al [47] agreed with this conclusion.

The co-pyrolysis of sewage sludge with 40 wt% mixed wood was very effective in controlling and masking the pungent smell generated during the pyrolysis reaction. The bio-oil produced also had a sweet smell. There was also an increase in the energy content of biochar from the co-pyrolysis process compared to the lower energy content from the sludge. The co-pyrolysis with 40 wt% mixed wood was more economical and applicable compared to rapeseed and straw.

The thermal stability tests of the sewage sludge pyrolysis oil proved to be more stable in the 20 wt% biodiesel samples compared to the 10 wt% methanol samples. Biodiesel can be added to the pyrolysis oil to delay polymerisation reactions and improve some of the properties.

The Lister diesel engine tests using the pyrolysis oil blends were successfully carried out without engine alterations. The pyrolysis oil blends had lower NOx and CO emissions compared to biodiesel alone. However the brake thermal efficiencies of the blends were lower than that of biodiesel and diesel.

The use of sewage sludge pyrolysis oil in a combined heat and power system for power production is possible. The profitability of such a system is mainly dependant on the government renewable incentives. Without these, any company would think twice about such processes. Although the pyrolysis oil is viewed as the valuable pyrolysis yield, the quantity produced from the intermediate pyrolysis process is very low compared to fast pyrolysis process. The economic evaluation carried dependents largely on the amount of pyrolysis oil produced and for this reason the prices of electricity per kWh are relatively high. The scenario of high electricity per kWh was also found by New Hampshire [130] and Peacocke et al [137]. It should be noted that a higher pyrolysis oil production from another biomass such as rapeseed would make the process profitability, if the analysis is based on the price of electricity. This is because the pyrolysis of rapeseed yields larger quantities of organic phase (pyrolysis oil) compared to sewage sludge. The pyrolysis process can be carried out for other reasons such as converting waste to energy and obtaining valuable chemicals.

11.2 RECOMMENDATIONS

The pyrolysis of sewage sludge yields large amounts of biochar. The use of alternative processes such as gasification would be idea for utilising this pyrolysis product. Comparison of gasification and intermediate pyrolysis process can be done to determine the best technology for utilising the energy in sewage sludge. The economics of both should be compared to determine the best possible technology that would be ideal for this waste.

Chapter 7 has proved some of the potential benefits of the sewage sludge char to soil application; however the information obtained is limited and needs further work. Field trials can be undertaken to determine the impact of sewage sludge biochar on crop growth, micro-organism growth, soil fertility and long term effects. This information would then help governing bodies such as the environmental agency to permit wide application of this pyrolysis product.

Successful engine tests have been carried out with 30 wt% and 50 wt% sewage sludge pyrolysis oil blends with biodiesel. Further investigation can be carried out by increasing the concentration of the pyrolysis oil blend to 60, 70, 80, 90 and 100 wt%. The performance and emissions of these can be compared to the lower pyrolysis oil fractions and diesel or biodiesel. The impact of these tests on engine components such as the cylinder, injector and filter can be investigated.

The bio-oil obtained from the co-pyrolysis of sewage sludge with wood, rapeseed and straw can be investigated for engine applications. Engine performance and emissions can be investigated and compared to that of sewage sludge pyrolysis oil. The co-pyrolysis process can also be expanded upon by increasing the fractions of wood, rapeseed or straw to 50, 60, 70, 80, 90 wt%. The properties of the product yield can be investigated. There is great potential of utilising wood and sewage sludge even if other biomass are not considered. There is also an opportunity to investigate the co-pyrolysis of sewage sludge with other biomass apart from those reported in this thesis.

Although the old Lister engine used for testing the pyrolysis oils is robust and able to test various blends. Its injectors, filters and compressors are not designed for the pyrolysis oils and this causes problems such as blockage during engine operations. It is therefore recommended to use specially designed engines or engine modifications or specific materials of construction that are able to handle the corrosiveness and viscosity of the bio-oil.

The bio-oil obtained from the pyrolysis of sewage sludge has a strong pungent smell. This might limit its applications to users or even abandoning most of its application. The bio-oil has proven to have a great energy content however its application might be limited due to the smell. It is therefore recommended to investigate alternative methods that could be used to reduce or remove the smell that would enable the acceptance for various applications.

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APPENDIX 1: TGA ANALYTICAL METHODS

A1.1. ANALYTICAL METHOD USED FOR PROXIMATE ANALYSIS

The proximate analysis method applied for these experiments was adapted from Stahl et al [137]. The analysis was TG/MS was purged with helium gas for 1 hour to remove any presence of oxygen within the system. The helium gas was set to run at 60 ml/min for 1 hour. The proximate analysis contents of moisture, char and volatile matter, and ash content were carried out as described below;

Moisture content: To analyse this, the sewage sludge sample was dried for 1 hour so the program was set to run from 25 to 105 °C at 10 °C/min and the temperature was kept isothermal at 105 °C for 1 hour.

Char and volatile matter: The TG was run from 105 to 500 °C at 20 °C/min and the temperature was kept constant at 500 °C for 10 min. Char was produced as a product of pyrolysis at 500 °C. The char content was then calculated from the mass before and after the pyrolysis process. The mass loss step change verifies the volatile matter.

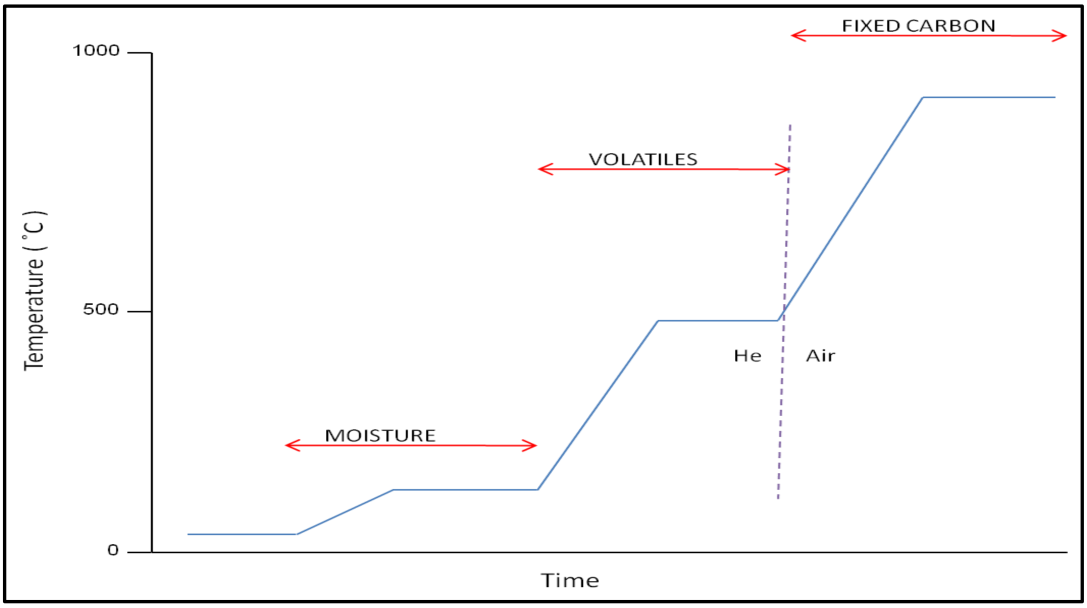


Figure A1.1: Proximate analysis method used for TG-MS

Ash content: To determine the ash content, the purge gas was switched from helium to air in order to allow combustion to take place. For this analysis, the TG was ran from 500 to 900 °C at 20 °C/min in air and the temperature kept constant at 900 °C for 1 hour to guarantee complete combustion.

