OPTIMISATION AND MODELLING OF PYROLYSIS PROCESSES FOCUSED ON THE TREATMENT OF MUNICIPAL SOLID WASTE SCALED TOWARDS DECENTRALISED ENERGY FROM WASTE SYSTEMS

By

Penny Challans

B.Eng (Mech), M.Sc (Energy)

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Cardiff School of Engineering
Cardiff University, Wales, United Kingdom
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Abstract

Energy from Waste (EfW) technologies are beneficial for both energy generation and as a waste management option. However they face significant challenges due to the heterogeneous nature of municipal solid waste. The overall aim of the research reported in this thesis was therefore to explore some of the problems which hinder the development of commercial scale EfW technologies. A laboratory scale pyrolysis reaction rig has been developed to investigate the effect of temperature, residence time and fuel type on the pyrolysis products. Investigations were also undertaken to establish the composition of gas produced from the pyrolysis of typical waste feedstocks in two commercial scale pyrolysis rigs. An empirical model has been developed to predict the pyrolysis behaviours on a larger scale and comparisons have been made with data from the commercial scale rigs.

The research findings showed that the majority of the reduction of mass during pyrolysis occurred within the first 5-10 minutes with a loss of up to 70 % at 550 °C and up to 77 % at 700 °C for paper, newspaper and cardboard. Paper, newspaper and cardboard behaved similarly with solid, liquid and gaseous fractions of approximately 33 %, 53 % and 13 % respectively. Products from the plastics components varied significantly; PET produced the highest gaseous products (42 %) and HDPE produced the highest solid products (45 %). An increase in pyrolysis temperature increased the gaseous products from paper to 34 % to the detriment of liquid and solid yields. The main gases produced from the pyrolysis were found to be CO_2, CO and H_2, except for the pyrolysis of PVC where the main gases produced, from the high content of hydrochloride, were not identified in this study. An increase in pyrolysis temperature was found to increase the production of CO and H_2. The gas produced from commercial rig 1 mostly consisted of CO_2 due to the low temperature and the addition of air to the pyrolysis chamber. The gas produced from commercial rig 2 consisted of high volumes of CO and H_2 suggesting the rig was operating at a temperature above 550 °C. An empirical model was developed based on laboratory data to allow prediction the effect of a change in MSW composition on the pyrolysis gas. It was found that the addition of newspaper to a waste mix led to a higher production of CO and therefore a higher HHV.

In general, the results of this study suggest that the laboratory scale pyrolysis rig used in this study and the empirical models developed, can be employed to predict the behaviour of larger scale commercial pyrolysis systems. However, further experimental investigation on the pyrolysis behaviours of mixed waste samples, especially plastic fractions, is hereby proposed.

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List of Abbreviations

EfW	Energy from Waste
MSW	Municipal solid waste
DEFRA	Department for Environment, Food and Rural Affairs
ROC	Renewables Obligation Certificate
WID	Waste Incineration Directive
CHP	Combined Heat and Power
TGA	Thermogravimetric Analysis
PE	Polyethylene
HDPE	High Density Polyethylene
PS	Polystyrene
PET	Polyethylene Terephthalate
PVC	Polyvinyl Chloride
IPA	Isopropanol
ppm	parts per million
GC	Gas Chromatography
CCE	Carbon Conversion Efficiency
CGE	Cold Gas Efficiency

Nomenclature

Symbol	Definition	Unit
AC	Ash content	% wt
FC	Fixed carbon	% wt
MC	Moisture content	% wt
VM	Volatile matter	% wt
LHV	Lower heating value	MJ/kg, MJ/Nm^3
HHV	Higher heating value	MJ/kg, MJ/Nm^3
CV	Calorific Value	MJ/kg
CCE	Carbon Conversion Efficiency	%
CGE	Cold Gas Efficiency	%
x	Residence time	Minutes
y	Mass remaining after pyrolysis	%
z	Pyrolysis temperature	°C

CHAPTER 1 INTRODUCTION

There are significant benefits of Energy from Waste (EfW) technologies from both the recoverable energy and the reduction of waste. It is not currently possible to prevent, re-use or recycle all municipal solid waste (MSW). As set out in the waste hierarchy, shown in Figure 1.3, EfW is the next most viable option. As well as this, the need to reduce waste sent to landfill and to develop renewable energy sources has led to a huge potential for EfW to effectively deal with the remaining waste. EfW recovery processes have several benefits including the prevention of some of the negative greenhouse gas impacts that are associated with the landfill of waste. As well as reducing these emissions, the energy generated reduces the dependence on fossil fuel power generation and contributes towards the UK renewable energy targets.

The term 'Energy from Waste' covers a range of processes which recover value from the waste. Some of these processes extract the energy directly whereas others convert waste into different types of fuel for later use. These processes include direct combustion, gasification, pyrolysis, plasma arc and anaerobic digestion. These processes and their place in the waste hierarchy are not well understood by the public with perceptions often influenced by incomplete or outdated information. These negative public perceptions can act as significant barriers to the acceptance of EfW technologies leading to objections to proposals for these facilities from local communities. Overcoming these barriers and negative perceptions by insuring information is available, trusted and understood, is key to the development of the EfW industry.

Using waste to produce energy is not a new concept; basic forms of the process have been used to heat water for centuries. However, the main form of waste treatment has historically always been landfill and due to the availability of suitable cites created by past mineral extraction the development of alternative waste treatment routes in the UK has lagged behind other parts of Europe. Early waste incinerators, which were primarily for waste disposal, were viewed very negatively by the general public. Many of these plants were forced to close after tighter emissions controls were brought in during 1989. However, the introduction of landfill tax and targets for the diversion of biodegradable waste from landfill led to a drive in the development of a new generation of energy from waste plants to include energy generation in addition to waste management as a key part of their process. The introduction of the Waste Incineration Directive [1] now recast into the Industrial Emissions

Directive [2] means all current plants burning waste have to meet stringent emissions limits, emissions monitoring, waste reception and treatment standards.

1.1 ENERGY

Over the last few decades there has been increasing concern over the availability of energy sources as well as the environmental impact of current energy sources and energy production processes. With a decline in the output of North Sea oil and gas, increased environmental concerns as well as the substantial loss of generating capacity due to the closure of nuclear and coal-fired power stations there needs to be a significant increase in the production of energy from renewable and other sources to continue to meet the UK's energy demands. Future energy supplies need to be secure, diverse, affordable and low-carbon however the principal concern for the government is to secure major funding to enable the development of new technologies and generation.

Concern over global warming and climate change is continuing to increase with strong evidence that recent global warming can't be explained by natural causes alone. Greenhouse gas emissions, such as carbon dioxide and methane, have been found to warm the Earth's atmosphere leading to higher sea levels and more frequent extreme weather events like storms and heat waves. These are expected to become more severe in the coming decades leading to government targets, through the Climate Change Act [3], to cut greenhouse gas emissions by at least 34 % by 2020, and by 80 % by 2050 below the 1990 baseline.

Energy sources and production will play a significant part in meeting these greenhouse gas emissions targets. In 2013, renewable sources constituted 5.2 % of the UK's energy sources [4]. This needs to increase to 15 % by 2020 to meet the EU's renewable energy target for the UK as set out by the 2009 Renewable Energy Directive [5]. Figure 1.1 shows the electricity generation from renewable sources from 2003 to 2013 [6].

Large scale EfW processes would help to meet greenhouse gas emissions targets and renewable energy targets as well as meeting the demand for energy in the UK. Small scale energy from waste could be invaluable to businesses, communities, etc to produce their own energy therefore avoiding reliance on diminishing UK supplies and increased energy prices. There has already been a great increase in the energy produced by EfW plants but with further support, funding, research and improved technologies there is great potential for this to increase even further. EfW has great potential as a partially renewable energy source.

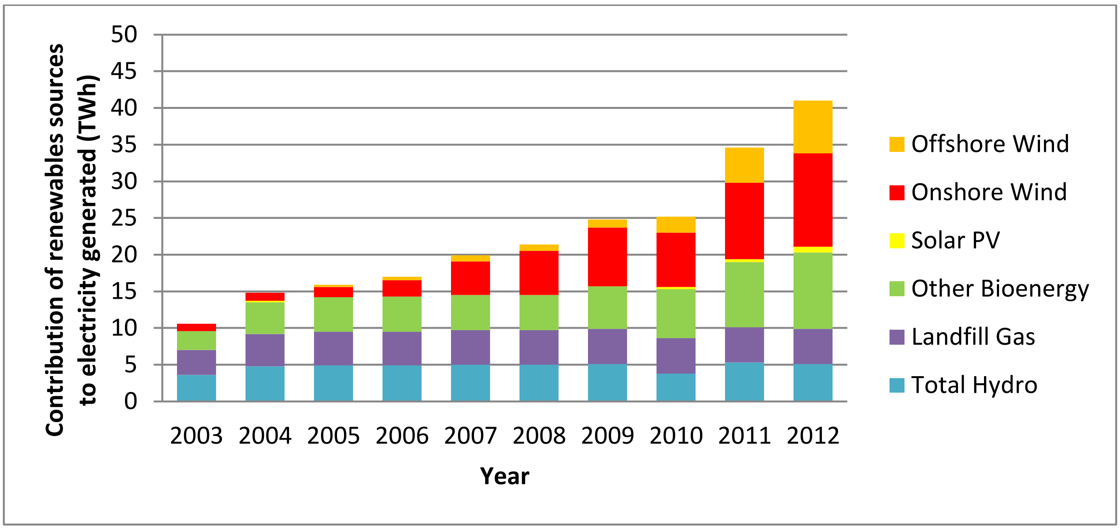


Figure 1.1: Renewable electricity generation from key technologies from 2003 to 2013 as presented by the Department for Energy and Climate Change [6]

1.2 MUNICIPAL SOLID WASTE

MSW, mostly consisting of everyday items, refers predominantly to household waste although also includes waste from schools, hospitals and businesses. It does not include industrial, agricultural, medical or radioactive wastes. The properties and composition of MSW can have a great effect on the type of technology used for EfW processes, the process mechanisms and the products of the process. The volume of each type of waste produced from various sectors and areas is also an important factor in determining the best waste management option.

In the year leading up to September 2011, the UK produced a total of 23.4 million tonnes of household waste, 40.3 % of this was recycled, re-used or composted [7]. This is an average of 452 kg of waste generated per person per year with 182 kg of this recycled, re-used or composted [8]. The amount of municipal waste sent to landfill decreased by 9.4 % from 2008 to 12.5 million tonnes in 2010. Figure 1.2 shows the municipal waste management methods in England over the past 10 years. A small increase in EfW can be seen alongside an increase in recycling. Although the volume of waste sent to landfill is decreasing, further improvements in technologies and processes for both recycling and for EfW could greatly reduce this even more. EfW has great potential to divert more waste from landfill whilst still leaving plenty of room to increase the volume of waste sent to recycling.

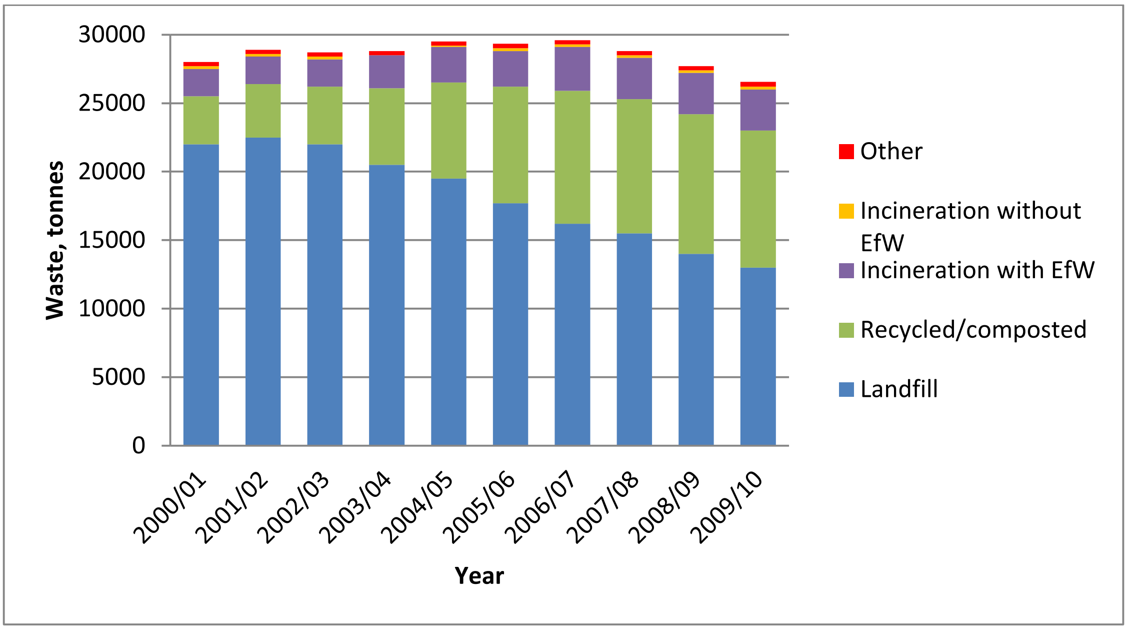


Figure 1.2: Municipal waste management methods in England from 2000 to 2010 as presented by the Department for Environment, Food and Rural Affairs [8]

In 2009/10, 13.9 million tonnes of municipal waste, 52.3 % of the total produced, had value recovered from it through recycling, composting, reuse, EfW or fuel manufacture. This is a rise from 49.0 % (13.4 million tonnes) in 2008/09. There was also an increase in the percentage of waste incinerated with energy recovery from 12.2 % in 2008/09 to 13.6 % in 2009/10 [8]. This is a great improvement, although there is the potential for these figures to be increased even further with more research, better technologies and more plants.

Increasing the volume of waste sent to EfW alone is not enough to improve the UK's waste management strategy to meet government targets. It should be used as part of a combined waste management strategy as set out in the waste hierarchy, shown in Figure 1.3. This classifies waste management options according to their desirability with the aim of extracting the maximum benefits from products and generating the minimum amount of waste. The hierarchy gives top priority to the prevention of waste, followed by re-use, recycling and then other types of recovery; this includes energy recovery through gasification and pyrolysis.

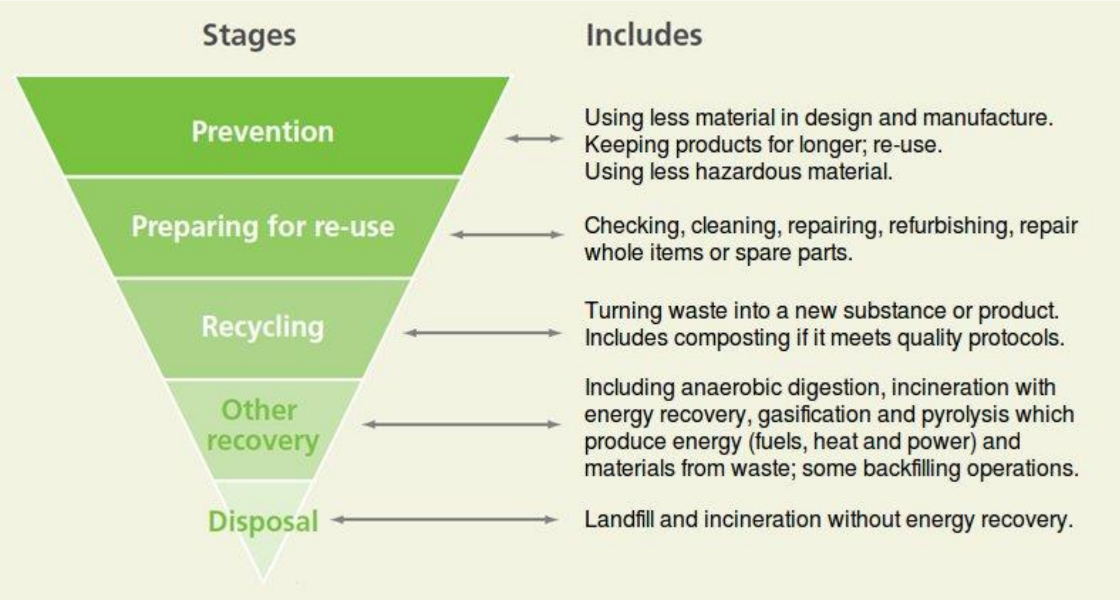


Figure 1.3: The waste hierarchy as presented by the Department for Environment, Food and Rural Affairs [7]

As the waste hierarchy states the best option is to prevent the production of waste in the first place. This is not always possible and is unlikely that the production of waste will ever be completely eliminated. There is, however, a lot more that could be done to reduce the volume of waste that is produced. This can vary from simple solutions such as reducing the volume of food waste and food packaging to opportunities to prevent waste within businesses and across supply chains.

Where the prevention of waste is not possible, the next desirable option is to re-use it. This can be done by encouraging people and businesses to re-use goods via charity shops, re-use networks and second hand goods markets. Manufacturing also plays an important role as ensuring products are made to be more durable, repairable, re-usable and recyclable can greatly cut down on the amount of waste being created.

After re-using waste, the next most desirable option is recycling. There has been a great increase in the volume of waste that can be recycled in recent years although more can still be done to increase this further. Manufacturing can again play an important role by ensuring the reduction of hazardous, harmful and difficult to recycle substances in products and materials. Although, recycling can be a viable option, it is only possibly for certain materials and if more energy is consumed and more greenhouse gases emitted in the recycling process than if a new product was manufactured it becomes a less beneficial alternative. Continuing research is needed in order to reduce the costs of recycling as well as to increase the products that can be recycled.

Despite the increase in waste prevention, re-use and recycling, there is still a significant volume of waste sent to landfill. This has led to energy recovery technologies becoming more prominent in order to recover value from this waste and avoid the least desirable option on the waste hierarchy of waste disposal. These technologies include anaerobic digestion, combustion, pyrolysis and gasification with energy recovery and materials recovery. Although the second least desirable option, there is still potential for these processes to divert even more waste from landfill without hindering other waste management options higher up the waste hierarchy which are more desirable. As waste prevention, re-use and recycling options improve, residual waste will eventually become a diminishing resource. This is however, a long way off and in the meantime there is plenty of opportunity to retrieve more value from the waste that is currently sent to landfill through energy or materials recovery, especially if more efficient technologies can be employed to maximise the energy recovered from it.

Landfill should be a last resort as a waste disposal option. The burial of waste is the oldest form of waste treatment but has significant environmental impacts. This is especially true for biodegradable wastes which produce significant greenhouse gas emissions leading to the importance in diverting them from landfill. The production of methane and the potential contamination of groundwater and soil during landfill usage are of great concern. These environmental impacts can continue to persist long after the closure of landfill sites. Alongside this, there are impacts on wildlife habitats, dust, odour and noise pollution and an increasing lack of available space in the UK.

In some cases it can be clearly demonstrated that there is a better environmental outcome to deviate from the waste hierarchy. The EU's Waste Framework Directive states that this can be the case for recovering energy from certain waste streams [9]. It must, however, be taken into account that despite the potential for environmental benefits and carbon diversion over sending waste to landfill, energy recovery can also produce greenhouse gas emissions. The net carbon impact of all of these processes must be taken into account when deciding waste management strategies. This greatly depends on the composition and availability of waste and the technologies utilised.

1.2.1 THE LANDFILL DIRECTIVE

In 1999, the European Union issued a directive on the landfill of waste with the aim to prevent and reduce the negative effects on the environment caused by landfill as far as possible [10]. This was gradually brought into force from 2002 in the UK to give UK industry time to adapt. The directive outlines strict controls on the landfill of waste and also has important implications for waste handling and waste disposal. The UK now imposes a landfill tax upon biodegradable waste that is put into landfill with a target of reducing figures to 35 % of 1995 levels by 2020. It also introduced a ban on the co-disposal of hazardous and non-hazardous waste in landfills and tighter site monitoring and engineering standards. Since 2007, all non-hazardous waste must be pre-treated before being put into landfill in order to reduce its volume, hazardous nature, facilitate handling or to enhance recovery.

1.2.2 MUNICIPAL SOLID WASTE COMPOSITION

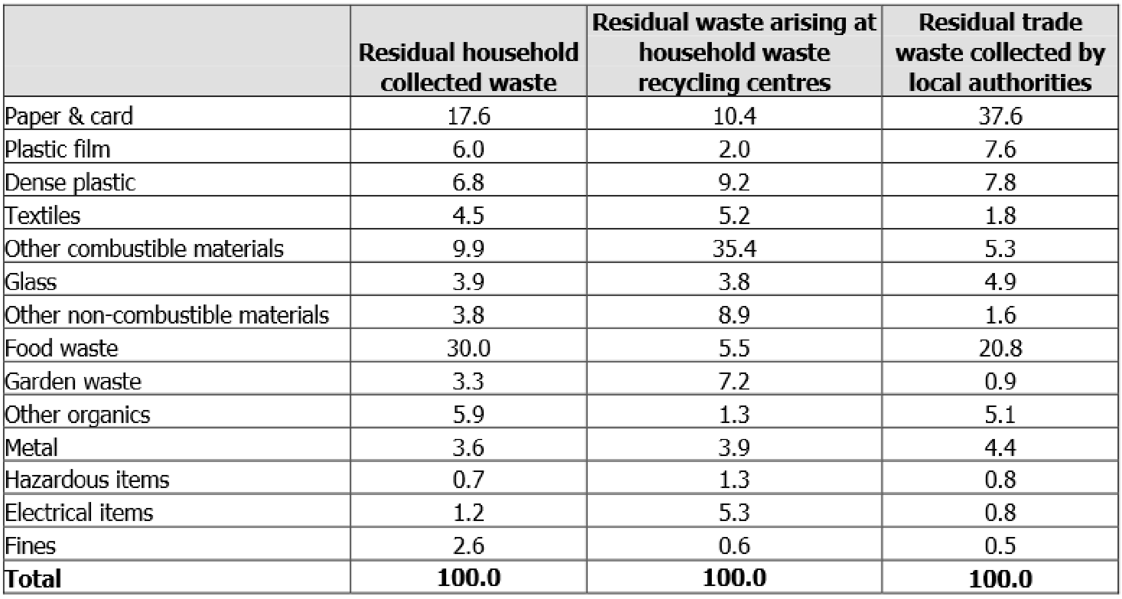
The composition of MSW varies greatly from country to country as well as varying significantly throughout the year. This can have a significant effect on EfW processes and products as well as other waste treatment options. In the UK, there can be a wide variation in MSW depending on how each council separates waste for collection. Most areas now have collections for recycling, food waste, garden waste and residual (black bag) waste however there is still a variation in the types of waste accepted under each category.

In a study by the Waste Resources Action Programme, the composition of 240 tonnes of municipal waste was analysed in all 22 local authorities in Wales [11]. Studies were conducted during summer as well as during winter in 2009. Table 1.1 shows the composition of the main residual waste streams as found by the study.