A1.2. INTERPRETATION OF RESULTS FOR PROXIMATE ANALYSIS

The moisture content, char and ash content were determined using TG/MS by applying the proximate analysis method described A1.1. The analysis method described a TGA curve in form of Fig.A1.2. Fig.A1.2 shows different sections of the graph; the first part of the graph shows the moisture content, the second part shows the volatile content during pyrolysis in absence of oxygen at approximately 500 ˚C while the last part of the graph from 500 to 900 ˚C indicates weight loss due to char oxidation. Results for different sewage sludges are displayed in Fig.A1.3.

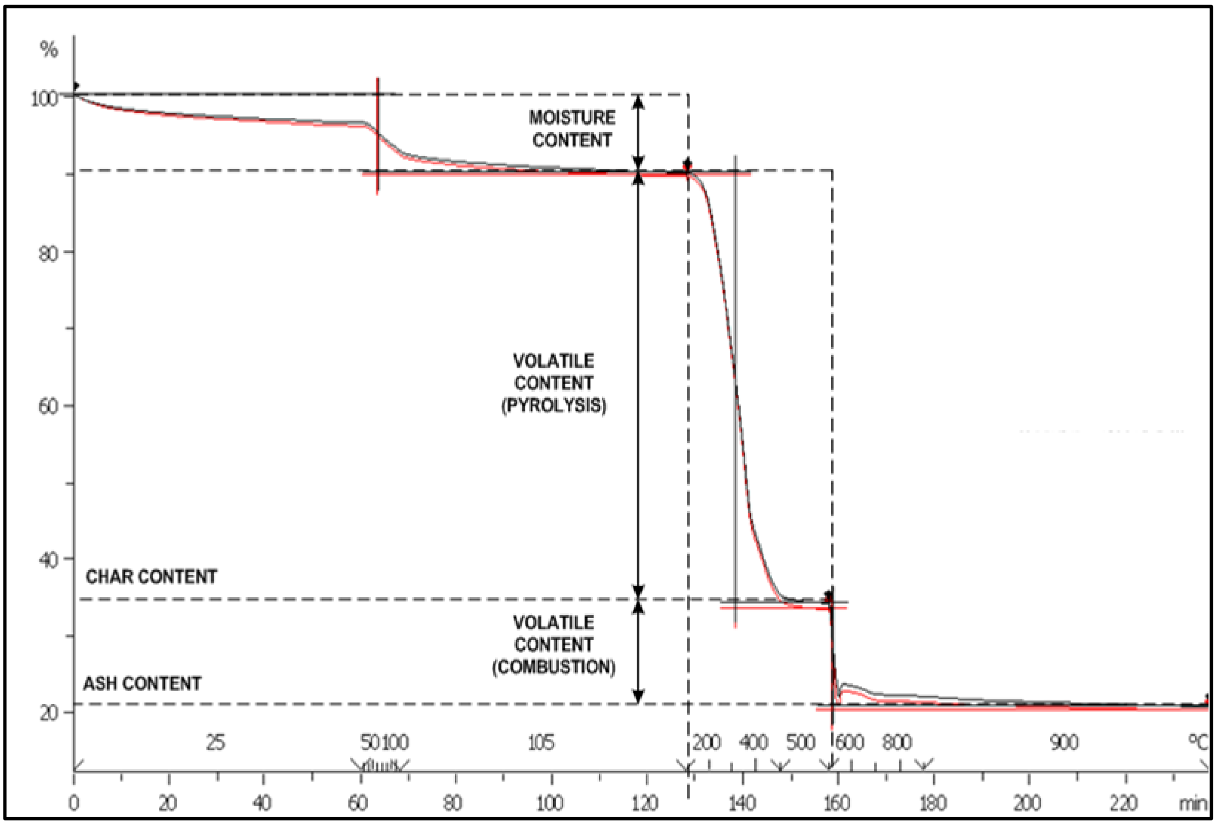


Figure A1.2: The proximate analysis interpretation from the TGA curve

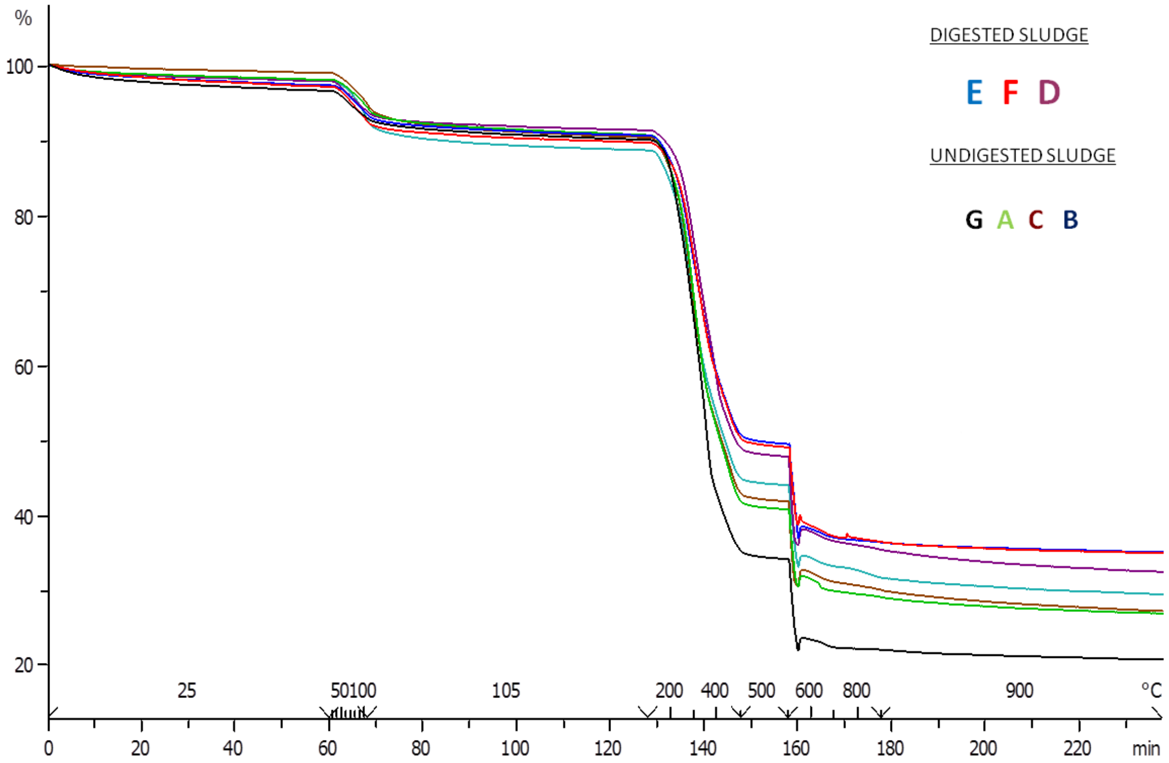


Figure A1.3: TGA curves for the various sludges

Table A1.1: The table shows the results obtained from Fig.A1.3

SAMPLE		**PYROLYSIS**		**COMBUSTION**	
		Yields of 105 -500 °C		Yields of 500– 900 °C	
	Moisture (wt %)	Volatiles (wt %)	Char (wt %)	Char (wt %)	Ash (wt %)
UNDIGESTED SLUDGE					
G	10.08	56.00	33.94	13.40	20.54
	10.55	56.33	33.12	13.08	20.03
A	9.04	51.19	39.77	14.99	24.78
	9.42	49.98	40.60	13.90	26.69
C	9.82	48.56	41.65	14.66	26.99
	9.61	48.48	41.95	14.86	27.10
B	11.50	44.65	43.83	14.58	29.25
	10.66	45.61	43.80	14.28	29.51
DIGESTED SLUDGE					
D	8.75	43.59	47.64	15.42	32.22
	7.74	43.27	48.98	15.15	33.83
E	9.54	41.13	49.33	14.44	34.89
	9.48	41.03	49.48	15.80	33.59
F	10.51	40.68	48.81	14.16	34.75
	12.66	39.32	48.03	13.75	34.34

A1.3. ANALYTICAL METHOD FOR THE PYROLYSIS PROCESS

In order to perform the pyrolysis process, the TG-MS was set to run using the following steps;

- Oxygen removal – at 25 °C, Helium was set at 60 ml/min for 1 hour to ensure pyrolysis conditions
- Pyrolysis run – TG was run from 25 to 500 °C at 20 ˚C/min
- Isothermal 500 ˚C – TG was run at 500 °C for 15 minutes

The decomposition behaviour displayed in form of a DTG curve shown in Fig.A1.4 and Fig.A1.5 were obtained for the undigested and digested sludge.

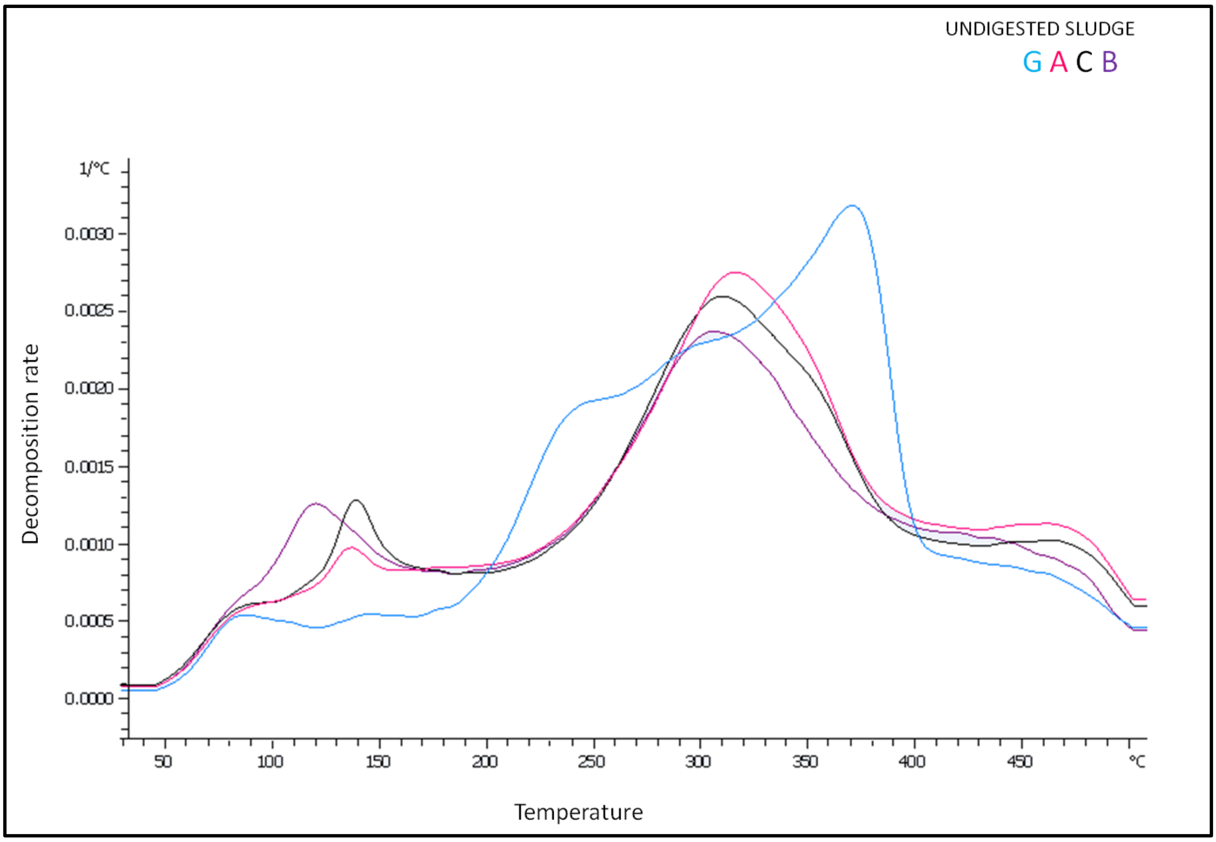


Figure A1.4: Decomposition rate of the undigested sludges

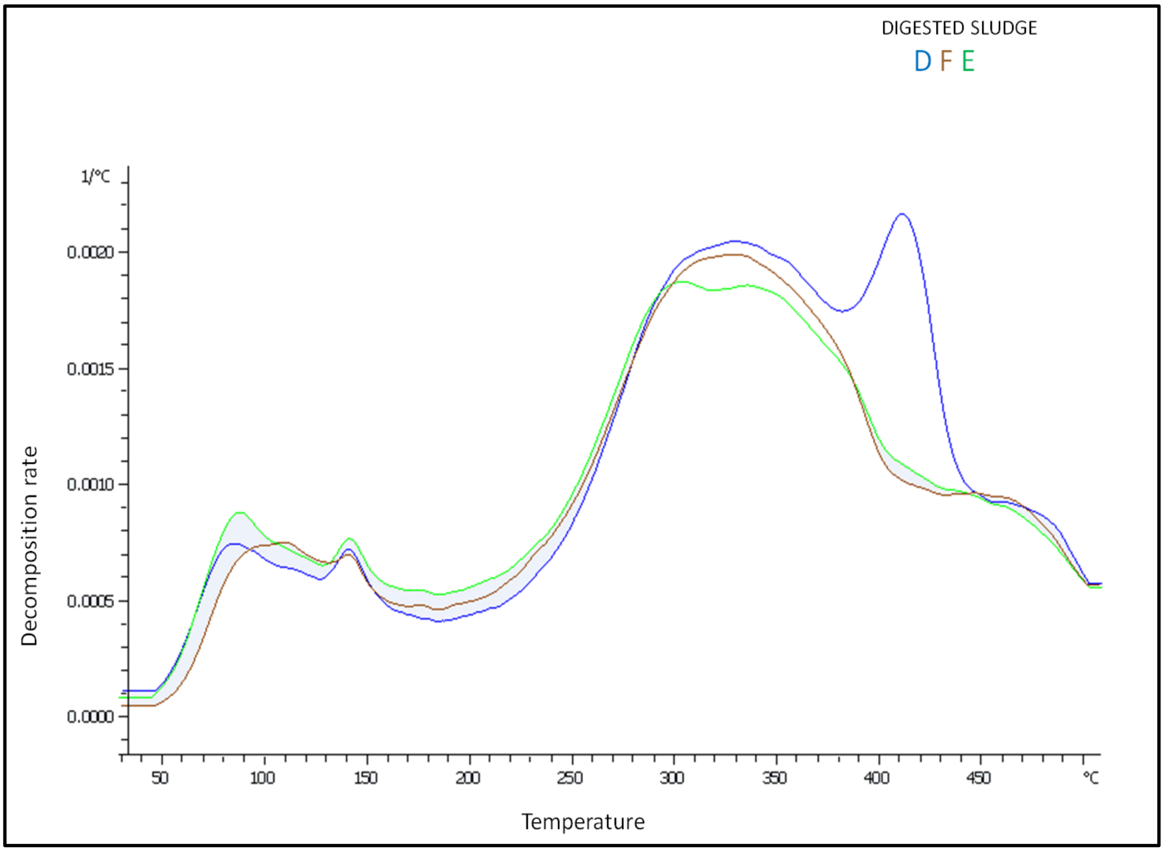


Figure A1.5: The decomposition behaviour of digested sludge

APPENDIX 2: STABILITY TESTS - GCMS CHROMATOGRAM AT 60°C AFTER 168H

A2.1. The spectra of pure pyrolysis oil at 60 °C after 168 h and compounds detected

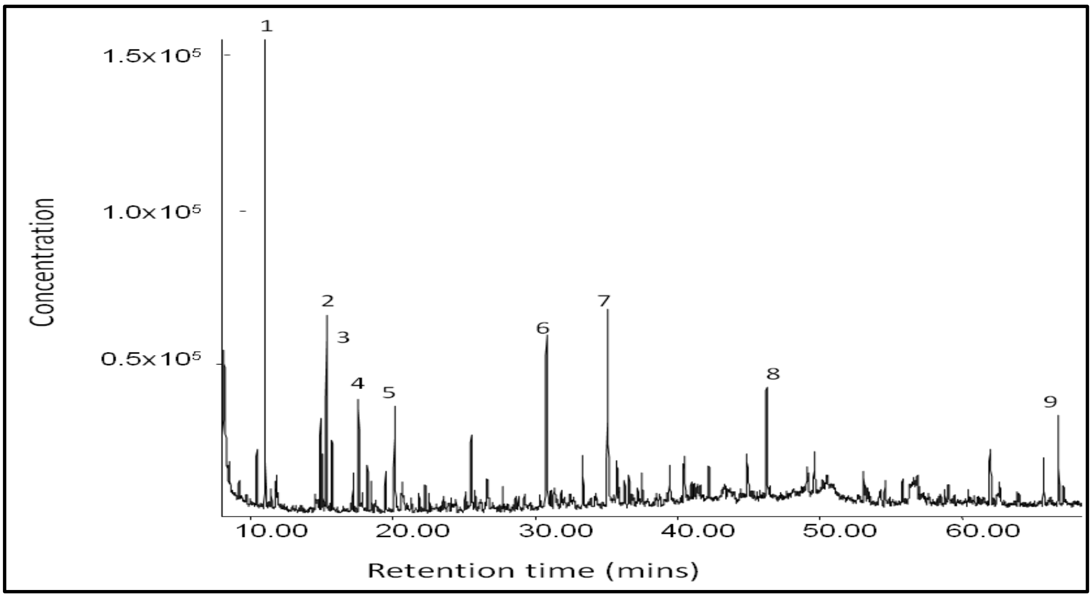


Figure A2.1: The spectra for the pyrolysis oil at 60 °C after 168h

Table A2.1: Compounds detected in the pyrolysis oil at 60 °C after 168 h

Peak number	Retention time (min)	Compound name
1	11.08	Methyl benzene
2	15.39	Ethyl benzene