The study found that residual household collected waste mostly comprised of food waste followed by paper and card. As expected, larger items were recorded at recycling centres where 35.4 % of waste was classed as ‘other combustible materials’, which includes wood. Trade waste was found to vary greatly depending on the type of trade. The majority of waste from restaurants was food waste where as mostly paper and card was collected from retail premises and offices. As well as the varied composition of current MSW, this composition can vary drastically over time. An increase in recycling could lead to a lower percentage of paper, card and plastics in MSW available for EfW processes and an increase in anaerobic digestion or composting could lead to a lower percentage of food waste.

Therefore, EfW technologies would either need to be adaptable to these different feed stocks or separate technologies are needed to be designed and built for the specific feeds.

Table 1.1: Composition (% wrt weight) of residual waste in Wales [11]



	Residual household collected waste	Residual waste arising at household waste recycling centres	Residual trade waste collected by local authorities
Paper & card	17.6	10.4	37.6
Plastic film	6.0	2.0	7.6
Dense plastic	6.8	9.2	7.8
Textiles	4.5	5.2	1.8
Other combustible materials	9.9	35.4	5.3
Glass	3.9	3.8	4.9
Other non-combustible materials	3.8	8.9	1.6
Food waste	30.0	5.5	20.8
Garden waste	3.3	7.2	0.9
Other organics	5.9	1.3	5.1
Metal	3.6	3.9	4.4
Hazardous items	0.7	1.3	0.8
Electrical items	1.2	5.3	0.8
Fines	2.6	0.6	0.5
Total	**100.0**	**100.0**	**100.0**

1.2.3 GOVERNMENT AIMS AND THE DEVELOPMENT OF ENERGY FROM WASTE

1.2.3.1 GOVERNMENT AIMS

In 2011, the Department of Environment, Food and Rural Affairs (DEFRA) produced a review of the UK Government Waste Policy [7]. This review states the government's support for efficient energy recovery from residual waste in order to provide environmental benefits, economic opportunities and a reduction in carbon emissions. The aim of the UK government is to get the most energy out of residual waste, as opposed to getting the most waste into energy recovery. Landfill should only be used as a last resort and only for waste where there is no better use. The Government aims to overcome these barriers by ensuring EfW and its place in the waste hierarchy is valued and understood by the public, businesses and households in the same way as re-use and recycling. It will also be important to ensure that any waste management legislations do not have negative consequences on the development of the EfW industry.

Further to this in February 2013, DEFRA produced a guide to EfW and a revised edition in 2014 [12] with the aim of increasing understanding of the process, the role it can play in the sustainable management of waste and how it can relate to other waste management options. The Government's main aim is to prevent the production of waste in the first place and reduce the volume of residual waste. However, energy recovery will remain important as a means to divert non-reusable or recyclable waste from landfill as well as an important means of energy generation. There is currently a clear gap between the potential of EfW and the delivery. The Government aims to improve this by facilitation change with further support and incentives for energy recovery to prevent valuable resources going to landfill.

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

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

1.2.3.2 PUBLIC OPINION

EfW can often be a controversial topic with many protests and campaigns against current and future plants. One of the barriers to EfW facilities being accepted in waste management systems is public concern over emissions [13]. EfW is often confused to incineration which has a poor historical image in the UK with the emissions of incinerators in the past causing pollution as well as health concerns. The term 'incineration' is often used erroneously these days to describe all energy from waste processes reminding people of these past incinerators. These early incinerators were simply to burn waste to reduce its volume and were not as strictly regulated as current technologies whereas the new generation of energy from waste plants are closely regulated and designed to meet strict emissions standards as well as to provide low carbon energy.

The Government is working to remove these barriers by ensuring more information is available and that it is readily understood. The 'Energy from waste: a guide to the debate' mentioned above aims to educate and inform a wide variety of people including members of the public, planning officials, local and national government as well as financiers and technology developers [12]. Both energy production and waste management are complex areas that are rarely addressed with a simple right or wrong answer. Therefore, individual proposals need to be fully debated using all the available evidence with due consideration of the wider environmental impact. Developers are encouraged to engage with communities in the early stages before submitting planning applications in order to be responsive to their concerns.

A major focus of concern is often the potential impact on health of emissions from EfW plants. Unlike early incinerators, the emissions of current plants are strictly regulated and monitored although public perception of current technologies is often still damaged by the negativity surrounding old incineration processes. For current technologies, there are strict controls as set by the Waste Incineration Directive and the Industrial Emissions Directive with stringent limits for the number of potential pollutants as well as operating requirements which help to minimise pollution. In order to meet these limits, the emissions clean-up steps in current EfW plants ensure that they contribute only a small addition to local concentrations of air pollutants. In an assessment of the potential health impacts of the Exeter EfW plant, a review of studies into the emissions of EfW technologies and the impacts on public health was undertaken [14]. It was concluded that modern EfW technologies can be regarded as safe facilities and have a negligible impact on health and the environment.

Another key area of concern is the potential conflict between recycling and energy from waste. However, the Government's goal is to move waste up the hierarchy therefore, favour recycling before energy from waste unless there proves to be a better environmental option. In many European countries there are examples where EfW can coexist with high volumes of waste recycling, ultimately delivering a low volume of waste put into landfill. At a more local level, there is more of a risk that EfW could compete with recycling instead of complimenting it. It is therefore imperative that contracts, plants and processes are flexible enough to adapt to changes in volumes and composition of waste to ensure this conflict is avoided. EfW has been proven to support and not compete with recycling when managed effectively. The Government fully supports this and aims to move waste up the hierarchy as well to get the most energy out of residual waste rather than to get the most waste into energy recovery.

1.2.3.3 WASTE INCINCERATION DIRECTIVE

The Waste Incineration Direction (WID) relates to the standards, methodologies and technologies for the incineration of waste with the aim of minimising the impact of negative environmental effects as well as any effects to human health resulting from emissions [9]. It is designed to ensure all thermal treatment and EfW systems are operating under the same operational and technical constraints, demonstrating this compliance through verification testing and sampling. These constraints cover a range of aspects including the delivery mechanisms, furnace design, abatement plants, residue handling, monitoring equipment, emissions values and the types of waste permitted.

The Directive covers both incineration and co-incineration plants, with co-incineration plants including those where waste is either used as a fuel or is disposed of at a plant where the generation of energy is the main purpose. A plant is only included however, if it burns waste as defined in the Waste Framework Directive, this includes MSW, clinical waste, hazardous waste, general waste and refuse derived fuels.

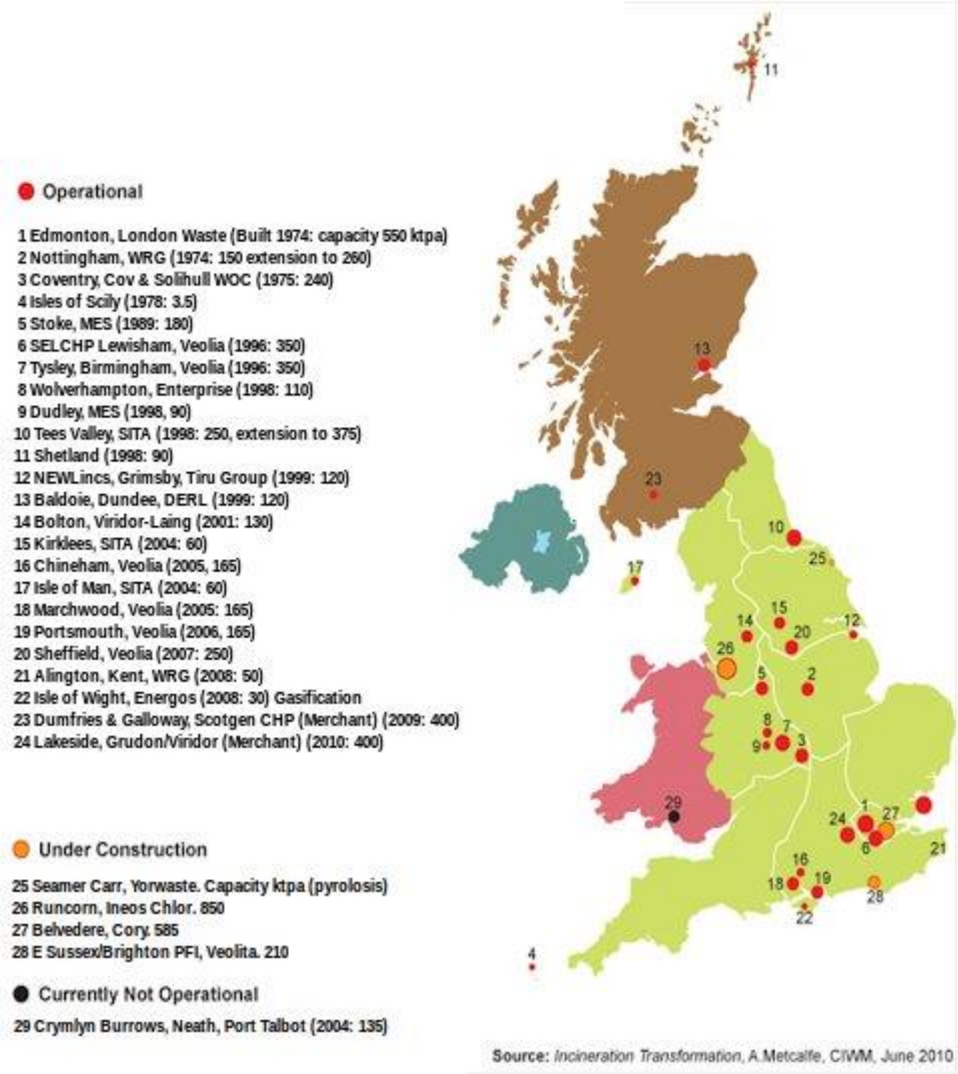
The most important requirements relate to the emissions limits for all facilities that thermally treat wastes. Maximum emissions levels were introduced for emissions to air of the most polluting and environmentally harmful parameters which are generated during the thermal degradation of wastes. Both daily and half hourly limit values for the following must be recorded:

- Total dust/particulates
- Total organic carbon
- Hydrogen chloride
- Hydrogen fluoride
- Heavy metals
- Dioxins
- Sulphur dioxide
- Nitrogen dioxide

To meet these strict limits, facilities must have flue gas cleaning plants to reduce the emissions of the above as far as is practically possible. There are also minimum requirements for combustion conditions, including the requirement for combustion of non-hazardous waste to be heated to 850 °C and to 1150 °C for hazardous waste for a minimum of 2 seconds in the secondary combustion chambers in order to ensure complete combustion of all potentially polluting substances. WID applies to almost all processes that burn or incinerate waste and generate emissions to the air from the process. Therefore, for gasification and pyrolysis WID will only apply to those plants where the purpose is the disposal of materials and the combustion of resultant gases.

1.3 ENERGY FROM WASTE PLANTS

Over the past decade there has been a rapid increase in the number of EfW plants commissioned in the UK, and there is potential for many more. Figure 1.4 shows EfW plants in the UK in 2010 with 24 operational and 4 under construction [15]. These figures have increased dramatically in the last few years. The Waste and Resources Action Programme has compiled a list of all operational EfW plants in the UK, last updated in February 2013 [11]. It gives details of 61 plants ranging in capacity from 450 – 2,000,000 tpa with output capacity ranging from 0.6 – 290 MWe. The output of these plants is either in the form of heat or electricity only or Combined Heat and Power (CHP). The input varies and includes waste wood, MSW, tyres, biomass, poultry litter and other animal waste.



Source: *Incineration Transformation*, A.Metcalfe, CIWM, June 2010

Figure 1.4: Energy from Waste plants in the UK, June 2010 [15]

1.3.1 SMALL SCALE ENERGY FROM WASTE PLANTS

EfW technologies that process under 100,000 tpa of waste are classed as ‘small scale’ [16, 17]. Those processing under 1,000 tpa of waste can be classes as ‘micro scale’. Many micro scale systems are modular in design; the units are mobile and can therefore be assembled where needed. There is great potential for small or micro-scale EfW technologies in a range of different sectors. The main benefit of such technologies is provision of on-site waste disposal and energy production. This eliminates the cost and environmental concerns associated with transporting waste as well as cost savings and security of the energy supply.

These small or micro-scale EfW technologies could be beneficial for commercial and industrial waste, for example mixed residual commercial waste with a similar composition to

MSW and individual waste streams where recycling is not a viable option. There is also potential for individual or small groups of businesses to exploit the value in their wastes using a small or micro-scale EfW technology and realise significant cost savings. Such technologies could be particularly beneficial for hospitals as the disposal of hazardous medical waste can be costly, whereas, with a small scale EfW unit on-site all waste could be disposed of safely and securely at a significantly lower cost than current medical waste disposal methods. Other potential customers could include large supermarkets or retail units, the military or rural communities.

Despite the potential, there have been some significant challenges with the development of small and micro-scale EfW technologies. One of the main challenges is the heterogeneous nature of MSW. This is less of a problem for larger rigs as the overall average composition of a larger proportion of waste is likely to be more uniform. For small scale facilities designed to process one or two bags of waste at a time it is a significant problem as the composition of waste from one bag to another can vary drastically.

Another of these challenges revolves around the ability of the technology to be scaled up from a pilot plant to a full scale facility. Although this is easier for micro-scale systems than larger technologies, it can still be a significant problem for small scale systems. Research and development of full-scale systems is much more time and cost consuming than trials on pilot scale technologies. Pyrolysis and gasification technologies have been shown to be one example where going from pilot plant trials up to full scale can be complex and problematic [18]. Overcoming these problems can often lead to extended development time and running costs. Funding is also a major factor which has led to problems for many small scale EfW start up companies over the past decade. In order to become commercial viable, technologies must have a proven reliability and be able to handle a changing, unpredictable waste stream over the course of its life time.

1.4 COMMERCIAL RIGS TESTED IN THIS STUDY

One of the original aims of this study was to use commercially operating thermal waste treatment processes to develop and investigate empirical rules for the processes occurring within the pyrolysis reactors. As a result of initial negotiations with 2 such manufacturers of thermal treatment processes that use pyrolysis as a primary mechanism, testing campaigns were arranged and completed. In total this came to around 40 hours of testing time on the processes at the company sites. It should be noted that during the completion of this PhD the companies themselves have undergone significant restructuring (for commercial reasons): and communication lines between the author and the companies have been lost. In one case the company has entirely discontinued the process, but continues to operate in other business sectors. For the reasons of commercial sensitivity it has been decided to anonymise any specific reference to these companies and describe the processes from an engineering perspective only. The purpose of these tests on commercial scale rigs is discussed in section 1.5.

1.4.1 COMMERCIAL RIG 1: MICRO SCALE BATCH PYROLYSER

Commercial Rig 1 tested in this study is a micro scale pyrolysis unit currently used for waste reduction, rather than energy generation. The process is shown as a schematic in Figure 1.5 with a photograph of the rig shown in Figure 1.6. It is aimed at use for high cost waste such as laboratory of clinical waste, remote locations or secure locations where waste collection can be difficult.

The unit operates as a batch process which involves warm up, pyrolysis, gasification and cool down followed by a flush of the system with water. As can be seen in Figure 1.5, the rig consists of a pyrolysis chamber with water and air inlets towards the top which are used to introduce air during the process as well as to introduce a water spray once the process is complete to steam clean the chamber. The water inlet and drainage points at the base of the chamber are used to flush out any solid residue remaining after the process. The gas produced from the process leaves the pyrolysis chamber and is passed through a catalytic converter, ash separator, heat exchanger and finally a water scrubber in order to clean the gas, remove particulates and recover energy in the form of heat.

All types of MSW can be thermally treated using the system, apart from metal and glass which remain in the pyrolysis chamber and can be recycled once the process is complete. There are some limitations on hazardous waste that can be treated using this process, for example full loads of fats or liquids, or batteries or radioactive wastes. There are also limitations on the acceptable proportions of some materials, for example a waste mix of 100 % plastics would not be possible due to the high volatile content. Within the unit, temperature sensors monitor every stage of the process allowing the automated control system to adjust the cycle time, set point temperature, air injection, energy and water usage automatically according to the characteristics of the waste load. The unit has a length of 2273 mm, height of 1250 mm, width of 811 mm and a weight of approximately 600 kg. The waste thermal treatment chamber has a volume of 100 litres and can take a load capacity of up to 8 – 10 kg of waste; hence this might be described as operating on a ‘micro scale’.

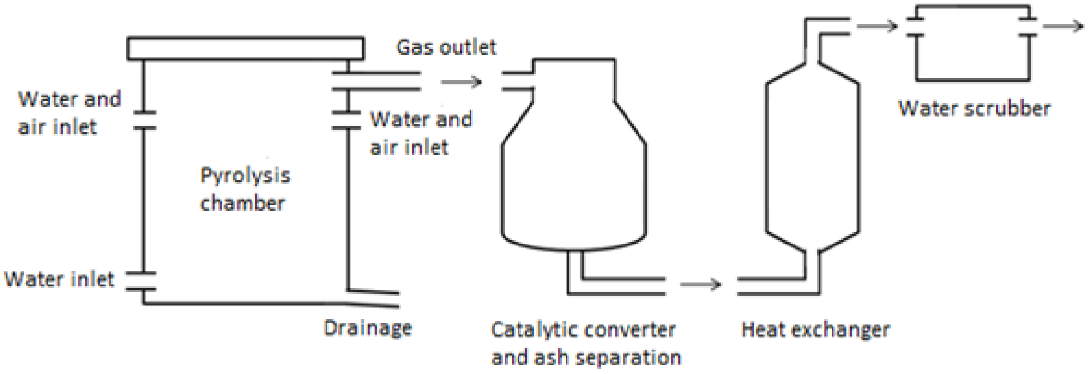


Figure 1.5: Schematic of commercial rig 1 process

Figure 1.6: Photograph of commercial rig 1, micro scale batch pyrolyser

1.4.2 COMMERCIAL RIG 2: SMALL SCALE SEMI-BATCH PYROLYSER

Commercial rig 2 tested in this study is a pilot small scale EfW technology developed from previous pyrolysis systems used for waste reduction on Royal Navy aircraft carriers. A schematic of the process is shown in Figure 1.7 and a photograph of the rig is shown in Figure 1.8. The waste or biomass is fed into the top of the pre-heated pyrolysis chamber via a conveyor belt. Ash is collected at the base of the chamber and the produced gas exits at the top. Further ash separation is undertaken to remove any particles in the gas before it is passed through the combustion chamber. For biomass, this gas can then be used in a heat exchanger or Organic Rankine Cycle. For non-hazardous waste the gas is processed further by passing through a residence chamber at a temperature of 850 °C for 2 seconds, for hazardous waste, the temperature of the residence chamber is increased to 1100 °C. As discussed previously, this is an EU requirement to ensure complete destruction of harmful dioxins.

The EfW unit has the potential to provide enough electricity for up to 50 homes or heat for up to 300 homes and could process up to 2,000 tonnes of waste a year. It is a decentralised system which can produce energy close to the source of the waste as well as offering customers complete ownership of their waste management process. This is potentially beneficial for a number of sectors including healthcare, retail and specialist facilities. The system is semi-continuous with waste shredded and then fed into the top of the pyrolysis chamber via a conveyor belt. The process can be adapted for biomass, non-hazardous or hazardous waste. No pre-sorting of waste streams is needed and no pre-heating required. There are limitations of the moisture content of the waste as a high moisture content greatly reduces the net thermal efficiency of the plant. The rig was still in development (at the time of the measurement campaign) with the aim of creating smaller versions, ideally down to single household size. Currently the energy produced by the plant is in the form of direct heat output, although it could also be coupled with a steam generator to produce electricity.

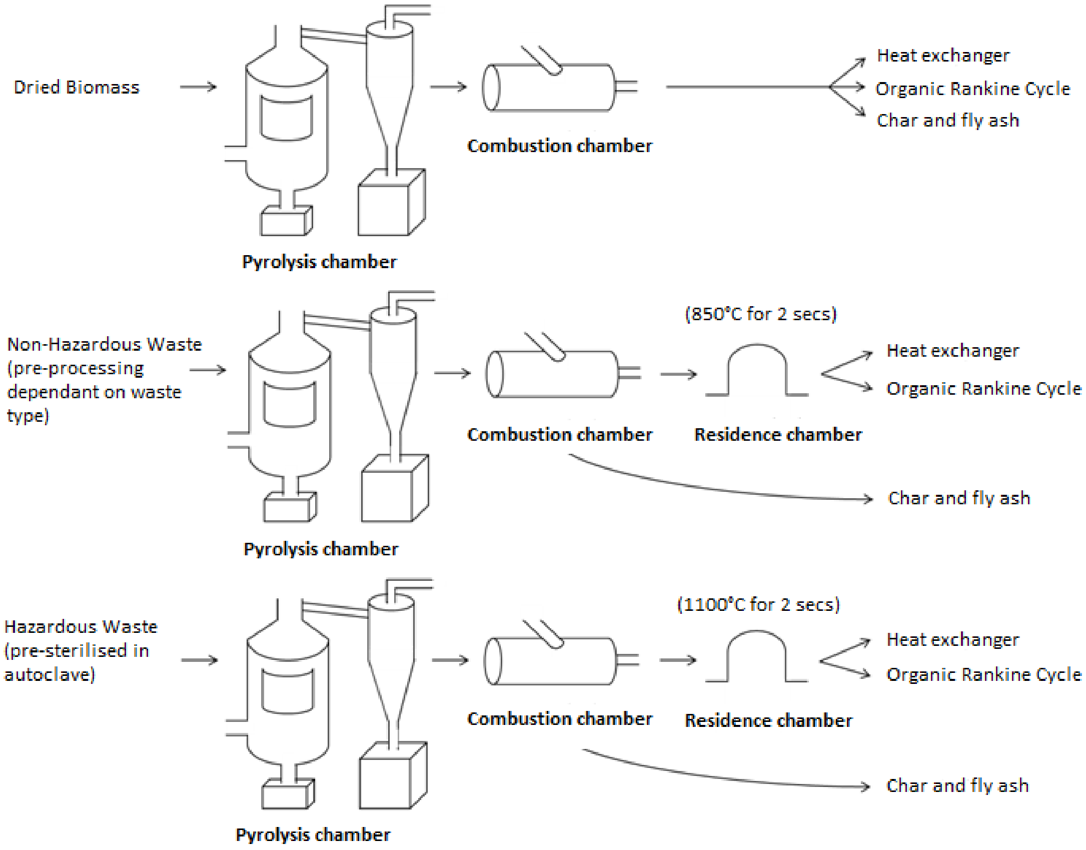


Figure 1.7: Schematic of the process of commercial rig 2: Small scale semi-batch pyrolyser

Figure 1.8: Commercial rig 2: Small scale semi-batch pyrolyser

1.5 PROJECT AIMS

As discussed above, EfW technologies are beneficial for both energy generation and as a waste management option. However, the development of such a process involves several challenges. One of the main challenges is the heterogeneous nature of MSW. The overall aim of the research reported in this thesis was therefore to explore some of the problems created by the pyrolysis of heterogeneous MSW which hinder the development of commercial small-scale EfW technologies. As well as this, the potential of using a laboratory scale pyrolysis reaction rig to predict the behaviour of larger commercial scale EfW pyrolysis systems has been established.