3	15.79	1,4 dimethyl benzene
4	17.64	Styrene
5	20.17	1-Decene
6	30.84	Phenol
7	35.12	4-methyl phenol
8	46.29	1H-indole
9	65.74	Hexadecanenitrile

A2.2. The spectra of 10% MeOH sample at 60 °C after 168 h and compounds detected

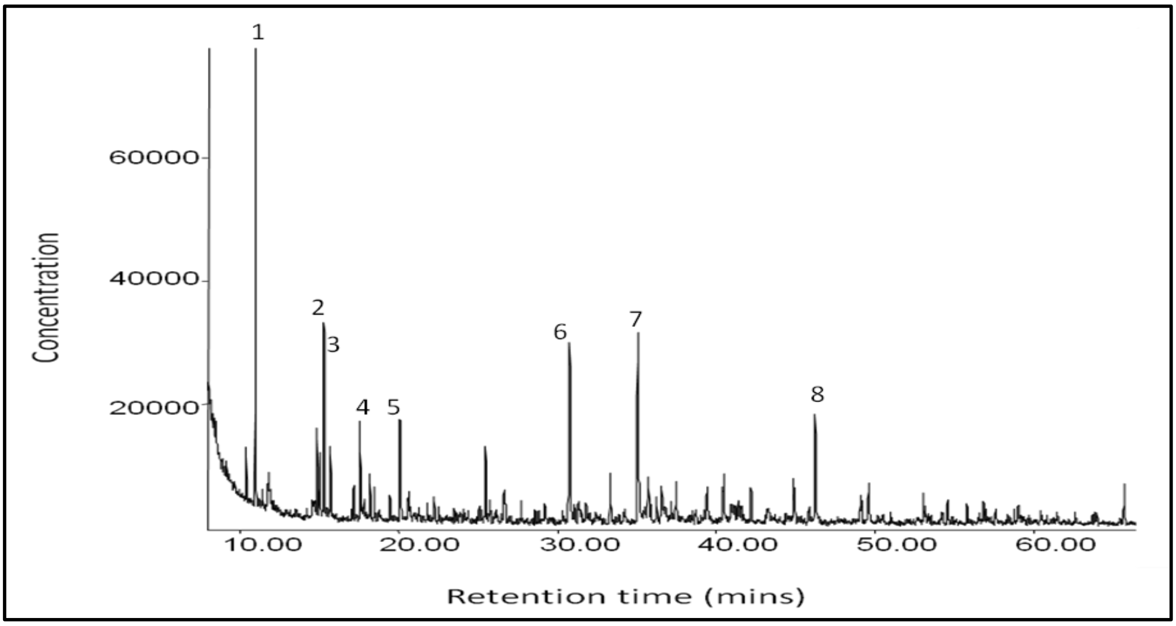


Figure A2.2: The spectra for the 10% MeOH sample at 60 °C after 168h

Table A2.2: Compounds detected in 10%MeOH sample at 60 °C after 168 h

Peak number	Retention time (min)	Compound name
1	11.05	Methyl benzene
2	15.37	Ethyl benzene
3	15.76	1,4 dimethyl benzene
4	17.61	Styrene
5	20.14	1-Decene
6	30.81	Phenol
7	35.10	4-Methyl phenol
8	46.26	1H-indole

A2.3. The spectra of 10% BD sample at 60 °C after 168h and compounds detected

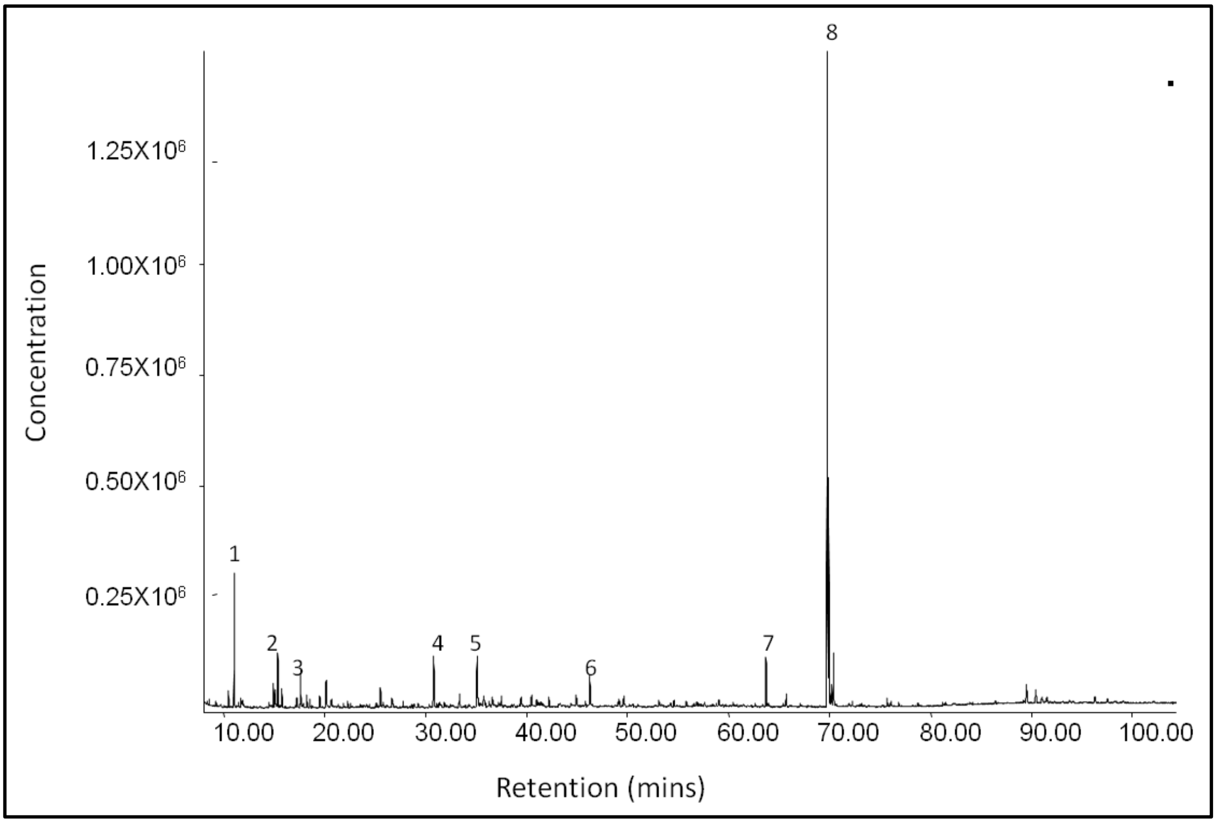


Figure A2.3: The spectra for the 10%BD at 60 °C after 168h

Table A2.3: The compounds detected in 10% BD at 60 °C after 168h

Peak number	Retention time (min)	Compound name
1	11.05	Methyl benzene
2	15.36	Ethyl benzene
3	17.62	Styrene
4	30.8	Phenol
5	35.09	4 Methyl phenol
6	46.25	1H-indole
7	63.70	Methyl ester, hexadecanoic acid
8	69.78	Methyl ester, 8-Octadecenoic acid