In order to achieve these aims, the following project objectives were established:

- To develop a laboratory scale pyrolysis reaction rig that can be used to simulate the pyrolysis of typical solid waste samples in larger scale commercial rigs.
- To quantify some of the process products from the pyrolysis of typical waste feedstocks with a focus on the mass reduction of waste.
- To quantify and investigate the composition of gas produced from pyrolysis of typical waste feedstocks in the laboratory scale pyrolysis reaction rig.
- To utilise an empirical modelling tool to highlight the likely performance of such systems on larger scales, given the data derived in the previous steps.
- To establish the composition of gas produced from pyrolysis of typical waste feedstocks in two commercial scale rigs.
- To therefore validate the overall modelling and experimental data and compare to data from commercial scale rigs to determine the applicability of this technology in decentralised energy systems.

1.6 THESIS STRUCTURE

Chapter 1 highlights the general overview of EfW as both an alternative energy source and a viable waste management option. Waste management problems, options and the use of MSW as an energy resource are discussed along with current EfW plants and technologies. This included the details of the two commercial scale rigs tested in this study. The aims of this research are also described.

Chapter 2 discusses previous research undertaken similar to that in this study. This includes the main chemical reactions involved in EfW processes as well as the effect of different MSW components on the product yields and the characteristics of the gas produced. The effect of the process temperature and the various research methods used has also been discussed.

Chapter 3 describes the MSW components and equipment used in this study. Experimental procedures are described in detail along with the study parameters and operating conditions. The accuracy and repeatability of the research for both laboratory investigations and studies on commercial scale rigs is also discussed.

Chapter 4 presents and discusses the experimental results obtained from this study for both laboratory investigations and studies on commercial scale rigs. Mass reduction, pyrolysis products and gas composition for different MSW components from laboratory investigations are explored. The gas composition from pyrolysis of mixed MSW in the commercial rigs is also discussed. Following this is a full discussion of the repeatability, errors and validity of the experimental data found in this study.

Chapter 5 presents and discusses the modelling results for the mass reduction of waste during pyrolysis based on laboratory data as well as the modelling results for the gas composition predicted for several different mixes of MSW. These gas composition predictions are then compared to the gas composition data obtain from investigations into the pyrolysis of mixed MSW on the commercial scale rigs.

Chapter 6 concludes the findings from the experimental investigations and the empirical model that was created in this study. The recommendations for future work on the pyrolysis of MSW are highlighted and discussed. Further improvements to the laboratory scale pyrolysis reaction rig that was used in this study are also proposed.

CHAPTER 2 LITERATURE REVIEW

2.1 INTRODUCTION

An extensive literature review has been undertaken to establish previous work that has been done within the research area of pyrolysis of MSW. This has included a review of work similar to that proposed in this study with the main focus on the pyrolysis of the main components of MSW. This has included investigations into the products from pyrolysis, the reduction of mass of the MSW components as well as analysis of the produced gases. A review of the effects that pyrolysis temperature and residence time and of MSW component characteristics have on the pyrolysis process. The pyrolysis of segregated waste and the effect of kinetic parameters has been studied extensively by previous authors [19-50]. However, the behaviour of fuels during pyrolysis can vary significantly with a difference in process mechanisms. The pyrolysis of various MSW components such as paper, newspaper and cardboard [39, 51-59], plastics [60-69], as well as textiles and food wastes [54, 70, 71] has also been investigated. Less research has been undertaken on the interactions of MSW components during pyrolysis [72-75].

Several methods have been used in previous research into these mechanisms including Thermogravimetric Analysis (TGA) [23, 39, 43, 44, 50, 55, 57, 58, 66, 74-78], laboratory scale reactors [22, 26, 38, 51, 56, 61, 62, 69, 71, 79-81], investigations on full-scale systems as well as modelling of the process [27, 46, 67, 76, 82-98]. There have also been various studies providing reviews of EfW technologies as well their technical, economic and environmental status [15-18, 99-106]. The main processes of EfW technologies are also described. The conclusions of this literature review have been used to establish the direction of this study, aid the design of the laboratory scale reaction rig, the experimental methodology and mathematical modelling of the laboratory data.

2.2 ENERGY FROM WASTE PROCESSES

2.2.1 COMBUSTION

The combustion or incineration of waste is already a mature and well established process. This involves a series of exothermic chemical reactions. The chemical equation for the stoichiometric reaction of carbon (C) in oxygen (O_2) is as follows:

$$C + O_2 \rightarrow CO_2 \qquad \text{Equation 1}$$

Incomplete combustion occurs when there is not enough oxygen present to allow the fuel to completely react to produce carbon dioxide (CO_2). The chemical reactions for sub-stoichiometric combustion, as stated by Higman and van der Burgt [107], are as follows:

$$3C + 2O_2 \rightarrow 2CO + CO_2 \qquad \text{Equation 2}$$

$$2C + O_2 \rightarrow 2CO \qquad \text{Equation 3}$$

The Boudouard reaction:

$$C + CO_2 \rightarrow 2CO \qquad \text{Equation 4}$$

The water gas reaction:

$$C + H_2O \rightarrow CO + H_2 \qquad \text{Equation 5}$$

The methanation reaction:

$$C + 2H_2 \rightarrow CH_4 \qquad \text{Equation 6}$$

The CO shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{Equation 7}$$

The steam methane (CH_4) reforming reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \text{Equation 8}$$

2.2.2 PYROLYSIS AND GASIFICATION

Advanced thermal treatments, such as pyrolysis and gasification have become increasingly popular for EfW technologies. Both processes turn waste into energy rich fuels through heating the waste under controlled conditions. Gasification, an exothermic reaction between a high carbon fuel and a carefully controlled and limited supply of oxidiser, is a type of incomplete combustion. A carbonaceous fuel is combusted at high temperatures in a closed tank environment with a limited supply of O_2. Due to the limited O_2, carbon monoxide (CO) and hydrogen (H_2) are produced instead of CO_2 and water (H_2O). Using this method, fuels such as coal, biomass, waste or coke can be partially combusted to produce a higher grade fuel. The gas product from gasification has a higher potential when used for energy production than the gas that would be produced from the direct combustion of the fuel.

Pyrolysis is similar to gasification in that it is a type of incomplete combustion occurring in a closed tank with a carbonaceous fuel, however, it requires a virtually O_2 free environment. In practise it is not always possible to achieve a completely O_2 free atmosphere due to the presence of O_2 within the fuel. The pyrolysis of organic materials produces combustible gases which include CO, H_2, CH_4 and other hydrocarbons as well as liquid products and a carbon rich solid residue. The gases produced can then be gasified or combusted to produce further energy. Pyrolysis has a long history in charcoal production from wood in an industrial scale. It has now become the basis of several methods under development for producing fuel from biomass or MSW. The process can be used to turn waste into a safely disposable substance or to produce syngas.

2.3 THE EFFECT OF MSW CHARACTERISTICS

As discussed in section 1.2.2 the typical composition of MSW can vary greatly with the heterogeneous nature of waste and there can be a wide variety of characteristics of each component. The properties of the fuel can have a huge impact on the processes of pyrolysis and gasification. Particle size, moisture content and volatile content can all influence the main process mechanisms such as rate of reaction as well as influencing which reactions take place. There can be specific limitations on the types of feedstock that can be processed by various pyrolysis and gasification technologies. Pre-treatment of the fuel can be necessary or desirable in order to aid the operation of the process. This can include removing certain items such as bulky, wet or low calorific value materials as well as processes to reduce the size or moisture content of particles entering the process.

2.3.1 FUEL COMPOSITION

The heterogeneous nature of MSW components presents a significant challenge to EfW technologies. Investigations to establish the chemical composition and characteristics such as moisture and ash content of each MSW component is therefore of great importance. As well as the significant variation in characteristics of different MSW components, there can also be a variation in characteristics of similar components. The plastic fractions of waste, for example, vary greatly in their composition. Even paper components can vary considerably leading to problems when comparing research, for example the comparisons between tissue paper and glossy paper. As part of this literature review, comprehensive data has been compiled on the ultimate analysis, proximate analysis and calorific value for the main components of MSW as found in the research reviewed in this study [10, 23, 28, 39, 41, 43, 55, 59, 66, 71, 72, 74, 75, 77, 78, 81]. This is shown in Appendix I.

2.3.2 PARTICLE SIZE

The particle size of the fuel may need to be controlled for some technologies using pre-treatment to reduce the size for either process consistency, or to remove bulky items. A smaller particle size increases the surface area of the fuel therefore greatly influencing the process mechanisms. Luo et al investigated the effect of particle size on the pyrolysis of individual MSW components. These were plastic, food waste and wood [79], and of mixed MSW [80]. A laboratory scale fixed bed reactor was used in order to evaluate the effects of particle size at different bed temperatures on product yield and composition. The fixed bed reactor had a height of 600 mm and outside diameter of 219 mm with a screw feeding system which fed samples continuously at a rate of 5 g/min. MSW samples were collected from a transfer station in Wuhan, China and were dried and crushed before being separated into three different size fractions; <5 mm, 5-10 mm and 10-20 mm. Results showed that smaller particles produced more gaseous products and less tar and char. Smaller particles of MSW also produced more H_2 and CO and were more favourable for gas quality and yield. A significant increase in gas yield and decrease in char and tar vapour was seen for all particle sizes of mixed MSW when the temperature was increased from 600 to 900 ˚C [80]. For the pyrolysis of single components of MSW, it also found that a smaller particle size increased the gas yields and production of H_2 and CO. The influence of particle size was found to be much more significant for the kitchen waste samples due to the higher fixed carbon and ash contents, and less for the plastic samples due to higher volatile content [79].

2.3.3 MOISTURE CONTENT

The moisture content of fuels can vary considerably depending on the type of fuel, its origin and treatment before it is used for pyrolysis or gasification. This can have a detrimental effect on EfW process and the quality of the fuel. The relationship between the calorific value and moisture content of typical waste and biomass components was investigated by Marsh et al [108]. It was found that an increase in the moisture content of a fuel leads to a decrease in the calorific value. It was stated that a typical low-value fuel would a dry calorific value of 15 MJ/kg would need a net moisture content of less than 35 % to be considered for EfW technologies. This is based on a dry calorific value of 9 MJ/kg. Waste derived fuels with a higher dry calorific value of 30 MJ/kg could have a moisture content of up to 45 % for the consideration in cement kiln applications. This could be increased to 65 % for consideration in EfW technologies [108].

Chen et al also investigated the effect of moisture content in MSW components, focusing on its effect on product composition and the lower heating value (LHV) of the syngas produced [22]. Polyethylene (PE), paper pulp and bamboo were pyrolysed using a laboratory scale fixed bed reactor. For paper and bamboo components, an increase in moisture content led to a decrease in the production of H_2 but an increase in tar yields. This also led to a decrease in the LHV of the produced gas with the highest LHV achieved for a moisture content of 0 %. This confirms findings by Marsh et al that an increase in moisture content reduces the calorific value of the fuel. This was not true, however for the pyrolysis of PE which produced the highest LHV of the syngas with a moisture content of 66.7 % [22].

2.4 MASS LOSS OF WASTE DURING PYROLYSIS AND PRODUCT YIELDS

The product yields from pyrolysis processes are of significant interest for EfW technologies. The desirable products vary greatly between technologies dependant on whether the gas, liquid or solid products are to be utilised for energy production. The reduction of solid waste is also an important factor due to the role of EfW as a waste management option. A number of studies have been undertaken to establish the thermal degradation behaviour of MSW components. The pyrolysis temperature is also an important factor as it has a varied effect on different components of MSW. It was stated by Cepeliogullar et al, that the thermal degradation of plastics occurred in a temperature range of 200-550 °C and for biomass a range of 120-800 °C [52]. It has been found by other researchers that biomass behaves similarly to paper, newspaper, cardboard and some food wastes during pyrolysis [23, 39]. Pyrolysis processes typical operate at a temperature between 400 and 800 °C [33].

2.4.1 PAPER, NEWSPAPER AND CARDBOARD WASTES

The thermal behaviour of glossy paper was investigated by Skreiberg et al using TGA and a macro-TGA [39]. The proximate analysis, ultimate analysis and calorific value of the glossy paper used are shown in Appendix I. A solid residue of 28 % was found from macro-TGA investigations performed with a sample of 200g pyrolysed in a N_2 atmosphere at a heating rate of 5 K/min up to a temperature of 900 °C. In TGA pyrolysis investigations, it was found that glossy paper started to release volatiles at a temperature of approximately 250 °C. A second stage of mass loss was observed which was attributed to the conversion of calcium carbonate ($CaCO_3$) to calcium oxide (CaO) and CO_2 [39]. $CaCO_3$ is a common additive to make paper glossy. This further highlights the challenges of the heterogeneous nature of MSW components.

The pyrolysis of paper was also investigated by Chen et al [23] using a TGA system. The paper studied by Chen at al had a lower ash content, higher fixed carbon and slightly higher volatile content of 10 %, 10 % and 80 % respectively compared to 25 %, 4. 5% and 70 % respectively for the glossy paper studied by Skreiberg et al [23, 39]. It was found by Chen et al that the main mass loss of paper occurred between 300 and 400 °C. This temperature range for the mass loss of paper was the same as that found by Singh et al in a TGA study of the pyrolysis of paper cup waste [55].

The syngas yield produced from the pyrolysis of paper was studied using a laboratory scale reactor by Ahmed and Gupta [51]. Samples of 35 g were pyrolysed at temperatures of 600 to 1000 °C. At all temperatures, a rapid increase in flow rate of the produced gas was found at the beginning of the process. This was followed by a rapid decrease until the flow rate reached zero. An increase in pyrolysis temperature led to a significant increase in the peak flow rate of the produced syngas increasing from approximately 2.4 g/min at 600 °C to nearly 12 g/min at 1000 °C [51]. This was attributed to the higher temperature allowing for the breakdown of long chains of hydrocarbons, therefore leading to an increase in the yield of syngas.

Wu et al used TGA to investigate the pyrolysis products from newspaper waste [58]. Two stages of mass loss were found; the first at temperatures between approximately 226 and 366 °C and the second between approximately 366 and 676°C. The first of these stages was attributed to the production of low and intermediate molecular mass volatiles such as H_2, H_2O and hydrocarbons. The second stage of mass loss was attributed to the conversion of C to CO and CO_2. The final residual mass was found to be 9.45 % of the initial sample [58].

2.4.2 PLASTIC WASTES

The pyrolysis of plastics is a complex process and varies significantly with the different plastic fractions of MSW. Kumar and Singh investigated the thermal degradation and cracking of high-density polyethylene (HDPE) with the aim of producing petroleum products [66]. It is stated that the pyrolysis of HDPE is usually conducted between 500 °C and 800 °C. This results in products of oil, gas, wax and solid residue. It was found that the thermal degradation of HDPE begun at approximately 380 °C and was complete at a temperature of 510 °C [66].

The composition and quantity of each of the products is dependent on the type of the plastic waste and the process conditions. It was found that at temperatures below 400 °C, the condensable products were low viscous liquids and above 450 °C, these became high viscous wax products. At a pyrolysis temperature of 550 °C, the pyrolysis products were found to be 8.83 % oil, 0.68 % solid residue, 52.02 % wax and 38.47 % gas/volatiles with respect to weight [66]. As the temperature increased, the pyrolysis reaction rate also increase leading to a decrease in reaction time. Faravelli et al [76] studied the thermal degradation of polyethylene (PE) and polystyrene (PS). It was found that PS degradation began at a temperature of approximately 360 °C [76], similar to that found for HDPE by Kumar and Singh [66]. For PE, the degradation temperature was found to be much higher at 410 °C. Total thermal decomposition was achieved at a temperature of 450 °C for PS and 550 °C for PE [76].

The pyrolysis products of HDPE were also investigated by Mastral et al using a laboratory scale fluidised bed reactor [69]. The gas yields and wax plus oil yields were established for pyrolysis temperature ranging from 640 °C to 850 °C. At the lowest temperature investigated of 640 °C the gas yield was found to be 33.5 % and the wax and oil yield was 68.5 % with respect to the mass of the sample. An increase in pyrolysis temperature up to 780 °C led to a significant increase in the production of gas to the detriment of wax and oil yields. A temperature increase from 780 °C to 850 °C led to a decrease in gas yields from 102.2 % to 89.1 % respectively and an increase in wax and oil yields from 9.6 % to 16.2 % respectively [69].

Investigations have also been conducted into the pyrolysis of various mixes of plastic wastes. Singh et al studied the pyrolysis of waste plastics derived from post-consumer MSW [78]. This mostly consisted of HDPE and Polyethylene Terephthalate (PET) although the exact composition is not stated. Thermal degradation was found to begin at approximately 410 °C and was completely by a temperature of approximately 480 °C. This is the same as the initial thermal degradation temperature for PE as found by Faravelli et al although complete degradation of PE required a higher temperature. Cepeliogullar et al [52] found that the thermal degradation of PET begun at 350 °C, this is slightly lower than the temperature of 410 °C for PE as found by Kumar et al [66].

Heikkinen et al also studied the pyrolysis behaviour of Polyvinyl Chloride (PVC) using TGA along with 40 other individual waste components [77]. It was found that all plastics, except PVC, reached a maximum rate of decomposition between 410 °C and 515 °C. PVC, as found by Chen et al [23], degraded in two stages. Heikkinen et al [77] found the first stage at 305 °C corresponded with the release of hydrogen chloride (HCl) due to dehydrochlorination. The second stage was observed at 468 °C and was attributed to the degradation of the remaining hydrocarbon residue. Due to the similarities in the pyrolysis behaviours tested, it was suggest that these plastics, with the exception of PVC, could be classed as one class. It is also suggested that PVC is separated from waste streams due to the release of hydrochloride. The temperature at which thermal degradation for PVC began, as found by Cepeliogullar et al, was 220 °C. This is slightly lower than the initial degradation temperature of 305 °C found by Heikkinen et al. Cepeliogullar et al also studied the gas yields produced from the pyrolysis of PET and PVC at 500 °C. These were found to be 76.9 % and 87.7 % respectively [52].

Polyester fabrics could also be classed under the plastic fractions of MSW. This was investigated along with PVC and PE by Chen et al using TGA [23]. The pyrolysis behaviour of polyester was found to be similar to that of PE with thermal degradation of polyester beginning at approximately 390 °C and 410 °C for PE. The thermal decomposition process was complete for polyester at approximately 410 °C and approximately 490 °C for PE. The pyrolysis behaviour of PVC was found to be very different with mass loss occurring in two stages; the first between 250 °C and 380 °C and the second between 400 °C and 550 °C [23].

2.4.3 FOOD WASTE

Along with paper, polyester, PVC and PE, Chen et al also investigated the pyrolysis behaviour of food waste [23]. The thermal degradation of dried orange peel and dried Chinese cabbage was investigated. For both of these, the majority of mass loss occurred at temperatures between 200 and 400°C with minimal further mass loss after this point [23]. This is similar to findings by Heikkinen et al [77] who studied the thermal degradation of bread, banana and starch using TGA. It was found that the majority of the mass loss of all of these samples occurred between temperatures of 209 and 346 °C.

2.5 ANALYSIS OF PYROLYSIS GASES

Experimental research into the pyrolysis of waste materials by other authors have shown the dominant gases to be CO, CO_2, H_2, H_2O and light hydrocarbons (C_1-C_4) [39, 56, 58, 69, 75, 78, 81]. These gaseous products have been found to vary significantly with pyrolysis temperature and fuel characteristics. The key advantage of pyrolysis, as well as gasification technologies is the ability to produce a CO and H_2 rich gas. As stated by Lupa et al [33], the most important gases for the consideration of energy generation from EfW processes are CO, CO_2, H_2O and H_2 with CO and H2 being the gases of most importance as they have a high calorific value (CV) of 10 and 13 MJ/kg respectively. Lupa et al established a heating value of 11-17 MJ/Nm3 from plasma-arc pyrolysis of waste [33]. This is comparable to other studies where values of 13-20 MJ/Nm^3 from the pyrolysis of waste [44], 5- 16 MJ/Nm^3 from the pyrolysis of biomass [40] and 13-15 MJ/Nm^3 also from the pyrolysis of biomass [25].

2.5.1 PAPER, NEWSPAPER AND CARDBOARD

As well as the quantity of gases produced from the pyrolysis of paper as discussed above, Ahmed and Gupta also investigated the composition of the produced gas [51]. The change in mass of H_2 production with pyrolysis time was recorded for pyrolysis temperatures of 600, 700, 800, 900 and 1000 °C. It was found that an increase in the pyrolysis temperature led to an increase in the production of H_2 and a decrease in the time of production. The gasification of paper was also investigated and found to produce higher volumes of H_2 than pyrolysis at the same temperature. It was also established that an increase in pyrolysis temperature led to an increase in the production of CO to the detriment of CO_2 production. The heating value of the produced gas therefore also increases with an increase in pyrolysis temperature. The energy yields from pyrolysis and gasification of paper were found to be similar at 600 °C, however at higher temperatures gasification led to higher energy yields. This was attributed to the absence of char gasification reactions at 600 °C and below [51].

The main non-condensable gaseous products from the pyrolysis of glossy paper were found by Skreiberg et al to be CO_2, CO, H_2, and lighter hydrocarbons such as CH_4, ethane (C_2H_6), acetylene (C_2H_2) and ethylene (C_2H_4) [39]. CaO was also produced due to the $CaCO_3$ present in the glossy paper as discussed above. Water vapour was also released but was not detected by the micro GC used to analyse the produced gases. The production of CO and CO_2 was found to peak at temperatures between 350 and 400 °C with a second peak above 600 °C caused by the thermal decomposition of the $CaCO_3$. At temperatures above 500 °C, the production of H_2 was found to increase although the production of the lighter hydrocarbons remained low.

Wu et al also found an increase in pyrolysis temperature led to an increase in the production of CO from the pyrolysis of newspaper, however it also led to an increase in the production of CO_2 [58]. At a pyrolysis temperature of 514 °C, the main gaseous products were found to be 0.32 % H_2, 5.29 % CO, 37.17 % CO_2, 20.57 % H_2O and 1.51 % for light hydrocarbons. At 668 °C, the gaseous products were 0.4 % H_2, 10.71 % CO, 56.77 % CO_2, 20.57 % H_2O and 2.11 % for light hydrocarbons [58].

2.5.2 PLASTICS AND TEXTILES

Singh et al found the main gases produced from the pyrolysis of a mixed plastic fraction of MSW were CO_2, CO, CH_4, and H_2O [78]. It was also found that an increase in the pyrolysis temperature led to an increase in the production of CO. Using a laboratory scale reactor, Conesa et al found the gas yield at a pyrolysis temperature of 800 °C to be 94 % of the original mass of HDPE. The composition of this produced gas was 20 % CH_4, 3.8 % C_2H_6, 37 % C_2H_4, 0.2 % C_3H_8, 4.7 % propylene, 0.3 % butane, 0.4 % butylenes, 2.2 % pentane, 24 % benzene, 2.1 % toluene, 0.01 % acetylene and 0.02 % xylenes and styrene [62].