A2.4. The spectra of 20% BD samples and compounds detected

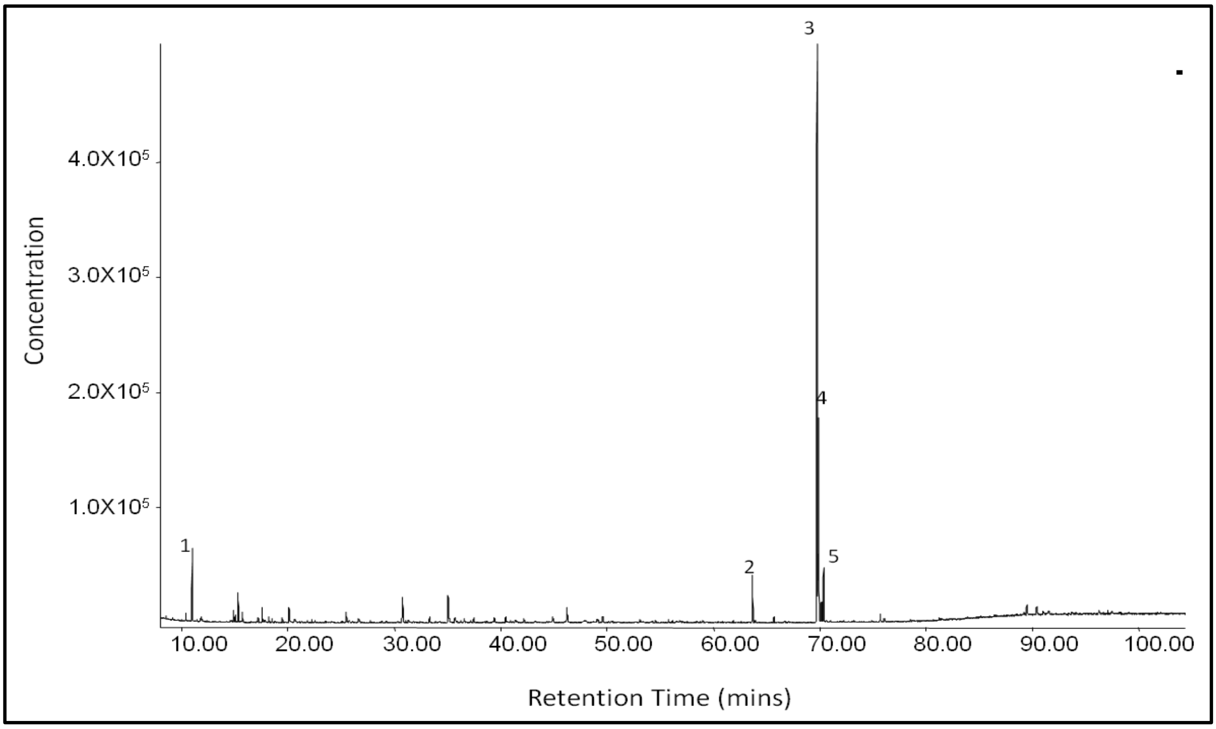


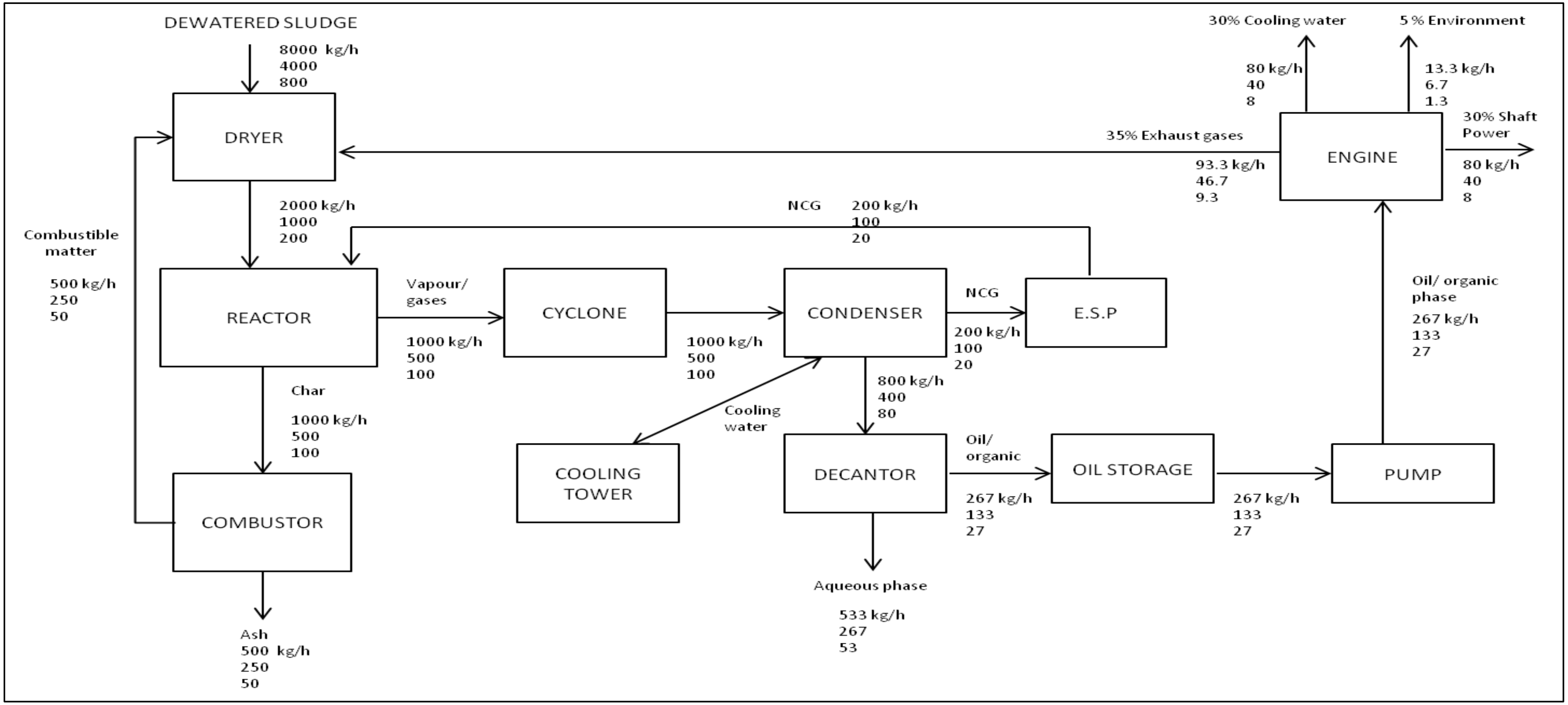
Figure A2.4: The spectra of 20%BD sample at 60 °C after 168h

Table A2.4: The compounds detected at 20%BD at 60 °C after 168h

Peak number	Retention time (min)	Compound name
1	11.03	Methyl benzene
2	63.68	Methyl ester, hexadecanoic acid
3	69.75	Methyl ester, 9-Octadecenoic acid (Z)-
4	69.89	9,12-Octadecadienoic acid (Z,Z)-
5	70.37	Methyl, 9,12,15-Octadecatrienoic acid

APPENDIX 3: ECONOMIC EVALUATION

A3.1. FLOW SHEET SHOWING MASS BALANCE FOR THE PROCESS



The mass balance and efficiencies used for the economic evaluation is shown in Table A3.1. The lower heating value of the pyrolysis oil was taken to be 37 MJ/kg.

Table A3.1: The pyrolysis oil possible energy distribution

Feed(kg/h)	Pyrolysis oil (kg/day)	MJ/day	MJ/yr (Energy)	30% for electricity(MJ/yr)	30 % of cooling water (MJ/yr)	35% Exhaust heat (MJ/yr)	5% Heat losses to the environment
2000	6400	236,800	78,144,000	23,443,200	23,443,200	27,350,400	3,907,200
1000	3200	118,400	39,072,000	11,721,600	11,721,600	13,675,200	1,953,600
200	640	23,680	7,814,400	2,344,320	2,344,320	2,735,040	390,720

A3.2 DRYING REQUIREMENTS FOR THE DEWATERED SEWAGE SLUDGE

Equation used to estimate the heat requirements for drying dewatered sludge

$$Q_{drying} = M_{ds}\ x\ W\ x\ [(Cp_{water}\ x\ \Delta T) + H_{vap}] + [M_{ds}\ x\ (1\text{-}W)]\ x\ Cp_{sludge}\ x\ \Delta T$$

Table A3.2: Assumptions and heat requirements made for drying the sewage sludge

			0.2 t/h	1.0 t/h	2.0 t/h
	UNITS				
Operating hours per year	[h/yr]	7920			
Assume 25% sludge dry mass content (M_{ds})	[kg/yr]	0.25			
(W) = water content in the sludge	[%]	0.75			
Hvap = Latent heat for vaporization of water(1 atm = 2257) instead of 2090		2257			
C_{pwater} = heat capacity of water	[kJ/kg K]	4.18			
$C_{psludge}$ = heat capacity of the sludge	[kJ/kg K]	1.83			
ΔT is the initial temperature of 15˚C to final temp of 100˚C	[°C]	85			
Dewatered sludge to meet reactor needs	[kg/h]		800	4,000	8,000
Q_{drying} per h	[kJ]		1,598,490	7,992,450	15,984,900
	[MJ/yr]		12,660,041	63,300,204	126,600,408
Assume char is used for drying. Combustible matter in the char excluding ash content	[kg/h]		50	250	500
Char produced per year	[kg/yr]		396,000	1,980,000	3,960,000
Energy from char (11MJ/kg)	[MJ/yr]		4,356,000	21,780,000	43,560,000
Heat from exhaust gases of CHP	[MJ/yr]		2,735,040	13,675,200	27,350,400
Surplus heat needed for drying	[MJ/yr]		5,569,001	27,845,004	55,690,008
Natural gas used for drying (85% efficiency)	[MJ/yr]		6,551,766	32,758,828	65,517,656
Cost of natural gas per year based on £0.0052 per MJ	[£/yr]		34,069	170,346	340,692

A3.3 REACTOR ENERGY REQUIREMENTS

The energy requirements of the reactor are calculated from the equation below;

$$\boldsymbol{Heat\ energy}: Q_e = (MCp\Delta T)_{char} + (MCp\Delta T)_{oil} + (MCp\Delta T)_{aqueous} + (MCp\Delta T)_{gases}$$

Where T_1 =100°C, T_2 = 400°C.