Mastral et al also investigated the composition of the gas produced from the pyrolysis of HDPE [69]. They found the main gaseous components were found to be H_2, CH_4, C_2H_4, C_2H_6 and other hydrocarbons ranging from C_3-C_{60}. It was found that the production of H_2, CH_4 and C_2H_4 increased with an increase in pyrolysis temperature from 640-850 °C. The production of other hydrocarbons such as C_2H_6, C_3 and C_4 increased with a temperature increase from 640-730 °C then decreased with a temperature increase from 730-850 °C. No CO or CO_2 was detected from the pyrolysis of HDPE [69]. Achilias et al also detected no production of CO or CO_2 from the pyrolysis of HDPE or from the pyrolysis of low density Polyethylene (LDPE) or Polypropylene (PP) [61]. The main gases identified were hydrocarbons as well as small quantities of H_2.

As discussed above, the behaviour of PVC during pyrolysis has been found to be significantly different to that of other plastic fractions of MSW. Zhou et al found the main gaseous products to be hydrochloride and benzene (C_6H_6) [75]. It was also stated that an increase in pyrolysis temperature favoured the production of aliphatic hydrocarbons. Yang et al [97] studied the pyrolysis behaviour of textiles in a fixed bed reactor. CO_2 and CO were found to be the main gases produced. At pyrolysis temperatures above 450°C, the production of H_2 and CH_4 began with the production of H_2 found to increase with an increase in pyrolysis temperature.

2.5.3 FOOD WASTE

A study into the pyrolysis behaviours of kitchen based vegetable waste was undertaken by Agarwal et al using a laboratory scale packed bed reactor [71]. The vegetable waste was dried before pyrolysis at a range of temperatures from 400 to 800 °C. It was found that an increase in the pyrolysis temperature led to an increase in the production of H_2 and an increase in the volume of the overall gas produced. The results found by Agarwal et al are similar to those found in previous research into the pyrolysis of biomass [26, 38]. At 400 °C there was minimal production of H_2 and CH_4 and the main component of the produced gas was CO_2. The gas composition from pyrolysis at 500 °C was found to be similar although slightly higher volumes of H_2 and CH_4 were detected. This trend continued with an increase in temperature to 600 °C. At 800 °C, the main gas produced was still found to be CO_2 but a significant increase in the production of H_2 and CH_4 was recorded [71]. Any CO produced was not analysed. Zhou et al also found the main gaseous products from the pyrolysis of orange peel to be CO_2, CO and H_2O [75].

2.6 PYROLYSIS OF MIXED MSW

Due to its heterogeneous nature, the behaviour of MSW during pyrolysis is complex and varied and is dependent on the composition and characteristics of the waste. As well as this, the pyrolysis products are strongly influenced by the type of reactor, temperature and heating rate, pressure ranges and the presence of catalysts. These pyrolysis characteristics have been investigated using TGA by several authors [23, 39, 43, 44, 50, 57, 74, 75, 77, 78].

The pyrolysis of mixed MSW was studied by Velghe et al [44] using a semi-batch reactor. The MSW mixture contained carpet, residues of plastic, metal, drinks cartons, paper and different fractions of synthetic materials and an organic fraction. The main gases produced at the start of pyrolysis were found to be CO_2 with smaller amounts of CO and minor amounts of light hydrocarbons. The volumes of CO_2 and CO were found to decrease as the pyrolysis time increased.

As well as investigating the behaviour of MSW mixtures, research has also been undertaken to establish the interactions of individual MSW components during pyrolysis. It was report by Zheng et al [50] that interactions between similar components of MSW, such as paper, biomass and food waste, during pyrolysis was small, whereas interactions between PE and biomass was significant especially at higher heating rates. This was confirmed by Skreiberg et al [39] who also investigated the interactions of mixtures of paper, biomass and food waste using TGA. It was found that the gas composition from MSW mixtures showed relatively quantitative and qualitative summative behaviour based on that found for single components of MSW.

Faravelli et al [76] investigated mixing of PE and PS using TGA. It was found that if the mixing of the PE and PS was poor then the thermal decomposition of each polymer behaved independently. However, if the mixing of the polymers reached a molecular scale, partial interactions and co-pyrolysis was observed. Increased mixing of the components led to an increase in the volatilisation of the PE during the depolymerisation of the PS.

2.7 RESEARCH METHODS

A variety of methods have been used in previous work to research pyrolysis behaviour. The majority of this has been undertaken using TGA, with a smaller number of studied undertaken using laboratory scale reactors. There has also been an increase in the number of different models developed to predict the pyrolysis behaviour of MSW.

2.7.1 THERMOGRAVIMETRIC ANALYSIS

TGA is a type of testing performed to determine changes in the weight of a sample in relation to the change in temperature. This analysis requires high precision in the measurement of weight, temperature and temperature change. It is one of the most common techniques used to investigate thermal behaviour and a significant amount of research into the pyrolysis of wastes has been undertaken using TGA.

The ease of use, short experimental time and high accuracy of results has made TGA a popular option for researching the pyrolysis behaviours and especially the thermal degradation of MSW. This can be especially beneficial for analysis of individual components of MSW. Heikkinen et al [77] used TGA to study the pyrolysis of 41 individual components of waste. If the pyrolysis of these individual components were investigated in a commercial scale rig this would take a significant amount of time and extremely high running costs. Even in a laboratory scale rig, this number of investigations would take a long time. TGA is therefore an important option for the analysis of MSW.

For TGA investigations, a very small sample size is used, usually around 10mg, which although allows for quicker reactions than the larger samples used for laboratory scale investigations. Although beneficial for individual components, this could cause problems for investigations on MSW mixtures due to the highly heterogeneous nature of waste and difficulties in getting an accurate representation of this in a sample of approximately 10 mg. As well as this problems could develop when scaling results up to represent commercial scale pyrolysis.

A macro TGA system was used by Skreiberg et al [39] to investigate the thermal behaviours of wood, demolition wood, coffee waste and glossy paper as individual components and in mixed samples. Data from this was compared to data achieved under the sample conditions with the same samples with a TGA. In TGA investigations, a sample size of approximately 2.75 mg was used. In macro TGA investigations a much larger sample size of 200 g was used. The macro TGA consisted of a cylindrical mesh basket which was connected to a balance and lowered into the cold reactor chamber before it was heated. The repeatability of experiments was found to be good, although uncertainty of some areas were found to be greater than those seen in TGA experiments.

For wood samples, it was found that pyrolysis occurred faster in TGA than in macro-TGA with mass loss mainly in a temperature range of 200-350 °C compared to 300-450 °C respectively. It was found that the heat and mass transfer limitations caused by the larger sample size caused a lag in the temperature evolution [39].

Yang et al [97] also studied the differences between the thermal degradation of MSW components using TGA compared with a packed bed reactor. A significant difference between the thermal degradation of samples during TGA and that during pyrolysis in the packed-bed reactor was found. The char yield in a packed bed reactor was 30-100 % higher than the char yield obtained from TGA tests at the same heating rate. This difference was attributed to tar cracking and repolymerisation which prevail during pyrolysis in the packed bed reactor [97]. The study by Yang et al has therefore shown the significant problems with using TGA data to predict the behaviour of pyrolysis on a larger scale.

2.7.2 LABORATORY SCALE PYROLYSIS

Research using laboratory scale gasifiers has been undertaken using a wide range of technologies and feed sizes. The design and development of laboratory gasifiers can be expensive and time consuming compared to TGA due to the much larger fuel sample size used. However, this larger sample size may be more beneficial when scaling results to represent the gasification reactions in a plant-scale gasifier. The majority of research using laboratory scale reactors has been undertaken using fixed bed reactors [22, 26, 51, 61, 71, 79-81] as well as this, research has also been undertaken using fluidised bed reactors [38, 56, 62, 69].

Ahmed and Gupta [51] investigated the syngas produced from the pyrolysis and steam gasification of paper using a laboratory scale fixed bed reactor. The produced gases were analysed using a micro GC. A sample size of 35 g was pyrolysed and gasified at temperatures of 600, 700, 800, 900 and 1000 °C. Data repeatability was found to be good [51].

A laboratory scale fixed bed reactor was also used by Luo et al [79] to investigate the effect of particle size on pyrolysis behaviours. A quartz reactor tube was externally heated by an electrical ring furnace. This was surrounded by an insulation layer. Difficulties were found in the accurate measurement of the temperature at the sample due to large temperature gradients within the sample. It was found that measurement of the quartz reactor tube was more accurate to approximately reflect the change in temperature of the sample.

The varied heat profile through samples was also found by Yang et al [97] in a study of slow pyrolysis in a laboratory scale packed bed reactor. The heating rate across the reactor was found to differ from the programmed wall heating rate significantly. The temperature was monitor using 3 thermocouples at different points in the reactor which held a sample of up to 1 kg. The temperature increase at the centre of the reactor bed was found to lag behind the temperature increase at the reactor wall. This difference was found to be as high as 200-250 °C.

Phan et al [19] also studied the effect of a larger mass of waste during pyrolysis focusing on the effect of the bed depth on the yields and properties of products using a fixed bed pyrolyser. It was found that the bed depth had a small influence on the products yields but a significant effect on the properties of the products. An increase in the bed depth was found to lead to an increase in the production of liquid products, and an increase in the production of CO.

2.7.3 MATHEMATICAL MODELLING

Mathematical models have often been used to establish the relationships between a set of variables for a wide variety of problems. This can be incredibly useful for research into EfW technologies. Values predicted by a model can then be compared with experimental data in order to establish the accuracy of the mathematical model and then used to predict the behaviour of the pyrolysis or gasification process. A number of models have been created for a variety of pyrolysis, gasification and combustion conditions for a wide variety of MSW mixtures and individual components [46, 76, 82, 86-92, 95-98, 103, 109].

The models developed have covered a wide range of pyrolysis behaviour as well as some which model the benefits of different EfW and biomass technologies. Murphy et al [103] investigated four technologies which produce energy from municipal solid waste (MSW). These technologies were: incineration, gasification, generation of biogas and utilisation in a combined heat and power (CHP) plant, generation of biogas and conversion to transport fuel. An empirical model was used to compare these technologies using a decision support software package which was written to model technical, economic and environmental conditions of waste to energy systems. It was found that gasification produced electricity with a maximum efficiency of around 34 %, suggesting that gasification of the residual component of MSW is more advantageous than incineration. It was concluded that gasification when compared to incineration, produces more electricity, requires a smaller gate fee and generates less greenhouse gas per kWh, when thermal product are not utilised.

Other models have been based on TGA and laboratory data in order to model the kinetic parameters of pyrolysis. At Zhejiang University, China, a TGA was coupled with a Fourier transform infrared spectroscopy (TG-FTIR) in order to study the pyrolysis of certain medical waste materials [110]. The FTIR was used to provide information on the mixture of product gases. Various medical materials were investigated including absorbent cotton and medical respirators. The objective of this investigation was to provide result to help develop a predictive medical waste pyrolysis model. Approximately 12 mg samples were tested after drying for 3 hours at 105 °C. It was concluded that further investigation was needed to establish the kinetic parameters in order to create a pyrolysis model that could predict yields and evolution patterns of volatile products using a CFD model. Further study was planned to determine the kinetic parameters for a pyrolysis model using the TG-FTIR pyrolysis equipment at several heating rates. A pyrolysis model based on parallel, independent, first-order reactions with Gaussian distribution of activated energies will be developed. From this a Distributed Activated Energy Model (DAEM) will be used to solve yield and rate of evolution for individual pyrolysis products with given kinetic parameters from the TG-FTIR analysis.

Zhejiang University went onto investigate the gasification characteristics of MSW using an artificial neural networks (ANN) model, along with Southeast University, Nanjing [46]. ANN models can be used to learn and recognise highly nonlinear relationships, the dispersed data can then be organised into a nonlinear model. This can be a useful method of predicting the gasification or pyrolysis characteristics of MSW. Xiao et al gasified wood, paper, kitchen waste, plastic and textiles in a fluidised bed reactor at 400-800 °C with an equivalence ratio range of 0.2-0.6. The model was found to have an accuracy of approximately ±15-25%.

Limited previous research has been undertaken which utilises prediction models for the pyrolysis of MSW, however, a significant amount has been undertaken for the pyrolysis and gasification of biomass which could show some similarities with the pyrolysis of MSW. Puig-Arnavat et al (Puig-Arnavat, 2010 #100) undertook a review of models used to predict the behaviour of biomass during gasification based on thermodynamic equilibrium, kinetics and ANN. The thermodynamic models were found to have an advantage as they are independent of the gasifier design so can be a useful tool for preliminary comparisons. However, highly accurate results cannot be achieved using this approach for all cases. A higher accuracy was found through the use of kinetic models however, some parameters create limits to their applicability to predicting the behaviour of different gasification plants.

Yang et al [97] used a laboratory scale slow heating packed bed reactor to study the pyrolysis of wood waste, cardboard and textiles. A mathematical model was then developed to simulate the heat and mass transfer and kinetic processes within the reactor. The pyrolysis yields were predicted along with their composition. The model was found to agree with laboratory data for the maximum levels of CO, CO_2, CH_4, H_2 and C_2H_4 produced. However, some gas peaks were shown in modelled data but not in laboratory data. This was attributed to non-uniformity across the reactor bed and insufficiently small sampling intervals [97]. The modelling approach used a function-group, depolymerisation, vaporisation, cross-linking (FG-DVC) model which was originally developed for coal pyrolysis. The functional group (FG) model describes the gas evolution and the group compositions of the tar and char. The reaction rates were assumed to follow first-order kinetics based on the Arrhenius equation of the form:

$$k_i = A_i \exp(\frac{-E_i \pm \sigma_i}{RT})$$

Where A_i is the pre-exponential factor, E_i is the activation energy and r_i the width of distribution in activation energies. Yang et al suggested that this modelling approach is greatly beneficial for the detailed prediction of product yields and their composition although it has mostly been validated against data obtained by TGA investigations. Yang et al went on to suggest that this modelling approach may be less beneficial for the modelling of data for larger particles or fuel batches. These difficulties are most likely due to the differences caused by the greater surface area of particles and larger masses which have been found to significantly increase the char yields. It was suggested that simpler reaction models may lead to a higher accuracy of data prediction for pyrolysis of MSW where the particle size or fuel mass is larger than that used in TGA investigation. A significant amount of further research is needed in order to sufficiently validate more complex models to model the pyrolysis or gasification of a larger mass. It has therefore been decided to utilise simple modelling techniques in this study in order to ensure a higher accuracy of correlation between modelled results and laboratory data for the pyrolysis of MSW samples larger than that used in TGA investigations.

2.8 SUMMARY

An extensive literature review has been undertaken on previous research into the pyrolysis behaviours of MSW as well as the research methods used. MSW has a heterogeneous nature which causes significant problems for EfW technologies. It was found from comparisons with previous research that even similar components of MSW can show a variation in composition. A list of the proximate and ultimate analysis of MSW components as reported in the literature is shown in Appendix I.

The particle size of MSW has been found to be important and can have a significant effect on results. This has shown the importance of using a consistent particle size to aid comparison of the behaviours of different components of MSW. The difference in particle sizes used in TGA, laboratory investigations or in commercial scale EfW plants therefore creates a significant challenge when comparing pyrolysis behaviours or scaling up laboratory data to full size plants. The moisture content of MSW has also been found to be an important consideration as it can have detrimental effects on the quality of the fuel and the efficiency of the process.

The loss of mass of all MSW components has been found to vary significantly with the pyrolysis temperature, residence time as well as for a difference in component. The reduction in mass occurs over a wide temperature range of approximately 160 – 800 °C [22, 23, 39, 51, 58, 66, 76, 77]. The pyrolysis temperature and residence time has also been found to have a significant effect on the pyrolysis products and the composition of the gas produced. The main gaseous products from the pyrolysis of MSW have been found to mainly consist of CO and CO_2 with smaller quantities of H_2, CH_4 and lighter hydrocarbons. An increase in pyrolysis temperature has been found to lead to an increase in the production of CO and H_2 and in some instances a decrease in the production of CO_2 [51, 58, 78]. The pyrolysis of plastics has been found to be complex and varied. The pyrolysis of HDPE produced no CO or CO2 [61, 62, 69] and the main gases produced from the pyrolysis of PVC were found to be hydrochloride and C_6H_6 [75]. Through the pyrolysis of mixed MSW it was found that interactions of similar components such as paper, biomass and food waste were small [39] but interactions between plastics and biomass or paper fractions were significant. It was found that some waste mixes pyrolysed together qualitatively and to some extent quantitatively showed a contribution from the pyrolysis of the individual components [39].

The majority of research has been undertaken using TGA as well as using laboratory scale equipment or through the development of mathematical models. However, this process uses a very small sample size of around 10 mg. This may cause problems when researching fuels such as MSW as it is not homogenous leading to inaccurate results especially if used to model a larger scale pyrolysis or gasification plant. A wide range of research has also been undertaken using laboratory scale pyrolysers and gasifiers. Comparisons between the results of these investigations can be difficult due to differences in the processes and equipment used however these investigations use a larger process (with most gasifiers larger than 1 metre) and sample size than that used in TGA tests making it easier to represent the heterogeneous nature of MSW as a fuel.

Following this literature review, it has been concluded that further research is necessary in order to optimise the pyrolysis processes using MSW as a fuel. The pyrolysis behaviours of the main components of MSW need to be established in order to allow for improvements to be made to EfW technologies. This would lead to an increase in process efficiency and to maximise the calorific value of the produced gas. In this study, an experimental investigation of the influence of temperature and time on the pyrolysis products of MSW components has been undertaken. A laboratory scale pyrolysis reaction rig has been developed to address a range of conditions.

CHAPTER 3 METHODOLOGY

3.1 INTRODUCTION

As shown in previous chapters, EfW technologies have the potential for both energy production and the diversion of waste from landfill. However, further research is still needed in order to further optimise the processes using municipal solid waste as a fuel. Following a literature review, it was concluded that optimum conditions need to be established in order to increase process efficiency and to maximise the calorific value of the produced gas. The process mechanisms and products needed further investigation with various MSW components as well as mixed waste samples. A laboratory scale pyrolysis reaction rig has been developed to address the effect of the main process mechanisms on the gas produced and establish a range of optimisation conditions. Kinetic data of the pyrolysis behaviour of MSW components and mixed MSW samples were determined, as well as an estimation of quantification of the process effluents. This data was then used to model the likely performance of larger scale systems.

CHAPTER 3 includes a review of the chosen research methods and design appropriateness of the investigation and how this will provide answers to the proposed research questions. In addition, details of the experimental procedure and equipment to be used are included as well as all data collection, analysis methods and a discussion of the accuracy of the instrumentation used. Results for the investigations described in this chapter can be found in Chapter 4 along with a discussion of the validity and reliability of the data. The empirical models developed from data from laboratory investigations are described and discussed in Chapter 5.

3.1.1 RESEARCH AIMS AND OBJECTIVES

As previously identified, the aim of this study was to explore some of the problems that are created by the heterogeneous nature of MSW during pyrolysis. The potential of using a laboratory scale reaction rig to predict the behaviour of larger commercial scale EfW pyrolysis systems has also been established. As shown in section 1.5, the project objectives were as follows:

- To develop a laboratory scale pyrolysis reaction rig that can be used to simulate the pyrolysis of typical solid waste samples in larger scale commercial rigs.
- To quantify some of the process products from the pyrolysis of typical waste feedstocks with a focus on the mass reduction of waste.
- To quantify and investigate the composition of gas produced from pyrolysis of typical waste feedstocks in the laboratory scale pyrolysis reaction rig.
- To utilise an empirical modelling tool to highlight the likely performance of such systems on larger scales, given the data derived in the previous steps.
- To establish the composition of gas produced from pyrolysis of typical waste feedstocks in two commercial scale rigs.
- To therefore validate the overall modelling and experimental data and compare to data from commercial scale rigs to determine the applicability of this technology in decentralised energy systems.

3.1.2 RESEARCH METHOD AND DESIGN APPROPRIATENESS

It has been decided to use a laboratory scale pyrolysis reaction rig in this study. There is great advantage in this over both TGA and tests on a commercial scale pyrolysis system. TGA has the advantage of being a more cost effective and a quicker way of obtaining results. However, it is limited by the necessity for a very small sample size, usually around 10 mg. Although this allows for faster reactions than the larger samples used for laboratory scale investigations, this can cause problems in representing heterogeneous fuels such as MSW. As well as this, the small sample size also creates difficulties when using results to model the behaviour of a commercial scale pyrolysis rig. Comparison between TGA tests and the pyrolysis of a larger sample size in a laboratory scale pyrolyser were made by Yang et al [97] and Skreiberg et al [39]. It was found that a larger sample mass had a significant effect on the thermal degradation behaviour compared to results from TGA tests, as discussed in section 2.7.1.

Another alternative would be to complete tests on a commercial scale rig. This has the advantage of improved relevance and reliability in the prediction of the behaviour of larger pyrolysis systems as results do not have to be scaled up as is the case with laboratory results or TGA. However, testing on a full scale rig does not allow for quantification of the behaviour of fuels on a fundamental level. As well as this, completing the full tests proposed within this research study on a commercial scale rig would be incredibly time consuming as well as prohibitively expensive.

It was therefore decided to design a novel laboratory scale pyrolysis reaction rig with the aim of representing a small section of the pyrolysis chamber of a commercial scale rig. Single components of waste were studied in order to establish how each component of waste reacts during pyrolysis. Data from this was then compared to gas analysis data from the pyrolysis of mixed MSW in two commercial scale pyrolysis rigs.

3.2 INSTRUMENTATION

3.2.1 THE PYROLYSIS REACTION RIG

The thermal behaviour of MSW components was studied using the custom built pyrolysis reaction rig. The laboratory scale pyrolysis reaction rig was designed, constructed and commissioned for this study using an adapted horizontal tube furnace. The furnace was heated by a wire element wound directly onto a fixed ceramic work tube. A removable steel boat, in which the sample was placed, sits inside this ceramic tube. The ceramic tube had a length of 330 mm and an internal diameter of 30 mm. The steel boat was 330 mm long, 20 mm wide and had a depth of 10 mm. The furnace had a maximum temperature of 1000 °C and a maximum continuous operating temperature of 900 °C. A separate control module connected to the furnace is capable of programming a set temperature, ramped to set-point, a delayed start as well as a process timer. The horizontal tube furnace is shown in **Error! Reference source not found.** and Figure 3.2.