The energy loss from the reactor was calculated shown below;

$$\boldsymbol{Heat\ loss}: Q_1 = M_{ss}HV_{ss} - (M_{char}HV_{char} + M_{bio-oil}HV_{bio-oil} + M_{gases}HV_{gases})$$

Where M and HV refer to mass flow rate and higher heating value, the subscripts ss, char, bio-oil and gases refer to dried sewage sludge, char from pyrolysis, bio-oil from pyrolysis and non condensable gases.

The heat required to raise the reactor is calculated from;

$$Q_1 = (MCpT)_{sludge} \quad (T_1 = 100\ °C,\ T_2 = 400\ °C)$$

Total heat required for the reactor was estimated from

$$Q_{Total} = Q_e + Q_1$$

Table A3.3: Assumptions taken for estimating the reactor requirements

	Cp(kJ/kg K)	HHV (MJ/kg)
Dried sewage sludge	1.83	15
Biochar	1	11
Bio-oil		
Pyrolysis oil	2.5	39
Aqueous phase	-	4.19
Non condensable gases		
CH_4	2.22	55
CO	1.02	10.1
CO_2	0.844	32.9

A3.4. SUMMARY OF THE HEAT REQUIREMENTS FOR THE DRYER AND REACTOR

Table A3.4: Total heat energy requirements for the dryer and the reactor

SUMMARY OF ENERGY REQUIREMENTS			
	0.2 t/h	1.0 t/h	2.0 t/h
	Drying [MJ/yr]		
Heat energy required per year	12,660,041	63,300,204	126,600,408
Heat energy available from char	4,356,000	21,780,000	43,560,000
Heat energy available from engine exhaust	2,735,040	13,675,200	27,350,400
Heat energy required from natural gas	5569,001,	27,845,004	55,690,008
Assume 85% efficiency of natural gas, total required	6,551,766	32,758,828	65,517,656
	Reactor [MJ/yr]		
Heat energy required per year	3,635,280	18,179,251	36,355,651
Heat energy available from non condensable gases	81,079	405,394	810,788
Heat energy required from Natural gas	3,554,201	17,773,857	35,544,863
Assume 85% efficiency of natural gas, total required	4,181,413	20,910,420	41,817,486

A3.5 LABOUR COSTS USING ULRICH'S METHOD

Table A3.5: Labour requirements for each unit

	Number of units	Number of operators required
Reactor	1	0.25
Cyclone	1	0
Condenser	1	0.05
Decantor	1	0.1
ESP	1	0.1
Pressure vessel/storage	1	0
Pump	1	0
Engine	1	1.4
Exhaust heat recovery	1	0
Heat exchanger	1	0.05
Dryer	1	0.15
Conveyor	1	0.1
Combustor	1	0.25
	Total	2.45

A3.6 PROFITABILITY ANALYSIS FOR THE PROCESS PLANTS

The profitability of the process plants was assessed using Table A3.6, A3.8 and A3.10. A positive net present value (NPV) is a good indicator for investment. However, it should be noted that Table A3.6 to Table A3.10 are based on the electricity prices shown in Table 10.14. These were found to be very high compared to the consumer price.

A3.6.1 EQUATIONS USED FOR PROTITABILITY ANALYSIS

- $Simply\ payback\ time = \frac{Total\ investment}{Average\ \ annual\ cash\ flow}$ [134]
- $Return\ on\ investment\ (ROI) = \left(\frac{Net\ annual\ profit}{Total\ investment}\right) * 100$
- $Annualised\ capital\ charge = \left(\frac{i(1+i)^n}{(1+i)^n} - 1\right)$ [134]

Assumed to be 12% discount factor over a plant life of 20 years. The annualised factor at 12% interest rate for 20 years is 0.134 [134]. The annualised factors at various interest rate and number of years are published in books and papers that avoid the use of the above equation.

A3.6.2. PROFITABILITY ANALYSIS FOR 0.2 T/H

Table A3.6: The profitability of the 0.2 t/h

	£/yr				
Main product revenues	742,453	Total fixed capital cost	£	1,609,646	
Natural gas costs for reactor	21,831				
Drying costs	34,069	Working capital	£	106,247	
Miscellaneous chemicals	10,625				
Nitrogen cost	5,940				
Sum of variable costs of production (VCOP)	94,295				
Labour costs	213,840				
Overheads	21,249				
Maintenance	21,249				
Lubrication oil	1302				
Sum of fixed costs of production(FCOP)	257,641				
ECONOMIC ASSUMPTIONS					
Tax rate					20%
Discount rate of capital cost					12%

Cash flow analysis

Project year	Capital expenditure (£)	Revenue (£)	Cost of making product(CCOP) (£)	Gross profit (£)	Depreciation	Taxable income (£)	Tax paid(£)	Cash flow (£)	PV of CF (£)	NPV(£)
1	1,609,646	742,453	351,936	390,516	0	390,516	78103	312,413	278940	278,940
2	106,247	742,453	351,936	390,516	0	390,516	78103	312,413	249054	527,994
3	0	742,453	351,936	390,516	160965	229,552	45910	344,606	245284	773,278
4	0	742,453	351,936	390,516	160965	229,552	45910	344,606	219003	992,281
5	0	742,453	351,936	390,516	160965	229,552	45910	344,606	195539	1,187,819
6	0	742,453	351,936	390,516	160965	229,552	45910	344,606	174588	1,362,407
7	0	742,453	351,936	390,516	160965	229,552	45910	344,606	155882	1,518,290
8	0	742,453	351,936	390,516	160965	229,552	45910	344,606	139181	1,657,470
9	0	742,453	351,936	390,516	160965	229,552	45910	344,606	124268	1,781,739
10	0	742,453	351,936	390,516	160965	229,552	45910	344,606	110954	1,892,692
11	0	742,453	351,936	390,516	160965	229,552	45910	344,606	99066	1,991,758
12	0	742,453	351,936	390,516	160965	229,552	45910	344,606	88452	2,080,210
13	0	742,453	351,936	390,516	0	390,516	78103	312,413	71597	2,151,807
14	0	742,453	351,936	390,516	0	390,516	78103	312,413	63926	2,215,733
15	0	742,453	351,936	390,516	0	390,516	78103	312,413	57077	2,272,810
16	0	742,453	351,936	390,516	0	390,516	78103	312,413	50961	2,323,771
17	0	742,453	351,936	390,516	0	390,516	78103	312,413	45501	2,369,272
18	0	742,453	351,936	390,516	0	390,516	78103	312,413	40626	2,409,898
19	0	742,453	351,936	390,516	0	390,516	78103	312,413	36273	2,446,171
20	-168,861	742,453	351,936	390,516	0	390,516	78103	312,413	32387	2,478,558

Simple pay back 4.9

A3.6.2.1 RETURN OF INVESTMENT FOR THE 0.2 T/H PLANT

Table A3.7: Return of investment based on electricity price shown in Table 10.14

No of years	Return on investment(ROI) %
1	18
2	36
3	56
4	77
5	97
6	117
7	137
8	177
9	177
10	197
11	217
12	237
13	255
14	274
15	292
16	310
17	328
18	346
19	365
20	383