Figure 3.1: A photograph of the horizontal tube furnace

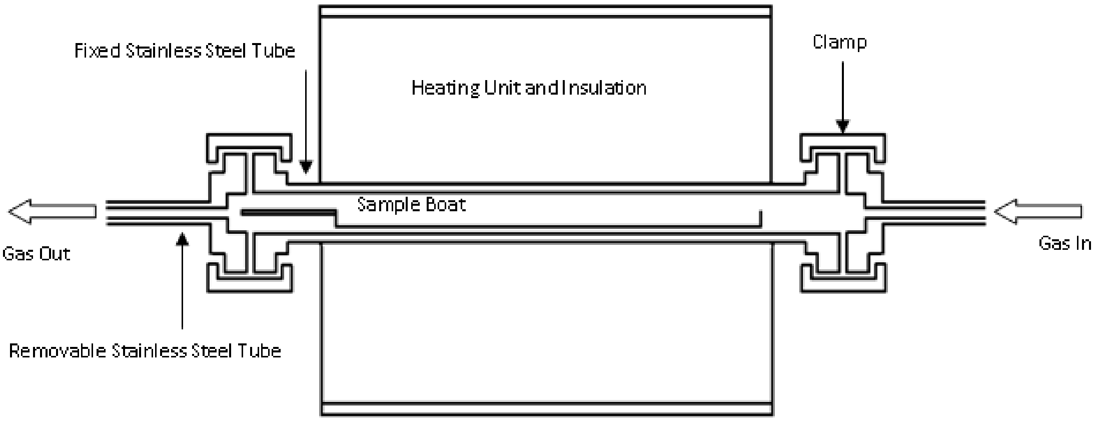


Figure 3.2: A schematic of the horizontal tube furnace (not to scale)

At both ends of the furnace, 6 mm stainless steel piping is attached using Swagelok fittings to provide a gas inlet and outlet. The gas inlet pipe is split into two after a short section to allow for the mixing of the reactant gases before entering the furnace, and connected to two calibrated Platon glass flow meters both with a range of 0-2 l/min to control the flow rate of both gases. These flow meters are then connected to an O_2 and a N_2 compressed gas cylinders using PVC tubing. The connection of these gas inlets enabled the rig to be used for a range of pyrolysis or gasification conditions. However, only the N_2 inlet was used in this study. Both gas cylinders were fitted with regulators as well as a flash back arrestor safety valve for the oxygen cylinder. Both flow meters were calibrated for air. A correction factor of 0.98 was used to allow for use with N_2 [111].

The 6 mm stainless steel piping at the gas outlet was connected to 6 mm PVC tubing which allowed for a gas tight connection to the glass bottles in the tar trap set up. A thermocouple, positioned at the end of the stainless steel exhaust pipe, was used to record the temperature of the released gases during preliminary testing to ensure the gas temperature was below 40°C to prevent damage to the gas analysers. For all runs, the temperature of the released gases at the beginning of the tar trap system was between 26 °C and 34 °C. Another thermocouple was used to ensure the temperature of the furnace was the same as indicated on the programming panel. These thermocouples were only used in preliminary testing and after every 20 hours of testing during the main testing to ensure any leaks in the system where minimised and did not affect the results. The complete pyrolysis reaction rig, pipe work, flow meters and Rosemount NGA 2000 gas analyser are shown in Figure 3.3 and Figure 3.4.

Figure 3.3: A photograph of the pyrolysis reaction rig with Rosemount NGA 2000 gas analyser

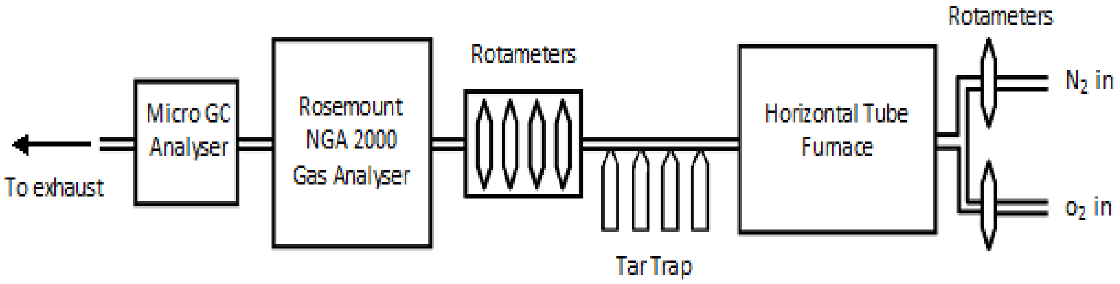


Figure 3.4: A schematic of pyrolysis reaction rig, tar trap and gas analysers

3.2.2 TAR TRAP AND GAS CLEANING

All exit gases from the reaction rig were passed through a tar trap and gas cleaning system before entering either of the gas analysers as shown in Figure 3.5. A photograph of the tar trap system can be seen in Figure 3.6. The main purpose of this was to avoid damage to the gas analysers by preventing tars from reaching them. In addition to this, the liquid products collected in the tar trap could be analysed and quantified. During preliminary experiments it was found that the gas at the exit of the furnace had already cooled sufficiently so no further gas cooling system was needed.

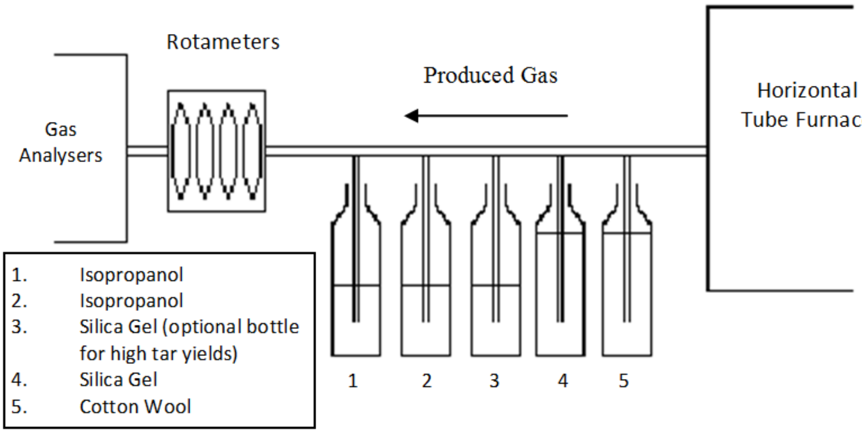


Figure 3.5: A schematic showing the set up of reaction rig, tar trap and gas analysers

Figure 3.6: A photograph of 5 Dreschel bottles used in the tar trap system

The gas filter and tar trap system consisted of four 250 ml gas wash borosilicate glass Dreschel bottles by Quickfit from Fisher Scientific. An extra bottle was used for pyrolysis investigations with plastic and textiles samples due to the high tar yields produced from these samples. The glass bottle heads were fitted with detachable plastic screw thread connectors, which allowed for easy fitting of flexible PVC tubing between bottles. Bottle 1 and 2 each contained 150 ml isopropanol (IPA), bottle 3 contained 100 ml silica gel and bottle 4 was filled half full of cotton wool. The optional extra bottle contained 100 ml silica gel. The IPA was used as a solvent to clean the gas by dissolving tar. IPA was used as the solvent for the experiment, as recommended in the international standard for tar and particle measurement in biomass producer gas by TarWeb.Net [112].

The silica gel was primarily used to collect any moisture from the gas to ensure no damage to the gas analysers; it also acted as an extra filter to collect any tar not dissolved by the IPA. The cotton wool in the final bottle allowed the gas to be visually checked in ordered to ensure no tars entered the gas analysers. If any colouration of the cotton wool was evident, the gas was not deemed cleaned enough to pass through the gas analysers. When this was the case, a further bottle of IPA was added before bottle 1. The likelihood of an extra bottle being needed was established during preliminary testing of each different sample. Figure 3.6 shows the set up of the Dreschel bottles used in the tar trap system. This photograph is from the pyrolysis investigation using a food waste sample. It can be seen that an extra bottle of silica gel has been added to the system. This was due to the high moisture content of the fuel so additional measures were taken to prevent moisture from reaching the analysers. During preliminary investigations it was determined that a change in the number of Dreschel bottles used in the tar trap system had no effect on the gas analysis results.

The IPA in bottles 1 and 2 was replaced after each experiment to ensure each run was conducted under the same conditions. Safety instructions for the use, storage and disposal of IPA were followed and are shown in Appendix II. The silica gel in bottle 3 was also changed for each run. This tar trap system was chosen as it can be easily adapted, is relatively simple to construct and filters the gas to the required standard without comprising analysis results. It is easily transported for any off-site testing. The tar trap system is discussed further in section 3.7.3 along with errors and repeatability of the system discussed in section 4.8.3.1.

3.2.3 GAS ANALYSERS

After the tar trap cleaning system, the PVC piping and connectors were used to split the gas through four Platon plastic flow meters which were used to measure the flow rate of the gas before entering the four inlet channels of the Rosemount gas analyser. Each of these flow meters had a range of 0-1 l/min. These readings give a good indication of how the flow rate of the produced gas increased or decreased with each sample and process variable. As these flow meters were calibrated for air and the composition of the produced gas flowing through them varied significantly throughout the run they were only used to give an indication of the flow rate, not an exact measurement. These flow meters were also used to ensure equal flow was sent through each channel on the gas analysers and gave an indication of any blockages.

3.2.3.1 ROSEMOUNT NGA 2000 GAS ANALYSER

An Emerson Process Management Rosemount Analytical NGA 2000 gas analyser module was used to measure the percentage of the volume of CO_2, CO and O_2. This is shown in Figure 3.7. It can also measure the CO produced in parts per million (ppm) although this channel was not used for these tests. The modular chemiluminescence analyser has a thermoelectrically-coded solid-state detector which ensures high stability. It has a fast response time reaching 90 % of full scale within 1 second allowing for continuous gas analysis data to be recorded.

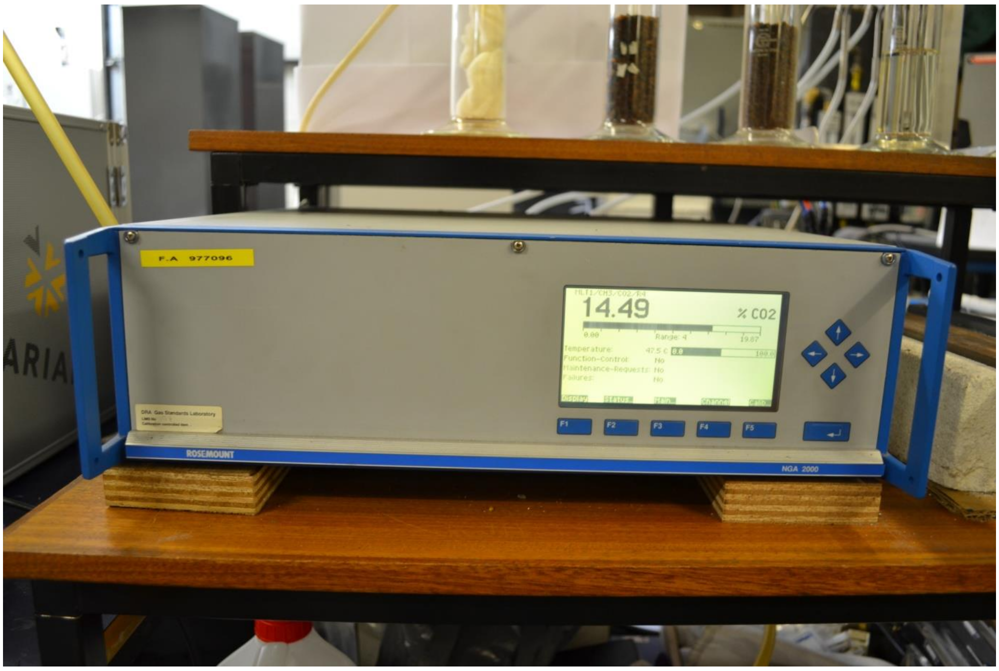


Figure 3.7: A photograph of the Rosemount NGA 2000 gas analyser

Readings were manually recorded every 15-30 seconds. Although this analyser does not measure other gases which are important to this investigation, such as H_2 and CH_4, the continuous readings allow for any small peaks or changes in the gas composition to be detected. During preliminary testing, the maximum and minimum volumes of CO_2, CO and O_2 produced from various fuel types and variables were estimated. The gas analyser was calibrated before every run using calibration gases for both of these estimated minimum and maximum values and set to zero using a N_2 purge through the analyser. Details of the calibration gases used are given in section 3.7.4.1. Safety data sheets for these gases can be found in Appendix III.

3.2.3.2 VARIAN CP-4900 MICRO GAS CHROMATOGRAPH

A Varian CP-4900 micro Gas Chromatograph (micro GC) was also used to determine the composition of the gas produced from pyrolysis and was connected to the outlet gas from the Rosemount analyser during laboratory investigations. This is shown in Figure 3.8. The micro GC was controlled with a Galaxie Workstation using software version 1.9.3.2. Gas was analysed using a pre-programmed method using the 2 chromatography channels. The first channel measured H_2, O_2, N_2, CO and CH_4 with argon as a carrier gas. During operation, the column injector temperatures were maintained at 70 °C and the column pressure at 150 kPa. The second channel measured CO_2, C_2H_6 and C_3H_8 with helium as a carrier gas. For this channel, the column temperature was maintained at 109°C at a pressure of 75 kPa.

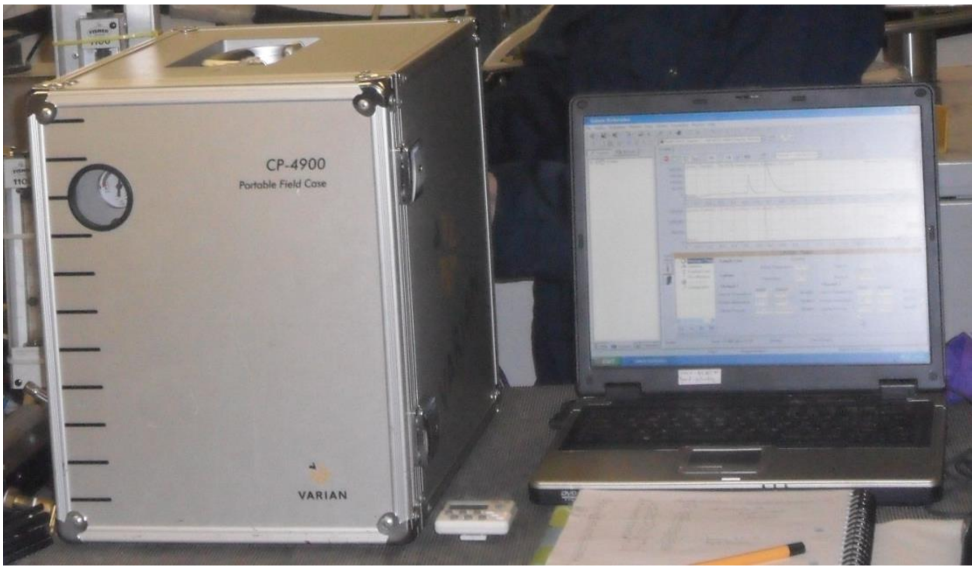


Figure 3.8: A photograph of the Varian CP-4900 micro GC and laptop set up during testing on commercial rig 1

The gas to be analysed must be a non-condensing gas with a temperature between 0 and 40 °C with a maximum input pressure of 200 kPa. Readings were taken and recorded approximately every 2 minutes before being exported to an Excel spreadsheet for data analysis. Although the micro GC measured a much greater range of gases, it cannot work continuously therefore limiting the number of recordings possible during each pyrolysis run. This could lead to some peaks or alterations in gas composition not being recorded although when used alongside the Rosemount analyser the time of peak gas composition can be established and it can be ensured that the micro GC is set to record at that exact time. When used together in this way, a fuller understanding of the composition of the output gas can be established. As with the Rosemount analyser, the results from preliminary testing were used to estimate the maximum and minimum values of these gases. The micro GC was calibrated at the beginning and end of every pyrolysis experiment using a calibration gas for the maximum values and was set to zero using a N_2 purge through the analyser.

3.3 PRELIMINARY TESTING

Preliminary testing of the laboratory scale pyrolysis reaction rig was undertaken to enable greater understanding of the performance of the rig as well as the effects of the main mechanisms of pyrolysis. The aim of this preliminary investigation was to highlight any areas needing improvement on the rig as well as to establish the range of variables to be tested within the main study, the optimum experimental procedures, data collection and analysis. Tests were firstly carried out using charcoal as fuel, due to its low volatile content, to enable the rig to be tested under relatively simple conditions. Following this, all fuel types were tested to establish any potential operating challenges, such as excess tar production leading to blockages. The potential ranges for gas production (maximum and minimum as a percentage of the output flow rate) were also established in order to calibrate both gas analysers with calibration gases suitable for these outputs.

The ranges for pyrolysis temperature and residence time were investigated in order to establish when optimum gas production occurs and also to highlight any areas of interest for further investigation. The particle size and sample size was also investigated to discover how a variety in these would affect the process and to decide the optimum particle and sample size to be used in experiments for the greatest gas production as well as for reliability, repeatability, practicality and safety reasons.

This preliminary testing was used to ensure that the proposed equipment set up, experimental procedures, data collection and analysis provided the required answers to the research questions. Following these preliminary investigations, the pyrolysis behaviours of a range of MSW components were investigated. Using the laboratory data collected, empirical model were developed for pyrolysis, based on the main process mechanisms.

3.3.1 SAMPLE SELECTION

3.3.1.1 MSW COMPONENTS

Preliminary testing was undertaken using charcoal for the majority of tests in order to investigate the behaviour of the reaction rig. Charcoal was used for these initial tests due to its low volatile content, therefore allowing testing of the reaction rig under simple conditions without any problems due to excess tar production. Tests were then run on the other MSW components to be used in the main investigation to establish any problems such as tar build up and blockages, as well as allowing an estimation of the volume and composition of gas produced. It was found that fuel type had a significant effect on the process mechanisms and products. It is therefore imperative that each MSW component sample used is as uniform as possible for all tests. All samples must be taken from the same source and exact same type of each component.

3.3.1.2 SAMPLE SIZE

The affect of sample size was investigated using samples of 2 g, 5 g and 10 g for each MSW component. After pyrolysis of 10 g samples, a significant variation could be seen along the length of the sample. This is attributed to the inlet gas cooling the sample at the inlet end of the sample boat. This is shown in Figure 3.9 with part A showing a 10 g sample and part B showing a 5 g sample. Using a thermocouple to test the temperature profile of the furnace, a slight variation in temperature due to cooling of the inlet gases was confirmed. Tests were repeated with 5 g samples placed in only half the sample boat furthest away from the gas inlet. This allowed for a more uniform temperature profile, as shown by tests using a thermocouple, across the sample. The scales used to measure the mass of samples had an accuracy of +/- 0.001 g, this is discussed in section 3.7.1.

However, tests with textile samples were found to produce a high volume of viscous tar which rapidly blocked up the gas outlet pipe from the furnace before reaching the tar trap system. To avoid this problem, a smaller sample size of 2 g waste was tested. The average residence time for tests with samples of 2 g were found to be too short for adequate gas analysis results using the micro GC, as readings from this could only be taken at 2 minute intervals as described in section 3.2.3.2. However, a sample size of 2 g did allow for gas analysis of textile samples without blocking of the gas outlet pipe. It was therefore decided to use a sample size of 5 g for all investigations, expect for textile samples when a sample size of

2 g was used. Although this does compromise the accuracy of comparing results for textile samples with results of other MSW component samples, it still gives a good indication of the behaviour of the component and the composition of the gas produced.

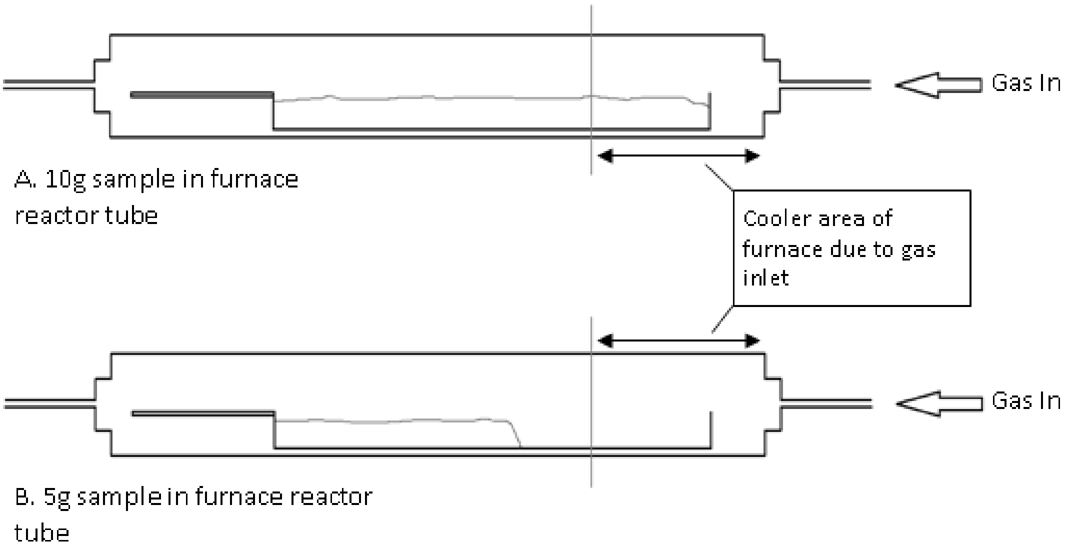


Figure 3.9: A schematic showing the positioning of the sample within the sample boat in the furnace reactor tube

3.3.2 TEMPERATURE

Preliminary testing of pyrolysis was undertaken using charcoal and paper samples at a range of temperatures from 300 °C to 900 °C at 100 °C intervals. It was found that pyrolysis at 300 °C and 400 °C was significantly slower than pyrolysis at higher temperatures and a low overall reduction in mass. The longer run time needed for pyrolysis at these low temperatures would lead to a fewer number of investigations possible due to the time constraints of this study. The low reduction in mass of these temperatures also indicated that there were limited pyrolysis reactions occurring. Pyrolysis at 800 °C and 900 °C led to a significant decrease in the residence time needed for the completion of pyrolysis reactions and an increase in the reduction in mass and therefore an increase in either the liquid or gaseous products. However, the shorter run time for pyrolysis at these higher temperatures caused problems in the accurate analysis of the gas composition as it was difficult to accurately record the rapidly changing composition that occurred, especially at the point of peak production of CO, CO_2 and H_2. Following this it was decided to use two main temperatures for pyrolysis testing of all MSW components. These temperatures were 550 °C and 700 °C. The choice of these temperatures is discussed in section 0.

3.3.3 RESIDENCE TIME

Preliminary testing was undertaken to investigate the mass loss during pyrolysis at 5, 10, 30 and 50 minutes. From this it was decided that it was not needed to test fuels after 30 minutes as reactions were complete and there was no further mass loss. Therefore, for mass loss experiments, residence times of 5, 10 and 30 minutes were chosen to be investigated.

For gas analysis investigations, samples were left to pyrolyse until the production of CO fell below 0.05 % on the Rosemount analyser in order to establish the behaviour of each fuel over the full reaction time. Any gas produced after this point was found to be minimal and therefore had a negligible effect on the final results. It was found that all MSW components investigated in this study completed pyrolysis reactions within a residence time of 20 minutes. All gas analysis investigations were therefore undertaken for a residence time of 20 minutes.

3.3.4 INSTRUMENTATION AND RIG DESIGN

During preliminary testing, the pyrolysis reaction rig and all other equipment was tested fully in order to highlight any improvements needed and also to establish any adjustments needed to either the instrumentation or the operating procedure. This was done to maximise the accuracy of results as well as to ensure ease of use and sufficient safety procedures. Preliminary testing was also used to ensure the reaction rig set up could be used to provide the required answers to the research questions and aims of this investigation.

Thermocouples were used to establish the temperature profile through the furnace. It was found that the gas entering the furnace had a cooling effect at that end of the sample boat so it was decided to place samples away from this end where the temperature profile was more uniform. The temperature of the outlet gases was also measured to establish if a gas cooling system was needed. The gas at the exit of the furnace was found to have a temperature of 60 °C and rapidly cooled to approximately 30 °C at the beginning of the tar trap system as the gas entered solvent bottle 1. By the end of the tar trap system the gas was at approximately room temperature and well within the specifications of 0-40 °C needed before entering the gas analysers. The reaction rig and gas pipe work were tested for any air ingress by passing a known calibration gas through the system and comparing with results from the gas analyser at the gas outlet. Any leaks were then found and fittings adjusted until the rig was airtight.

Preliminary testing was also undertaking using each of the MSW component samples under a range of conditions in order to establish an estimate of the volume and density of tar produced and any affect this had on the instrumentation or rig design. For some of the samples, mostly plastics, textiles and food waste, a high volume of tar was produced which highlighted problems with the tar trap system. For these samples, an extra bottle of IPA was needed to ensure the gas was cleaned sufficiently before entering the gas analysers. For food waste samples, an extra bottle of silica gel was used due to the high moisture content of the sample, to ensure no moisture reached the gas analysers. The affect of the tar trap system on the composition of the output gas was also established during preliminary testing. A known calibration gas was passed through the furnace with the tar trap system in place and again without it in place. No difference was found in the composition of the output gas which matched the composition of the input calibration gas. It was therefore concluded that the tar trap system would not affect the gas analysis results. This is discussed further in section 3.7.3.

The experimental operating procedure was also tested to ensure maximum accuracy, repeatability and reliability of results whilst ensuring safety. The final Safe Operating Procedure and Risk Assessment can be found in Appendices IV and V respectively.

3.4 SAMPLES AND VARIABLES

3.4.1 MUNICIPAL SOLID WASTE COMPONENTS

Eight components of MSW were selected for testing in this study based on the composition of MSW as shown in section 1.2.2. These components were: paper, newspaper, cardboard, PET (plastic drinks bottles), PVC (plastic sheet), HDPE (plastic milk bottles), textiles (50 % cotton, 50 % polyester) and an example of organic waste (raw potato). For all pyrolysis runs a sample size of 5 g was used expect for the pyrolysis of textiles samples as discussed in section 3.3.1.2. All MSW component samples were cut to an average size of 4 x 35 mm. This size was chosen as it is the same size as that produced by a standard cross-cut paper shredder. This allowed for simple processing of samples as well as being representative of the size of the waste that was pyrolysed in commercial rig 2. Paper, newspaper, cardboard, PVC, PET and HDPE samples were cut to size using a Q-Connect Q6CC cross cut paper shredder. Textiles samples were cut by hand and food waste samples were grated using a standard sized kitchen cheese grater. The accuracy of the size of samples as well as the source of each component is discussed in section 3.7.1.

Table 3.1: MSW components used in this study

MSW Component	Description
Paper	Office printer paper. Plain white, no ink. All samples from the same packet of paper.
Newspaper	Standard tabloid newspaper. All samples taken from the same paper.
Cardboard	Standard corrugated cardboard. No ink, labels or tape. All samples taken from the same cardboard box.
PET	Clear PET drinks bottle. No labels. All samples taken from the same bottle.
HDPE	White HDPE milk bottle. No labels. All samples taken from the same bottle.
PVC	PVC blow up lilo. No edges or seams. All samples taken from the same lilo.
Textiles	50 % polyester, 50 % cotton bed sheet. All samples taken from the same sheet.
Organic Waste	Raw potato. Samples taken from different potatoes of the same variety, freshly grated for each experiment.

3.4.2 TEMPERATURE RANGES

Following preliminary investigations it was decided to use two main temperatures for pyrolysis testing. These temperatures were 550 °C and 700 °C. This allows for comparisons with commercial rigs tested in this study as commercial rig 1 operates at approximately 550 °C and it is predicted that commercial rig 2 also operates at approximately this temperature. This is within the range for typical pyrolysis temperatures for the pyrolysis of MSW of 500-550 °C as reported by Chen et al [113]. It was also reported that at temperature of 700 °C and above the production of gas became more favourable. Therefore, all eight samples will be investigated at a pyrolysis temperature of 550 °C. Two samples of paper and PET, in order to represent the paper and plastic fractions of MSW, will also be pyrolysed at 700 °C. This is to give an indication of the effect of an increase in temperature on the pyrolysis process of these samples.

For mass loss investigations, paper has been tested at 300-900 °C at 100 °C intervals. This is same as preliminary testing undertaken using charcoal as a fuel which has been reported in the results alongside MSW components in chapter 4. Newspaper and cardboard were tested at temperatures of 550 °C, 625 °C and 700 °C. As the reduction of mass during pyrolysis was not the main objective of this study, the mass loss of al samples was not investigated. The accuracy of temperature measurements is discussed in section 3.7.2.

3.4.3 RESIDENCE TIME

For mass loss investigations a residence time of 5, 10 and 30 minutes were used. This can then be compared to the analysis of the raw fuel sample to give the reduction of sample mass with time at different temperatures. Following preliminary testing it was decided that it was not needed to test fuels after 30 minutes as the majority of reactions were complete and there was no further mass loss. For gas analysis investigations at 550 °C, the pyrolysis residence time was set at 20 minutes for all components. During preliminary testing it was established that there was negligible gas production after this time. For investigations at 700 °C, the pyrolysis of samples was left to continue until the production of CO fell below 0.05 % on the Rosemount analyser. After this point there was negligible gas production.

3.5 DATA COLLECTION

3.5.1 FUEL SAMPLE ANALYSIS

The results for fuel sample analysis investigations are presented and discussed in section 4.2. The errors and repeatability of these tests is discussed in 4.8.1. Numerical values are shown in Appendix VI.

3.5.1.1 PROXIMATE ANALYSIS

Raw fuel samples were characterised using proximate analysis to determine the moisture, ash, volatile matter and fixed carbon contents. Pyrolysed samples were also tested in the same way to determine volatile content after pyrolysis. This was carried out according to the following standards: BS ISO 17246:2010, BS ISO 3451-1:2008, BS ISO 2144:1997, BS ISO 638:2008. Standards were not available for all fuel types, where this was the case a standard for a similar fuel type has been used. For each of the proximate analysis tests, 1 g of each fuel sample was used. Each test was repeated three times and an average taken of results for each fuel sample.

For moisture tests, the sample was placed in an open crucible in a closed furnace at 105 °C for one hour. The mass lost during this is the evaporated moisture which is calculated by the difference in sample mass before and after. For ash tests, samples were placed in open crucibles in a closed furnace at a temperature and for a time specified in the above standards for each fuel to burn the sample until only ash remains. The ash content of the sample was then calculated by mass remaining of the sample. The volatile matter was established by placing samples in a closed crucible in a closed furnace at a temperature and for a time specified in the above standards for each fuel in order to only burn off the volatile matter. The volatile matter was then calculated by mass lost from the sample. The fixed carbon was calculated as the remaining mass of the original sample once the ash, moisture and volatile content have been subtracted.

3.5.1.2 TOTAL CARBON

A Leco CR144 Carbon and Sulphur analyser was used to measure the total C within each fuel sample. A sample of 0.35 g was placed in an open crucible within the Leco analyser furnace. The sample is combusted at 1350 °C in an O_2 rich atmosphere and any C present is converted to CO_2. The gas from the sample then flows into a non-dispersive infrared (NDIR) detection cell which measures the mass of CO_2 present. This mass is then converted to the percent of C based on the mass of the dry sample. The Leco analyser is controlled by an external PC using Windows based software. This software also calculates and presents the results.

3.5.1.3 CALORIFIC VALUE

The CV was established using a Parr Isoperibol 6200 Bomb Calorimeter. The Bomb Calorimeter measures the heat created by a sample when it is burned in an O_2 rich atmosphere in a closed O_2 bomb, which is surrounded by water, under controlled conditions. A sample of 1 g was placed inside the closed O_2 bomb within an insulating water jacket. The sample was ignited and combusted within the closed vessel and the heat created during this process transfers to the surrounding water. The temperature change of the water was recorded and from this the CV of the sample was calculated.

3.5.2 MASS LOSS AND PYROLYSIS PRODUCTS

The products from the pyrolysis of all MSW components were measured during pyrolysis investigations at 550 °C. Paper and PET were also investigated at 700 °C. Samples were pyrolysed for a residence time of 20 minutes or until the production of CO fell below 0.5 %. The gas flowing into the reaction rig and the gas out was recorded every minute using flow meters. As discussed above, the mass of the sample was recorded before and after each pyrolysis investigation in order to calculate the mass loss during the process. The mass of the sample boat, each bottle and piece of plastic tubing in the tar trap system and the exhaust pipe of the furnace was also recorded before and after each pyrolysis investigation to measure the mass of any tar produced. A visual description of the tar produced by each component was also recorded. Results for the mass reduction of samples are shown in section 4.3 and for pyrolysis products in section 4.4. The errors and repeatability of these tests are discussed in section 4.8.2 and section 4.8.3 and numerical values shown in Appendix VII.

3.5.3 GAS ANALYSIS

Gas analysis data was recorded for pyrolysis investigations at temperatures of 550 °C and 700 °C using both the Rosemount analyser and the micro GC described in sections 3.2.3.1 and 3.2.3.2 respectively. As the Rosemount analyser provides continuous gas analysis, data was recorded manually every 30 seconds. Data from the micro GC was recorded automatically by the PC based software every 2 minutes. The results for gas analysis investigations can be found in section 4.5. The errors and repeatability of these tests are discussed in section 4.8.4 and numerical values can be found in Appendix VIII.

3.5.4 SUMMARY OF EXPERIMENTS

Table 3.2: Summary of experiments undertaken with each MSW componentTable 3.2 shows a summary of all experiments undertaken in this study for each of the eight MSW components. Investigations into the mass loss of charcoal during pyrolysis have also been included.

Table 3.2: Summary of experiments undertaken with each MSW component

Experiment	Temperature, °C	Charcoal	Paper	Newspaper	Cardboard	PET	HDPE	PVC	Textiles	Food waste
Mass loss	300	x	x							
	400	x	x							
	500	x	x							
	550	x	x	x	x					
	625	x	x	x	x					
	700	x	x	x	x					
	800	x	x							
	900	x	x							
Pyrolysis Products	550		x	x	x	x	x	x	x	x
	700		x			x				
Gas Analysis	550		x	x	x	x	x	x	x	x
	700		x			x				

3.6 TESTING ON COMMERCIAL RIGS

3.6.1 COMMERCIAL RIG 1: MICRO SCALE BATCH PYROLYSER

Testing was undertaken using commercial rig 1 which is described in section 1.4.1. The aim of this trial was to quantify the composition of the product gases produced by the system and investigate how this changes for different components of MSW. Run 1 was undertaken using 100 % cardboard waste. This allowed for direct comparisons with laboratory data for the pyrolysis of a single MSW component. Following this, run 2 was undertaken using a waste mixture of 33 % cardboard and 66 % PET in order to establish the effects of a simple mixed waste sample with just 2 MSW components to give an indication of the possible interactions of both components and its effect on the pyrolysis process. This also allowed for comparisons with data predicted using the empirical model developed based on laboratory results for a simple waste mixture. The fuels for both runs are shown inside the pyrolysis chamber before each run in Figure 3.10.

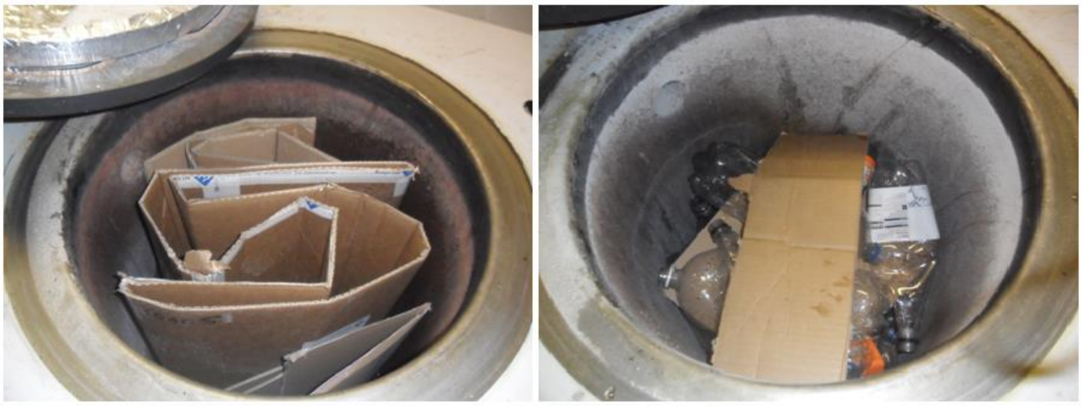


Figure 3.10: Photographs of the cardboard for Run 1 (left) and cardboard and PET for run 2 (right) in the pyrolysis chamber of commercial rig 1

The rig produces solid, liquid and gaseous products. This investigation focuses solely on the produced gas with the aim of comparing data to that found in laboratory investigations. The objectives of these on-site tests were to quantify the composition of the produced gas before it entered the catalyst.

3.6.1.1 INSTRUMENTATION

The tar condensate trap system used for commercial rig tests was the similar to that used in laboratory investigations as described in section 3.2.2 with the addition of a cooling unit and additional Dreschel bottles containing IPA. This was due to the higher volume of tar expected in commercial rig tests due to the higher mass of waste and the longer running time of investigations and to therefore ensure sufficient tar removal.

Product gas was sampled with a static tapping at the gas out-flow of the pyrolysis chamber. The sample then passed into a liquid removal section where it was cooled to -18 °C in IPA, forcing the condensation and removal of liquids in the gas stream. This included any moisture and organic liquids present. The tar trap system, shown in Figure 3.11, consisted of

3 Dreschel bottles of 250 ml capacity. Bottles were filled with 80 ml each of IPA. Further bottles, 1 with IPA, 2 filled with silica gel and 1 empty, as shown in Figure 3.12, were used to capture any remaining liquids in the gas stream. This empty Dreschel bottle was used for visual checks of the gas to ensure it was sufficiently clean before entering the micro GC. All Dreschel bottles and piping were cleaned thoroughly in between runs using IPA and water and the IPA and silica gel was replaced.

The cleaned gas was then drawn through a pump which controlled the rate of gas flow through the system. The pump provided a negative pressure to draw the sampled gas through the system. The module consisted of a flow meter valve and a positive displacement pump. The remaining cleaned, moisture free gas was analysed using the micro GC system described in section 3.2.3.2.

Figure 3.11: A photograph of the three Dreschel bottles inside freezer with 80 ml of IPA collecting tars during run 2

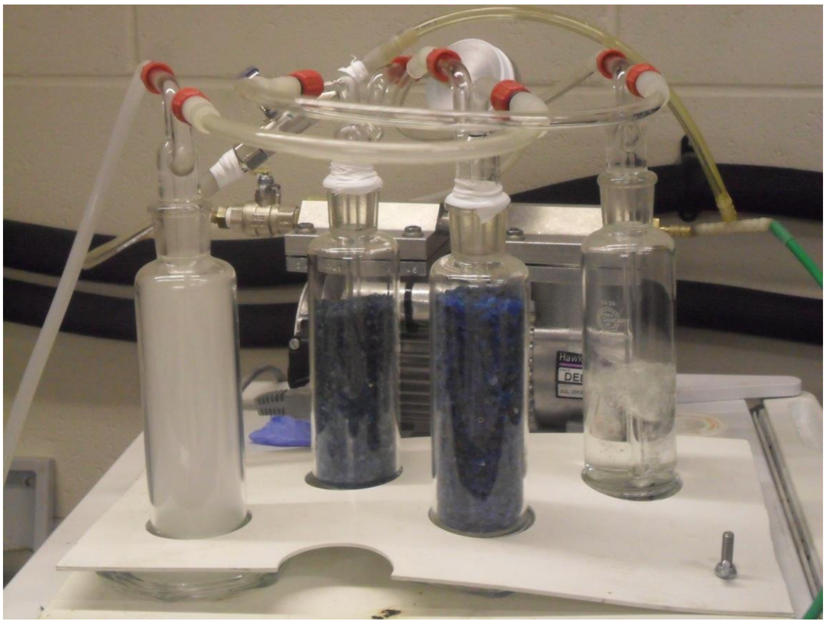


Figure 3.12: A photograph of the Dreschel bottles with IPA and silica gel outside the freezer during run 1

3.6.1.2 DATA COLLECTION

The product gas was analysed using the micro GC at approximately 2 minute intervals throughout the entire run of the rig system. The micro GC was calibrated every 30 minutes using the calibration gas stated in section 3.7.4.1. The control system of the rig recorded the temperature of the pyrolysis chamber as well as the flow rate of air into the chamber. Results are shown in section 4.6 and comparisons with predictions made using the empirical model based on laboratory data are shown in Section 5.2.3. Full numerical values are given in tabulated form in Appendix IX.

3.6.2 COMMERCIAL RIG 2: SMALL SCALE SEMI-BATCH PYROLYSER

Testing was also undertaken using commercial rig 2 which is described in section 1.4.2. As with the trial on commercial rig 1, the aim was to quantify the composition of the product gases produced by the system with the aim of comparing data to that found in laboratory investigations. Testing was undertaken using the following MSW mix:

Paper:	30 % mass
Cardboard:	40 % mass

- Plastics: 20 % mass
- Textiles: 10 % mass

3.6.2.1 INSTRUMENTATION

The analysis hardware and tar trap system set up for these on-site tests were identical to that used in on-site tests with commercial rig 1 as described in section 3.6.1.1. The product gas was analysed at the point at which the gas leaves the pyrolysis chamber.

3.6.2.2 DATA COLLECTION

The produced gas was analysed using the micro GC once the system was in stable operation with 10 samples analysed at each sample point. The micro GC was calibrated every 30 minutes using the calibration gas stated in section 3.7.4.1. The temperature of the pyrolysis chamber was not recorded although it was estimated to be approximately 550 °C during stable operation. Results are shown in section 4.7 and comparisons with predictions made using the empirical model based on laboratory data are shown in section 5.2.4. Full numerical values are given in tabulated form in Appendix X.

3.7 DISCUSSION OF ERRORS AND ACCURACY OF INSTRUMENTATION

During all investigations, the accuracy and reliability of results and the minimisation of errors were an important factor. In this section, the accuracy of all instrumentation used is discussed along with details of the minimisation of errors. Further discussion of errors along with a detail discussion and analysis of the validity and repeatability of results presented in this study can be found in section 4.8.

3.7.1 MUNICIPAL SOLID WASTE SAMPLE SELECTION

Preliminary testing showed that fuel type has a great effect on the pyrolysis processes. Therefore, it was ensured that each of the MSW component samples used in this study were from the same source and as homogeneous as possible. For laboratory investigations, all paper samples came from the same packet of computer printing paper, all newspaper samples were from the same newspaper and all cardboard samples were from the same corrugated cardboard box. For PET and HDPE components, the samples came from drinks bottle and milk bottle respectively. PVC samples came from the same plastic sheet and textiles samples from the same sheet of fabric. For food waste samples, a wide variety of components were available however, raw potato was chosen. This was not dried before pyrolysis so all potato samples were grated and placed straight into the sample boat for pyrolysis to prevent any drying in air occurring.

All samples were cut to the same size of approximately 4 x 35 mm and a sample size of 5 g was used for all tests apart from for textile samples when a sample size of 2 g was used. Paper, newspaper, cardboard, PET, HDPE and PVC samples were all cut using the same paper shredder. This was found to have an accuracy of +/- 0.1 mm. Textiles samples were cut by hand. This had a much lower accuracy of approximately +/- 2 mm. Potato samples were grated using a standard kitchen cheese grater. The width of these samples had a high accuracy of approximately +/- 0.5 mm, however the measurement of the length of the samples was found to vary by approximately +/- 5 mm. The scales used to measure the mass of samples as well as mass of sections of the tar trap system before and after pyrolysis had an accuracy of +/- 0.001 g.

As discussed previously, the composition of MSW is extremely heterogeneous. As well as this, each component can vary considerable in composition for example; the paper sample used in one study could vary in composition significantly compared to paper samples used in another study. This variety in composition is of even more importance for plastic samples which could vary due to different fillers used in the production process, and for food waste samples where there is a very wide range of types of food waste. To aid comparisons between previous works, as discussed in section 2.3, a list has been compiled of all reported proximate and ultimate analysis as well as the CV of the MSW components similar to those used in this study. This is shown in Appendix I. The repeatability of proximate analysis, total carbon and CV results in this study is discussed in section 4.8.1. Numerical values of these repeats can be found in Appendix VI.

3.7.2 THE PYROLYSIS REACTON RIG

During preliminary investigations, it was established that the pyrolysis reaction rig must be cleaned between investigations. This was due to build up of liquid tars inside the reactor tube. If these tars were not cleaned, and increase in temperature or the addition of air led to further thermal degradation of these liquid products and therefore gases produced. Before and after each investigation, N_2 was flowed through the heated pyrolysis reactor tube with no sample in place. The gas from the outlet of the furnace was analysed to ensure no gases other than N_2 were detected. If no other gases were detected it was deemed that no cleaning was needed. If other gases, usually CO or CO_2, were detected the rig was cleaned and the process repeated until no other gases were detected by the analysers. The reaction rig was also cleaned at the end of every day of testing. The rig was cleaned by increasing the temperature to 1000 °C and introducing O_2 into the reactor tube, this combusted any liquid or solid products remaining in the reactor tube. The reactor tube was also visually inspected between each run and the sample boat cleaned using IPA to dissolve any remaining tars.

The exact temperature of the inside of the reactor tube was established during preliminary testing using a thermocouple placed at the centre of the reactor tube. It was found that the reactor tube temperature was 40 °C lower than the set temperature when the set temperature was 550°C and 50 °C lower when the set temperature was 700 °C. The temperature stated elsewhere in this study is therefore the actual temperature of the reactor tube and the set temperature was increase accordingly. The temperature of the pyrolysis reactor tube was check at the beginning of each day of testing as well as whenever the set temperature was altered. As discussed in section 3.3.1.2, the inlet flow of N_2 caused some cooling of the reactor tube by the gas inlet. A small variation in temperature of approximately 30-40 °C was found with a gas flow of 0.6 l/min. This was investigated by recording the temperature at difference points across the length of the reactor tube with a range of flow rates of the input gas. With no gas flow, no temperature difference was recorded apart from in the last 5 cm of the reactor length. At a higher gas flow of 1 l/min, a larger temperature difference of 60-70 °C was recorded. The effect of this was minimised by placing the sample away from the gas inlet were a more uniform temperature profile was recorded.