A3.6.3 PROFITABILITY ANALYSIS FOR 1.0 T/H WITH RENEWABLE HEAT INCENTIVE

Table A3.8: Profitability analysis based on the electricity price in Table 10.14

	£/yr		
Main product revenues	1,350,918	Total fixed capital cost [£/yr]	3,363,322
Natural gas costs for reactor	108,804		
Drying costs	170,346	Working capital [£/yr]	222,001
Cooling water	6000		
Miscellaneous chemicals	22,200		
Nitrogen cost	29,700		
Sum of variable costs of production (VCOP)	416,154		
Labour costs	356,400		
Overheads	44,400		
Maintenance	44,400		
Lubrication oil	6,512		
Sum of fixed costs of production(FCOP)	451,713		

ECONOMIC ASSUMPTIONS

Tax rate	20%
Discount rate of capital cost	12%

CASH FLOW ANALYSIS

Project year	Capital expenditure (£)	Revenue (£)	Cost of making product(CCOP)(£)	Gross profit (£)	Depreciation	Taxable income (£)	Tax paid (£)	Cash flow (£)	PV of CF (£)	NPV (£)
1	3,363,322	1,350,918	867,867	483,052	0	483,052	96610	386,441	345,037	345,037
2	222,001	1,350,918	867,867	483,052	0	483,052	96610	386,441	308,069	653,106
3	0	1,350,918	867,867	483,052	336332	146,720	29344	453,708	322,940	976,046
4	0	1,350,918	867,867	483,052	336332	146,720	29344	453,708	288,340	1,264,386
5	0	1,350,918	867,867	483,052	336332	146,720	29344	453,708	257,446	1,521,832
6	0	1,350,918	867,867	483,052	336332	146,720	29344	453,708	229,863	1,751,694
7	0	1,350,918	867,867	483,052	336332	146,720	29344	453,708	205,234	1,956,929
8	0	1,350,918	867,867	483,052	336332	146,720	29344	453,708	183,245	2,140,174
9	0	1,350,918	867,867	483,052	336332	146,720	29344	453,708	163,612	2,303,785
10	0	1,350,918	867,867	483,052	336332	146,720	29344	453,708	146,082	2,449,867
11	0	1,350,918	867,867	483,052	336332	146,720	29344	453,708	130,430	2,580,297
12	0	1,350,918	867,867	483,052	336332	146,720	29344	453,708	116,456	2,696,753
13	0	1,350,918	867,867	483,052	0	483,052	96610	386,441	88,562	2,785,315
14	0	1,350,918	867,867	483,052	0	483,052	96610	386,441	79,074	2,864,389
15	0	1,350,918	867,867	483,052	0	483,052	96610	386,441	70,601	2,934,990
16	0	1,350,918	867,867	483,052	0	483,052	96610	386,441	63,037	2,998,027
17	0	1,350,918	867,867	483,052	0	483,052	96610	386,441	56,283	3,054,310
18	0	1,350,918	867,867	483,052	0	483,052	96610	386,441	50,253	3,104,563
19	0	1,350,918	867,867	483,052	0	483,052	96610	386,441	44,868	3,149,431
20	-222001	1,350,918	867,867	483,052	0	483,052	96610	386,441	40,061	3,189,493

Simple pay back **8**

A3.6.3.1 RETURN OF INVESTMENT FOR THE 1.0 T/H PLANT WITH RENEWABLE HEAT INCENTIVES

Table A3.9: Return on investment based on electricity sale price in Table 10.14

No of years	Return on investment(ROI) %
1	18
2	36
3	56
4	77
5	97
6	117
7	137
8	177
9	177
10	197
11	217
12	237
13	255
14	274
15	292
16	310
17	328
18	346
19	365
20	383

A3.6.4 PROFITABILITY ANALYSIS FOR 2.0 T/H WITH RENEWABLE HEAT INCENTIVE

Table A3.10: Profitability analysis for the 2.0 t/h based on the electricity price in Table 10.14

	£/yr		
Main product revenues	1,784,868	Total fixed capital cost [£]	4,937,514
Natural gas costs for reactor	217,433		
Drying costs	340,692	Working capital [£]	325,909
Cooling water	12,000		
Miscellaneous chemicals	32,591		
Nitrogen cost	59,400		
Sum of variable costs of production (VCOP)	879,550		
Labour costs	356,400		
Overheads	65,182		
Maintenance	65,182		
Lubrication oil	13,024		
Sum of fixed costs of production(FCOP)	499,787		

ECONOMIC ASSUMPTIONS

Tax rate	20%
Discount rate of capital cost	12%

Cash flow analysis

Project year	Capital expenditure (£)	Revenue (£)	Cost of making product(CCOP)(£)	Gross profit (£)	Depreciation	Taxable income (£)	Tax paid (£)	Cash flow (£)	PV of CF (£)	NPV (£)
1	4,937,514	1784868	1379337	405531	0	405531	81106	324425	289665	289665
2	325,909	1784868	1379337	405531	0	405531	81106	324425	258630	548295
3	0	1784868	1379337	405531	493751	-88220	-17644	423175	301208	849503
4	0	1784868	1379337	405531	493751	-88220	-17644	423175	268936	1118438
5	0	1784868	1379337	405531	493751	-88220	-17644	423175	240121	1358559
6	0	1784868	1379337	405531	493751	-88220	-17644	423175	214394	1572953
7	0	1784868	1379337	405531	493751	-88220	-17644	423175	191423	1764376
8	0	1784868	1379337	405531	493751	-88220	-17644	423175	170913	1935290
9	0	1784868	1379337	405531	493751	-88220	-17644	423175	152601	2087891
10	0	1784868	1379337	405531	493751	-88220	-17644	423175	136251	2224142
11	0	1784868	1379337	405531	493751	-88220	-17644	423175	121653	2345795
12	0	1784868	1379337	405531	493751	-88220	-17644	423175	108619	2454413
13	0	1784868	1379337	405531	0	405531	81106	324425	74350	2528763
14	0	1784868	1379337	405531	0	405531	81106	324425	66384	2595147
15	0	1784868	1379337	405531	0	405531	81106	324425	59271	2654418
16	0	1784868	1379337	405531	0	405531	81106	324425	52921	2707339
17	0	1784868	1379337	405531	0	405531	81106	324425	47251	2754590
18	0	1784868	1379337	405531	0	405531	81106	324425	42188	2796778
19	0	1784868	1379337	405531	0	405531	81106	324425	37668	2834446
20	-325909	1784868	1379337	405531	0	405531	81106	324425	33632.097	2868078

Simple pay back **13**

A3.6.4.1 RETURN OF INVESTMENT FOR THE 2.0 T/H PLANT WITH RENEWABLE HEAT INCENTIVE

Table A3.11: Profitability analysis for the 2.0 t/h based on electricity price shown in Table 10.14

No of years	Return on investment(ROI) %
1	18
2	36
3	56
4	77
5	97
6	117
7	137
8	177
9	177
10	197
11	217
12	237
13	255
14	274
15	292
16	310
17	328
18	346
19	365
20	383