To ensure there were no gas leaks within the reaction rig and pipe work system experimental runs were undertaken with the furnace turned off and with no fuel sample. Calibration gases were passed through the reaction rig system and the gas analysers were used to ensure the gas outlet was the same as the input calibration gas with no air contamination. This process was repeated once a week during testing and also whenever any adjustments were made to the reaction rig to make sure no leaks were present and therefore no contamination of the gas analysis data during experiments. The pyrolysis reaction rig was also tested in this way before and after each investigation with the pyrolysis reaction rig heated up. This was to ensure there was no contamination from the previous investigation present in gas analysis results for the next. Details of calibration gases can be found in section 3.7.4.1.

3.7.3 TAR TRAP AND GAS CLEANING SYSTEM

The affect of the tar trap system on the composition of the output gas was also established using preliminary testing. Calibration gases were passed through the furnace and compared to the composition of the output gases measured using the gas analysers with the tar trap in place and then without under the same conditions. No difference was found in the composition of the output gas, which was found to match the known composition of the input calibration gas. It was therefore concluded that the tar trap system would not affect the gas analysis results.

The tar trap was also tested in this way with an extra bottle of IPA in place before Bottle 1 to establish any affect this had on the gas analysis data as this extra bottle was needed for the plastic samples under some conditions to ensure the gas was sufficiently clean to prevent damage to the gas analysers. No change in composition or volume of gas was found with the bottle in place or without so this does not affect the accuracy of results.

In order to ensure that there were no losses in the tar trap system through evaporation of IPA, the masses of all parts of the tar trap system were recorded before and after a time of 20 minutes with no sample in the furnace, which was heated to 550°C. This was repeated for investigations with samples of paper, newspaper, cardboard and PET. It was found that any mass loss from IPA in the first two bottles was collected in the silica gel of the third bottle. Results for this are shown and discussed in section 4.8.3.1.

3.7.4 ROSEMOUNT AND MICRO GC GAS ANALYSERS

Both gas analysers used in this study had specific requirements in order to maintain accuracy of gas analysis. For both, the sampling gas was required to be between 0 °C and 40 °C. A thermocouple was used to measure the temperature of the gas at the point at which it left the tar trap system before it reached the analysers. This was found to be approximately

15-18 °C dependant on room temperature therefore no gas cooling system was needed and it may be assumed that the temperature of the exit gas has negligible effect on its composition.

The micro GC required an environment with less than 95 % humidity and a temperature of 0-50 °C. This was only a potential problem during testing on commercial rig 1 where no heating was available and testing was undertaken during adverse weather conditions. The temperature of the area surrounding the micro GC was monitored throughout investigations and was found to be between 3 and 5 °C and therefore within the operating conditions of the micro GC. During laboratory investigations the temperature of the area surrounding the micro GC varied from approximately 10 – 20°C and during testing on commercial rig 2 was approximately 18 °C. The micro GC has a percentage error of less than 0.5 % for C_3H_8 at a level of 1 mol %. The Rosemount analyser also had an accuracy of +/- 0.5 % of the full scale of gas at a constant temperature. Further discussion of the errors involved in gas analysis results and the repeatability of investigations can be found in section 4.8.4.

3.7.4.1 CALIBRATION GASES

The Rosemount gas analyser was calibrated daily and the micro GC analyser calibrated before and after each run using certified calibration gases obtained from Scientific and Technical Gases Ltd. Using results from preliminary testing, the maximum and minimum values of H_2, N_2, CO, CO_2, O_2, CH_4, C_2H_6 and C_3H_8 for various MSW component samples and process variables were estimated. The calibration gases used were based on these minimum and maximum values. Maximum and minimum calibration gases from BOC were used to calibrate the Rosemount gas analyser; these were calibration gas 1 and 2. A calibration gas from Scientific and Technical Gas Ltd. was also used to calibrate the micro GC analyser; this was calibration gas 3. All calibration gases had a balance of N_2 and were certified with an uncertainty of +/- 5 %. The composition of these calibration gases are shown in Table 3.3. Both analysers were also set to zero as part of each calibration using a N_2 purge through the reaction rig. Both analysers were calibrated before and after every investigation. During tests on commercial scale rigs, the micro GC was calibrated every 30 minutes during investigations as well as before and after testing. Safety data sheets for these calibration gases can be found in Appendix III.

Table 3.3: Calibration gas composition, vol. %

Gas	Calibration Gas 1	Calibration Gas 2	Calibration Gas 3
CO	0.1	4	15
CO_2	1	15	15
O_2	1	20	-
H_2	-	-	15
CH_4	-	-	5
C_2H_6	-	-	2
C_3H_8	-	-	2

3.8 SAFETY

All tests were undertaken under strict safety conditions. The following personal protective equipment was worn for all pyrolysis tests, as detailed in these appendices; laboratory coat, welding gloves, safety goggles, and steel toe capped boots. Safety information for IPA can be found in Appendix II and for calibration gases in Appendix III. The safe operating procedure for laboratory tests can be found in Appendix IV. A risk assessment for laboratory tests can be found in Appendix V.

For commercial rig tests extra care was taken to ensure the safety of all personnel and equipment involved as these tests were off-site on previously unmeasured apparatus. Tests were planned thoroughly with staff operating both commercial rigs before the commencement of any measurement to ensure appropriate safety procedures were in place. As for laboratory investigations, personal protection equipment was worn. Risk assessments for off-site tests at both commercial rigs are shown in Appendices XI and XII.

3.9 SUMMARY

As discussed in previous chapters, further research is needed to establish the effect of different MSW components on the pyrolysis process and therefore predict the behaviour of each component during pyrolysis of mixed MSW in commercial scale rigs. A laboratory scale reaction rig has been used to obtain kinetic data of the pyrolysis process and investigations have been undertaken on two commercial scale pyrolysis rigs.

Eight components of MSW were chosen to give an indication of the effect of fuel type on the process at a pyrolysis temperature of 550 °C. These components were: paper, newspaper, cardboard, PET (plastic drinks bottles), PVC (plastic sheet), HDPE (plastic milk bottles), textiles (50 % cotton, 50 % polyester) and food waste (raw potato). Mass loss during pyrolysis was also investigated for paper samples from 300-900 °C and for newspaper and cardboard samples at 500, 625 and 700 °C.

A horizontal tube furnace was adapted into a pyrolysis reaction rig with gas inlet and gas outlets fitted. A tar trap system was developed and fitted to the gas outlet to collect tar from the process and ensure the gas was clean enough before entering the gas analysers to prevent damage. Gas analysis data was collected at regular intervals throughout experiments. The CV, carbon content and proximate analysis of each MSW component was also established.

To maximise the accuracy and repeatability of experiments, it was ensured that all MSW component samples were from the same source, as homogeneous as possible and shredded or cut to the same size. All instrumentation and equipment was tested during preliminary testing and amended where needed in order to provide the most accurate and repeatable results. Data collection methods were also tested during preliminary testing and relevant British Standards followed for proximate analysis, total carbon and CV testing. Both gas analysers were calibrated regularly using appropriate certified calibration gases, and sampling conditions for both analysers were met, and correct operating procedures followed to ensure accurate and repeatable results.

The results obtained in these experiments have been used to create an empirical model with the aim of predicting the behaviour of larger commercial scale pyrolysis systems. All results and discussions of findings are shown in Chapter 4 along with discussion of errors and reliability, and mathematical modelling is shown in Chapter 5.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 INTRODUCTION

In this chapter the research findings obtained from the experimental study are presented and discussed. The results for the characterisation of the fuel samples are shown in section 4.2, with the results of effect of mass loss and pyrolysis products shown and discussed in sections 4.3 and 4.4 respectively. Following this the effect of fuel type, temperature and residence time on the composition of pyrolysis gas is discussed in section 4.5. The results from experimental studies on commercial rigs are shown, discussed and compared with laboratory experimental data in section 4.6 for commercial rig 1, and section 4.7 for commercial rig 2. This chapter also includes discussion of the reliability and repeatability of experimental results and sources of errors within the study in section 4.8. Further discussion of laboratory and commercial rig investigations can be found in Chapter 5 along with empirical modelling of laboratory data.

4.2 CHARACTERISATION OF MSW FUEL SAMPLES

For all fuel samples the moisture, ash, volatiles and fixed carbon content was found using the proximate analysis techniques described in section 3.5.1.1. The total carbon in each sample was found using the Leco CR144 Carbon and Sulphur analyser described in section 3.5.1.2 and the calorific value was found using the bomb calorimeter described in section 3.5.1.3. Discussion of repeatability and errors for these results are shown in Section 4.8.1. Numerical values of all repeats can be found in Appendix VI.

The proximate analysis of the samples is shown in Figure 4.1 and the total carbon and calorific value shown in Table 4.1. The proximate analysis of charcoal has also been included as this was used during preliminary testing for mass loss investigations. It can be seen that there is significant variability in the composition of each MSW component sample. The plastic samples of PET, PVC and HDPE have the highest percentage of volatiles, as do the textile samples due to the 50 % polyester content. Paper, newspaper and cardboard samples all have a similar composition and the highest percentage of ash compared to the other components. The food waste component was found to have the highest moisture content, as expected. It can be seen that charcoal has a significantly higher content of fixed carbon and significantly lower content of volatiles. It is for this reason that it was used for preliminary investigations in order to assess the performance of the reaction rig under simple condition with a low volatile fuel.

The homogeneity of these MSW component samples creates challenges for EfW processes. The high moisture content of the food waste component will release excess O_2 during pyrolysis. The higher ash content found in paper, newspaper and cardboard will lead to a greater mass remaining after the pyrolysis process as discussed later in this chapter. The high volatile content for the plastic samples and for the textile samples will have a significant effect on tar production as well as the rate of reactions during pyrolysis as described later in this chapter.

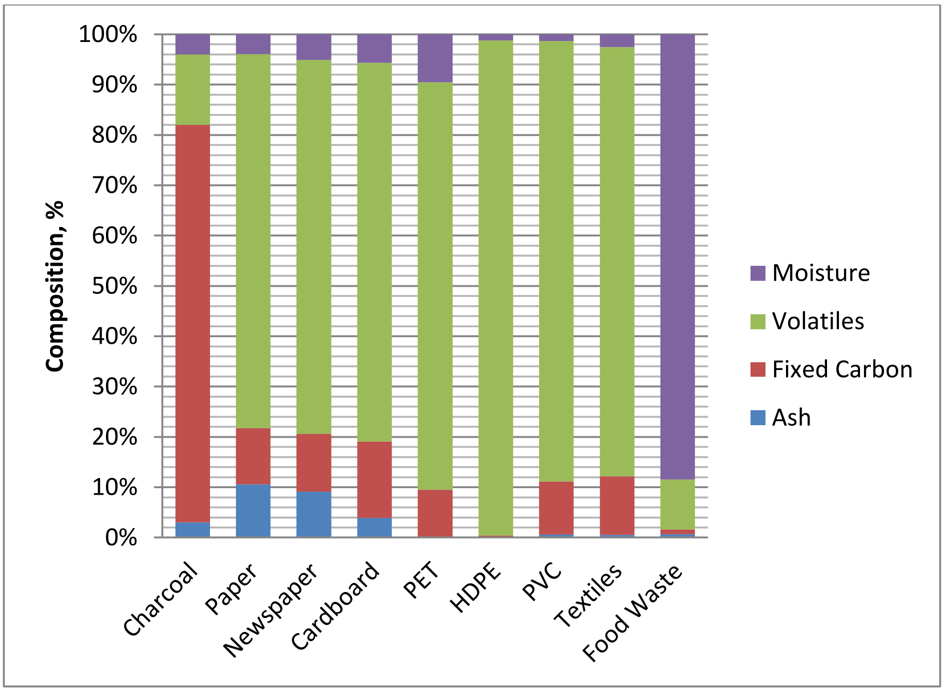


Figure 4.1: A graph to show the fixed carbon, moisture, ash and volatile content as a percentage of mass of raw samples

It can be seen in Table 4.1 that the plastics have the highest calorific value, followed by textiles. This is due to the 50 % polyester content of the textiles used in this study. All results shown are on a wet basis, apart from the total carbon and calorific value for the food waste sample which were done on a dry basis due to the significantly high moisture content. The proximate analysis, total carbon content and calorific value of samples used in this study has been compared to values stated in literature, this is shown in Appendix I along with ultimate analysis as found by various studies.

Table 4.1: Total carbon and calorific value of raw samples

	Total Carbon: %	CV: MJ/kg
Paper	29.17	12.90
Newspaper	32.20	15.49
Cardboard	31.58	16.20
PVC	40.10	44.15
HDPE	86.01	46.30
PET	63.12	46.20
Textiles	45.79	28.10
Food Waste (dry sample)	41.04	16.50

4.3 MASS LOSS

As paper, newspaper and cardboard have the highest ash content out of all MSW samples tested in this investigation it was decided to focus the investigation to mass loss of these three samples as these samples would have the greatest effect on the reduction of mass of MSW mixtures. These results were then compared with results for charcoal samples found during preliminary testing, hence using charcoal as a control sample, given its low volatile matter content. The mass loss of other samples during pyrolysis at 550 °C for 20 minutes is discussed in section 4.4.1.

The percentage of sample mass remaining at 5, 10, 30 and 50 minutes for 550 °C, 625 °C and 700 °C was found using the experimental methods described in section 3.5.2. The errors and repeatability of these results are discussed in section 4.8.2. Further analysis and empirical modelling of mass loss data can be found in Chapter 5.

4.3.1 EFFECT OF RESIDENCE TIME ON MASS LOSS

Figure 4.2 shows how the pyrolysis residence time affects the percentage of original sample mass remaining in the sample boat at 5, 10 and 30 minute intervals for 550 °C. Figure

4.3 shows data for the sample mass remaining at 625 °C and Figure 4.4 shows data for pyrolysis at 700 °C. For this data, 100 % represented the mass of the raw sample; this was 5 g for all mass loss experiments. The mass remaining of paper, newspaper and cardboard samples at each of the three temperatures was also recorded after 50 minutes and is shown in each of the respective graphs.

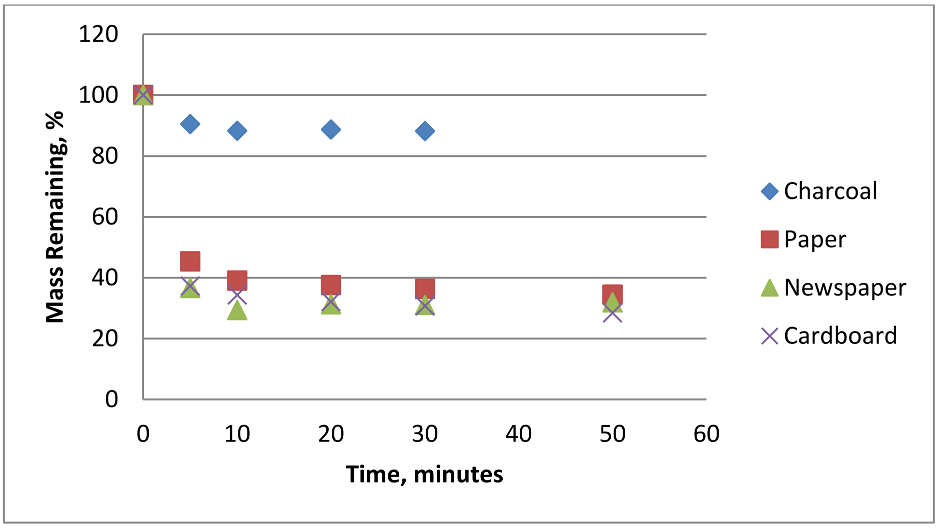


Figure 4.2: A graph of the change in percentage of mass remaining with time for samples pyrolysed at 550 °C

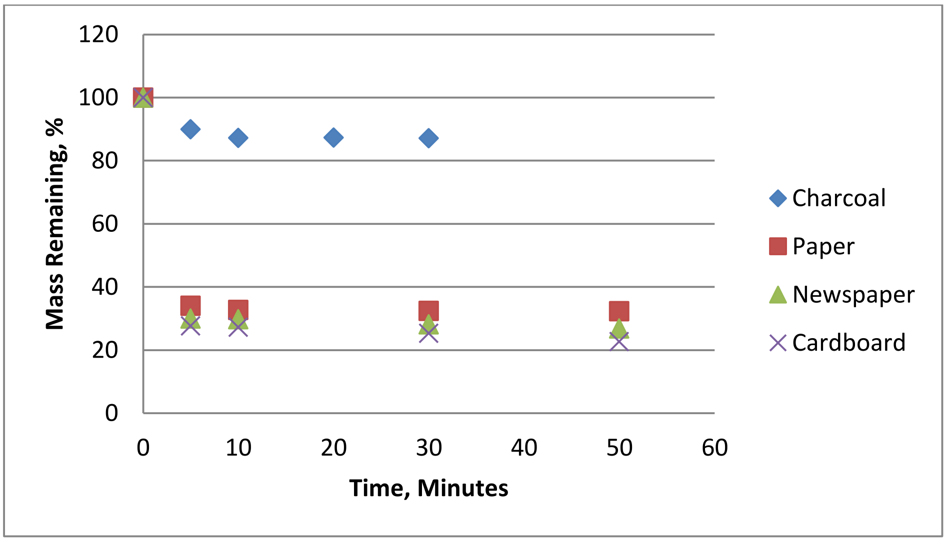


Figure 4.3: A graph of the change in percentage of mass remaining with time for samples pyrolysed at 625 °C

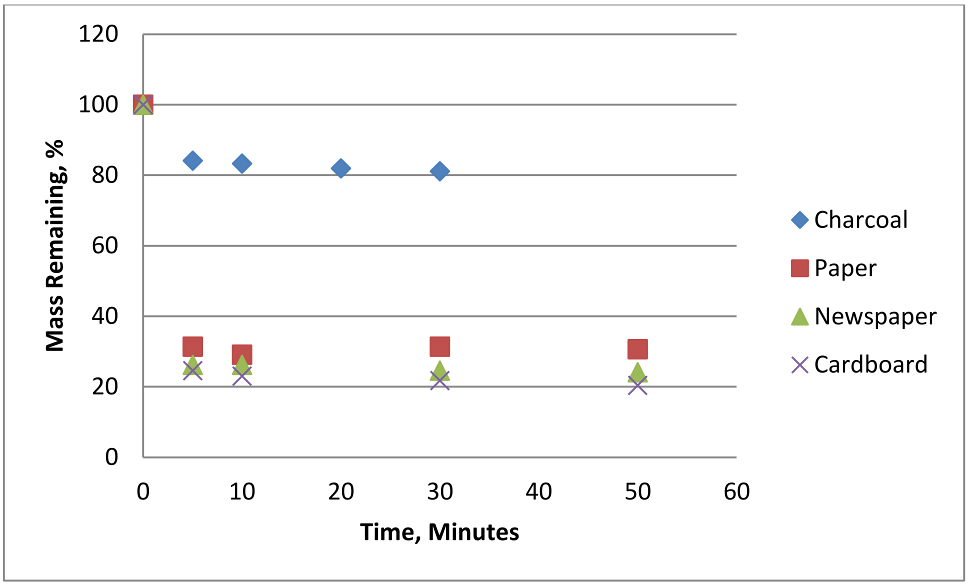


Figure 4.4: A graph of the change in percentage of mass remaining with time for samples pyrolysed at 700 °C

It can be seen that for all temperatures there is little change in the sample mass after 10 minutes and a rapid decrease in mass in the first 5 minutes of pyrolysis. This is also shown by gas analysis data, shown in section 4.5.1, as there is very little gas produced after 15-20 minutes of pyrolysis at 550 °C for all samples. These results are discussed further in section 5.1 where they are used to develop an empirical model.

4.3.2 EFFECT OF TEMPERATURE ON MASS LOSS

Figure 4.5 shows how the pyrolysis temperature affects the percentage of original sample mass remaining in the sample boat after 5 minutes of pyrolysis from 300-900 °C for paper and charcoal and from 550-700 °C for newspaper and cardboard. Figure 4.6 shows data for the sample mass remaining after 10 minutes and Figure 4.7 shows data for the sample mass remaining after 30 minutes. The data recorded for the mass loss of paper, newspaper and cardboard at 50 minutes is not shown as there was negligible difference compared with data for a residence time of 30 minutes. For this data, 100 % represented the mass of the raw sample; this was 5 g for all mass loss experiments.

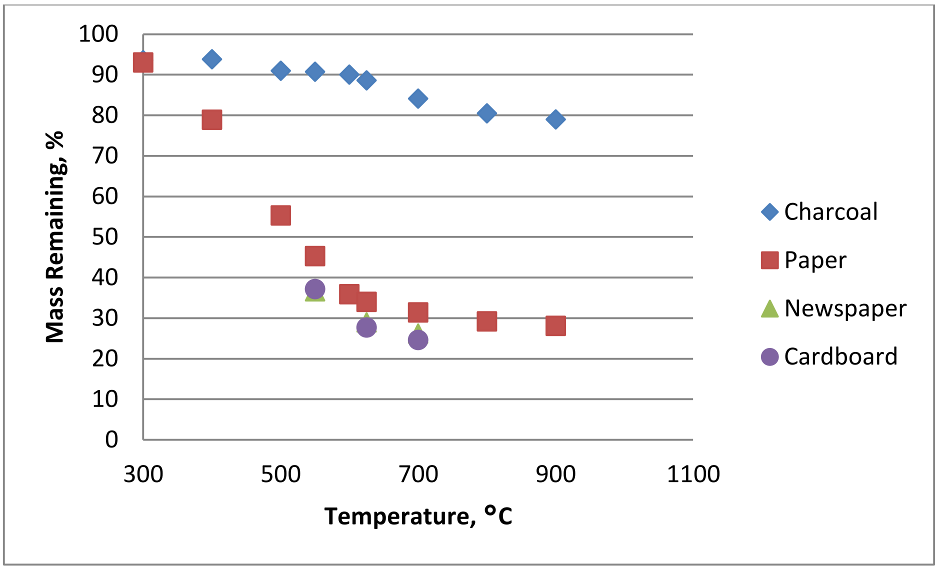


Figure 4.5: A graph of the change in percentage of mass remaining with temperature for samples pyrolysed for 5 minutes

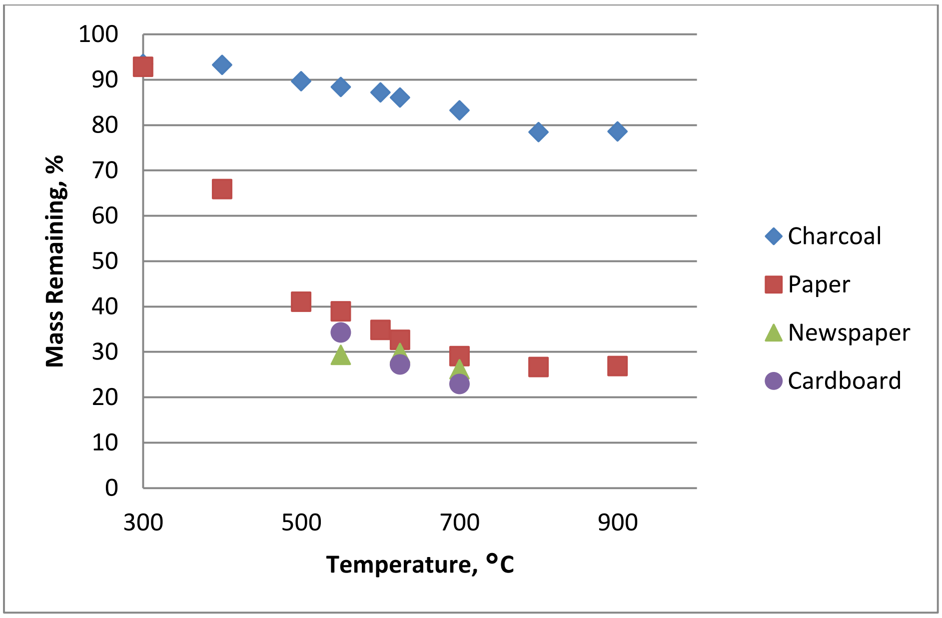


Figure 4.6: A graph of the change in percentage of mass remaining with temperature for samples pyrolysed for 10 minutes

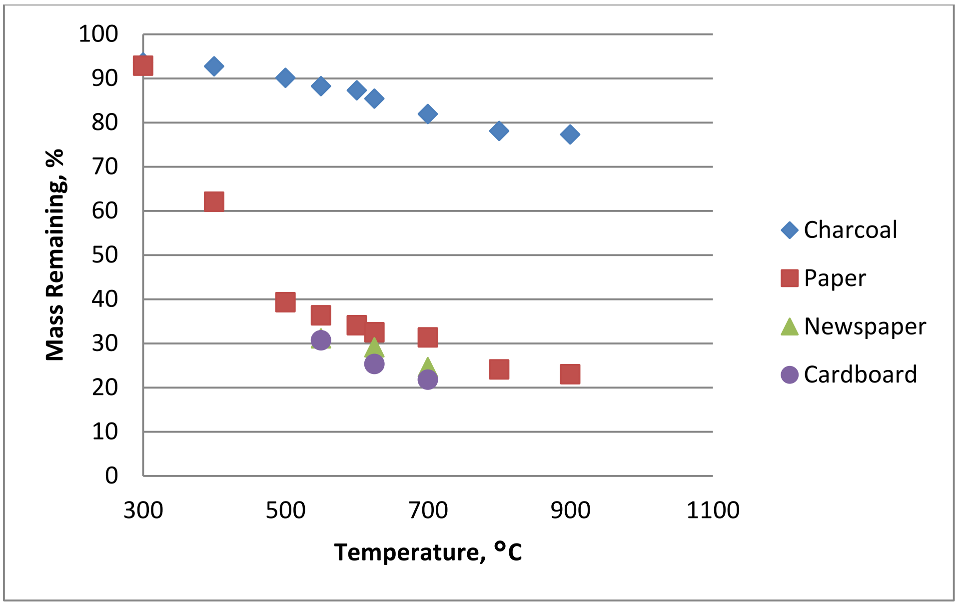


Figure 4.7: A graph of the change in percentage of mass remaining with temperature for samples pyrolysed for 30 minutes

It can be seen for all temperatures that there is little change in the sample mass above 800 °C and a rapid decrease in mass between 300 and 500 °C for paper, newspaper and cardboard samples. The mass remaining for each fuel sample for each pyrolysis time all follow a similar sigmoid trend. This sigmoid trend can be seen especially for charcoal. For paper it can be seen that the top curve of the sigmoid function occurs below 300 °C so does not appear on these graphs.

This sigmoidal trend is not comparable with TGA results as reported by various authors [23, 39, 43, 44, 50, 55, 57, 58, 66, 74-78]. TGA data shows a rapid loss of mass over a small range in temperature. Both Chen et al [23] and Singh et al [55] found the majority of mass loss from paper pyrolysis occurred between 300 and 400 °C. Results from this study show a more gradual loss in mass over a wide temperature range from approximately 300-800 °C. This is attributed to the larger sample mass used in this study and therefore the increase in time needed for heat transfer through the larger mass of the sample. This is comparable to the difference found between the mass loss of samples using TGA and a laboratory scale pyrolyser by Yang et al [97]. This is discussed further in section 4.4.2 along with discussion of the pyrolysis products and in section 5.1 where empirical models have been developed for the mass loss of paper, newspaper and cardboard in order to extrapolate laboratory results and predict mass loss behaviour at a range of pyrolysis temperatures and residence times.

Although the overall behaviour of the mass reduction during pyrolysis is not comparable, the initial temperature at which samples begin to lose mass, and therefore thermal degradation begins, is comparable with previous work. In a TGA study into the pyrolysis of paper by Wu et al, it was found that mass loss for paper samples began at a temperature of 214 °C although the percentage of mass remaining didn't drop below 99% until approximately 290 °C [57]. The sigmoidal trend for the mass reduction of paper as found in this study can be extrapolated for temperatures below 300 °C. The initial temperature of thermal degradation can be estimated at approximately 200-250 °C which is comparable with the temperature found by Wu et al. This is discussed further in section 5.1.1.

Data found in this study is also comparable to that found by Skreiberg et al [39] where it was found that 28 % of the original mass of 200 g of paper remained after pyrolysis up to 900 °C. In this study, the mass remaining of paper after pyrolysis at 900 °C was found to be 28.1 % for a residence time of 5 minutes and 26.9 % for a residence time of 10 minutes. Despite differences in the pyrolysis of samples as Skreiberg et al used a macro-TGA which heated the sample up at a slow heating rate than in this study and a larger sample size was used; this shows good compatibility between results.

The data found in this study has been used to create an empirical model to predict the percentage of mass remaining for any pyrolysis time from 0 – 50 minutes at any temperature between 300 and 900 °C. This is shown and discussed in Chapter 5 along with further comparisons between this laboratory data and data from investigations of the same waste samples using TGA by other authors in section 5.1.1.

4.3.3 CARBON AND VOLATILE LOSS

Table 4.2 shows the percentage of total carbon and volatiles remaining, with respect to mass, for the pyrolysis of paper, newspaper and cardboard at 550 °C, 625 °C and 700 °C for 5, 10, 30 and 50 minutes.

Table 4.2: Carbon and volatiles remaining after pyrolysis at 550, 625 and 700 °C for 5, 10, 30 and 50 minutes

		550 °C		625 °C		700 °C	
	Pyrolysis Time	Carbon	Volatiles	Carbon	Volatiles	Carbon	Volatiles
	Minutes	% remaining wrt mass of carbon or volatiles in original sample					
Paper	5	51.57	50.19	38.30	37.16	38.04	7.80
	10	45.41	41.02	38.03	36.83	37.49	6.74
	30	43.01	34.77	37.49	35.16	37.10	2.81
	50	41.20	33.00	37.45	34.56	36.03	2.23
Newspaper	5	41.22	33.84	34.54	31.26	30.64	11.57
	10	38.30	33.10	33.90	30.03	30.31	9.78
	30	37.08	32.21	33.63	28.67	27.92	7.54
	50	34.04	31.16	31.62	23.20	26.73	6.92
Cardboard	5	46.74	61.37	40.83	25.50	37.68	14.49
	10	44.45	50.23	38.85	23.41	35.88	13.88
	30	43.49	41.18	37.47	23.06	35.08	9.72
	50	43.01	30.96	35.36	22.90	31.26	8.83

It can be seen that temperature had a greater affect on the volatile loss than time with an increase to 700 °C reducing the volatiles remaining for paper after 5 minutes of pyrolysis to 7.8 % compared to 50.19 % for paper at 550 °C. The change in volatiles was not as profound for cardboard samples as it was found that 11.57 % remained after 5 minutes at 700 °C compared to 33.84 % which remained at 550 °C. The carbon and volatile loss of samples is discussed further in section 4.4.1.

4.4 PYROLYSIS PRODUCTS

The solid, liquid and gaseous products from the pyrolysis of 5 g samples at 550 °C for 20 minutes have been investigated. The total gaseous products were calculated using the assumption that no N_2 was consumed or produced during the pyrolysis of all samples and therefore the flow rate of N_2 in was equal to the flow rate of N_2 out. From this, and gas analysis data from the micro GC, the flow rate of each gas identified by the analyser was established. The N_2 content of MSW components similar to those used in this study can be found in Appendix I. This was found to be 0.1 % or less for all components accept for coated paper as reported by Wu et al [57]. A discussion of the errors incurred in this data can be found in section 4.8.3. The total volume of any unidentified gases was then calculated by subtracting the sum of the identified gases from the total volume of gas produced. The identities of these unidentified gases are discussed in section 4.4.2.

The solid products were taken to be the mass of the sample remaining in the sample boat after pyrolysis. The liquid products were calculated by difference with the assumption that any mass of the sample not converted to either solid or gaseous products had been converted to liquid products. The pyrolysis products for paper and PET samples were also investigated at 700 °C. The solid pyrolysis products are shown and discussed in section 4.4.1, the gaseous products in section 4.4.2 and the liquid products in section 4.4.3. A mass balance of all products is shown in section 4.4.4. A discussion of all errors incurred in the measurements and calculations of pyrolysis products can be found in section 4.8.3.

4.4.1 SOLID PRODUCTS

The solid pyrolysis products were measured as the mass of the original 5 g sample remaining in the sample boat after 20 minutes of pyrolysis. Figure 4.8 shows how much of the solid product from the pyrolysis of each sample is made up of the ash content of the raw sample as found in section 4.2. It can be seen that even though paper, newspaper and cardboard have the highest ash content, the majority of the solid pyrolysis product is not made up of ash. For the plastic samples of PET, HDPE and PVC it could be seen after each experiment that the sample had pyrolysed and only char or tar was left in the sample boat. This is the same for the textiles samples. For food waste samples there was very little mass remaining compared to the other samples. This is due to the very high moisture content of the raw sample and can be attributed to moisture loss during the early stages of pyrolysis.

For paper, newspaper and cardboard samples, the remaining mass that is not due to the ash content is most likely unreacted sample. This assumption coincides with the results shown in section 4.3.3 for the mass of carbon and volatile matter remaining in the sample after pyrolysis. These results show there is still approximately 30-40 % of unreacted carbon and volatiles present after 20 minutes of pyrolysis for paper, newspaper and cardboard. For these samples, this unreacted carbon and volatiles is most likely due to the surface of the sample pyrolysing and turning to char, which then inhibits the sample below from reacting. This was also observed visually once the remaining sample had cooled after pyrolysis.

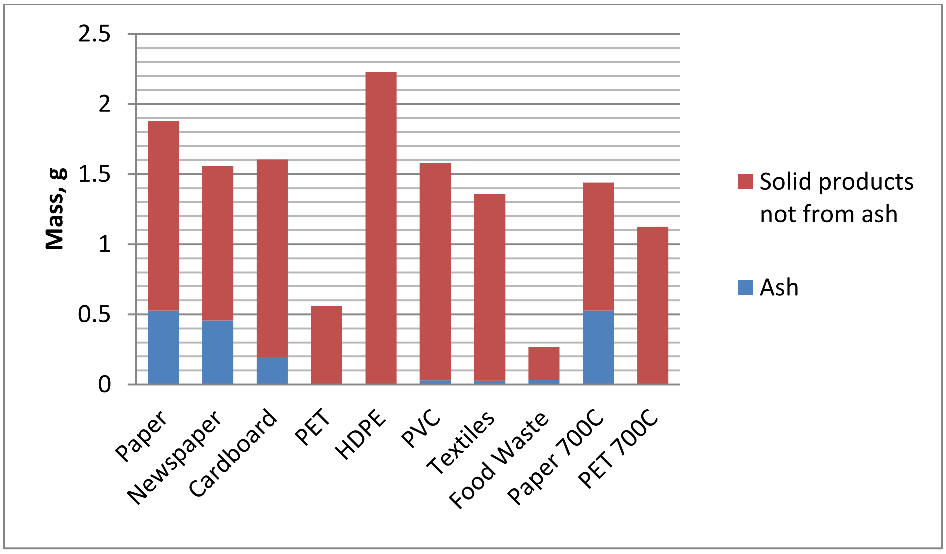


Figure 4.8: A graph of the ash content and other solid products from pyrolysis of samples at 550 °C and of paper and PET at 700 °C

For PET and PVC, the solid mass remaining after pyrolysis is most likely due to liquid pyrolysis products remaining in the sample boat and either pyrolysing further or cooling to a solid state once the sample boat was removed from the furnace. This was observed visually during investigations and leads to an inaccuracy in the measurement of solid and liquid products as, in this investigation, liquid products have been measured as solids. This is discussed further in section 4.8.3. For HDPE, the sample boat contained a white powdered substance which was a filler used in the production of the plastic. The high mass of solid product for HDPE is partly attributed to this and partly attributed to wax products remaining in the sample boat after pyrolysis and measured as solid products. Kumar et al [66] found that 52 % of the original mass of HDPE was turned into wax during pyrolysis at 550 °C. Mastral et al [69] also found high wax and oil products from the pyrolysis of HDPE with 68 % of the original mass during the pyrolysis of HDPE at 640 °C. This confirms the assumption that wax products in this study have been counted as solid products. For the textile samples, it could be seen during investigations that the remaining solid mass was partly due to unreacted sample and partly due to liquid products remaining in the sample boat.

It can be seen that an increase in temperature from 550 °C to 700 °C led to a decrease in solid products from the pyrolysis of paper and the solid products for PET increased from 0.56 g at 550 °C to 1.13 g at 700 °C. For paper, this is due to the higher temperature leaving less unreacted sample after pyrolysis as discussed above. For PET, this is mostly due to the increase in temperature pyrolysing more of the liquid products and converting it to char and gas before the liquid products had a chance to leave the furnace and enter the tar trap system. This then leads to a higher mass of solid products remaining in the sample boat and higher inaccuracies in the measurement of liquid and solid products as discussed previously.

4.4.2 GASEOUS PRODUCTS

Figure 4.9 shows the gaseous products that were identified by the gas analysers and the unknown gases not identified by the gas analysers. This graph is shown in litres rather than mass in order to minimise errors produced from converting the unknown gas to mass from the litres calculated from the micro GC data. The unidentified gases were calculated by subtracting the total volume of gases identified by the micro GC from the calculated value for the total volume of gases produced. The gases identified by the micro GC were CO, CO_2, H_2, CH_4, C_2H_6 and C_3H_8.

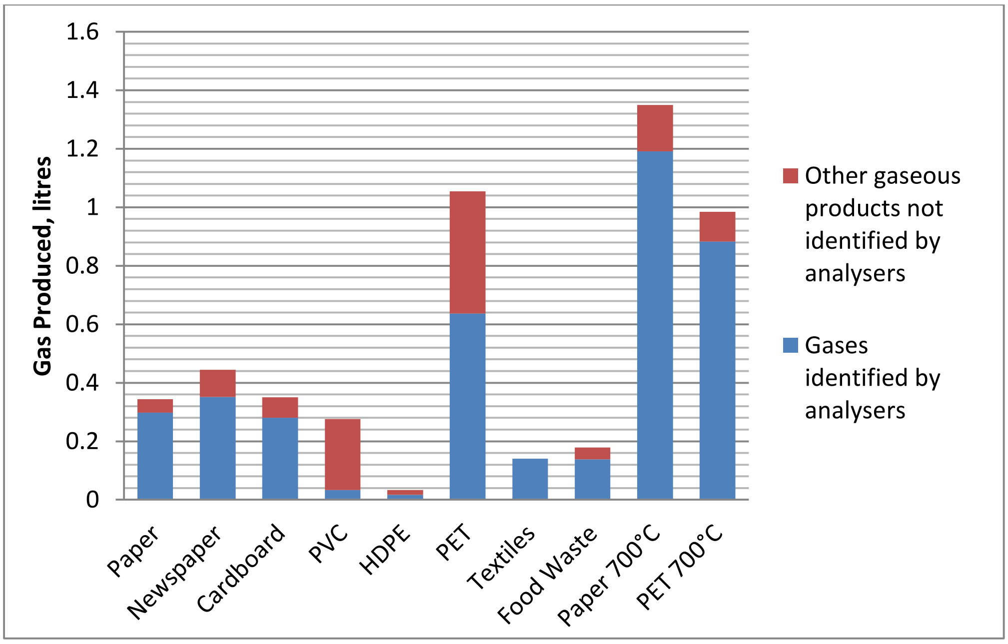


Figure 4.9: A graph to show the litres of identified gaseous products and unidentified gaseous products for the pyrolysis of samples at 550 °C and for paper and PET at 700 °C.

It can be seen that paper, newspaper and cardboard samples produced similar quantities of gaseous products, with newspaper samples producing slightly higher volumes of both identified and unidentified gases. It can also be seen that an increase in pyrolysis temperature significantly increased the volume of gaseous products; this is confirmed by previous research into the pyrolysis of paper [39, 51, 58]. The effect of temperature on the gaseous products of pyrolysis is discussed further in section 4.5.6.

The high volume of gas produced from the pyrolysis of PET is confirmed by Cepeliogullar et al. in a TGA study where it was found that the gas yield from the pyrolysis of PET at 500 °C was 76.9% [52]. This is significantly higher than the 43 % found in this study. Cepeliogullar et al also studied the gas yields obtain from the pyrolysis of PVC at 500 °C; this was found to be 87.7 %. Results found in this study did not follow this trend and a lower gas yield of 13.2 % was recorded. Previous research shows that the thermal degradation of PVC occurs in two stages with the maximum decomposition occurring between 410 and 515 °C [77]. This was established using TGA. It is suggested that more energy, and therefore a higher temperature, is needed for the thermal decomposition of PVC in the laboratory scale fixed bed reactor compared to TGA process due to the larger sample size and temperature profile throughout the sample. As discussed in section 4.3.2, this was also found by Yang et al [97] in an investigation which compared TGA data to that from a laboratory scale packed bed pyrolyser where it was found that the char yield in a packed bed pyrolyser can be 30-100 % higher than the char yield from TGA tests. This was attributed to the temperature profile throughout the rig and the sample as well as possible tar cracking and repolymerisation during pyrolysis. A higher char yield would lead to a decrease in the percentage of gas yields. The lower percentage of gaseous products from PET and PVC in this study can therefore be attributed to the larger sample size. The comparisons made by Yang et al between TGA and a laboratory scale pyrolyser are discussed further in section 5.1.1.

It can also be seen in Figure 4.9 that comparatively low volumes of gases were produced from the pyrolysis of HDPE, textiles and food waste. For the food waste samples this was attributed to the very high moisture content of the raw samples. As samples were not dried before pyrolysis, the majority of mass loss was due to moisture and therefore included in the mass of liquid products. The low volumes of gaseous products for both HDPE and textiles samples is most likely attributed to the production of thick wax or tar which was observed during investigations with these samples. This wax or tar caused several blockages within the pipe work for the output gas and tar trap system leading to the need to repeat experimental runs. Data shown in this study is for runs where complete blockages did not occur, however, it is likely that the thick wax or tar produced caused partial blockages in the system and therefore slightly inhibited the produced gas reaching the gas analysers leading to a lower volume of gas recorded for these samples. It is therefore assumed that gas production from both HDPE and textiles samples may have been higher than those recorded. This was also suggested by Yang et al [97] who found the gas yields from the pyrolysis of textiles to be approximately 30-43%. Kumar et al [66] found that the pyrolysis of HDPE at 550°C produced 38.47% of gas and volatiles and Mastral et al [69] found that the HDPE pyrolysis at 640°C produced 33.5% gas.

Figure 4.9 also shows that a significant volume of gases were produced that were not identified by the micro GC, i.e. not CO, CO_2, H_2, CH_4, C_2H_6 or C_3H_8. Skreiberg et al found that the pyrolysis of paper also produced small volumes of C_2H_2 and C_2H_4 [39]. Wu et al [58] also found that hydrocarbons were produced from the pyrolysis of newspaper with 1.51 % produced at 514 °C and 2.11 % produced at 668 °C. This increase in the production of hydrocarbons from paper with an increase in pyrolysis temperature was also found in this study.

It can be seen that PET produced the highest percentage of unidentified gases at 550 °C. However, an increase in pyrolysis temperature to 700 °C reduced the litres of unidentified gases produced. In a study into the pyrolysis of HDPE, Mastral et al [69] found that the production of some hydrocarbons, such as C_2H_6 and C_3-C_4 increased with an increase in pyrolysis temperature up to a temperature of 730 °C and then decreased with further increases in temperature. This was attributed to further cracking leading to the production of gas compounds of lighter molecular weight. This is comparable with the lower volume of unidentified gases detected in this study from the pyrolysis of PET at 700 °C.

Figure 4.9 also shows that the pyrolysis of PVC produced a significant volume of unidentified gases. In a study of the thermal degradation of PVC, Marongui et al concluded that the degradation process was very complex due to the presence of chloride as well as the complexity and formation of polyaromatic hydrocarbons [68]. The unidentified gases from the pyrolysis of PVC in this study are therefore attributed to hydrocarbons and other gases produced from the chloride fraction of the sample that were not identified by the gas analysers. Dimitrov, et al also found hydrocarbons were present in the gas produced from the pyrolysis of recycled PET bottles and found the main pyrolysis products to be: CO_2, acetaldehyde, benzene, vinyl benzoate, benzoic acid,, divinyl terephthalate, 4-(vinyloxycarbonyl) benzoic acid, ethan-1,2-diyldibenzoate [63].

The gases produced that were not identified by the micro GC can therefore be assumed to be hydrocarbons other than CH_4, C_2H_6 and C_3H_8 that were not collected in the tar trap system. The tar trap system had a maximum temperature of approximately 30-40 °C, therefore the unidentified gases were assumed to be hydrocarbons that are in a gaseous state at this temperature. Table 4.3 shows the melting points, boiling points and state at 40°C for a range of hydrocarbons. Molecules with strong intermolecular bonds have higher boiling points as more kinetic energy is needed to break these bonds to allow the molecules to escape the liquid as gases. It can be seen that CH_4, C_2H_6, C_3H_8, C_4H_{10} (butane) and pentane (C_5H_{12}) would be expected to pass through the tar trap. Any heavier hydrocarbons from Hexane (C_6H_{14}) to Eicosane ($C_{20}H_{32}$) would remain as a liquid and collect in the tar trap system. CH_4, C_2H_6, and C_3H_8 were identified by the micro GC analyser so therefore it can be assumed that any unidentified gases are most likely hydrocarbons including C_2H_2, C_2H_4, C_4H_{10} and some C_5H_{12}, dependant on exact temperature of the tar trap system, although this is not a comprehensive list. The hydrocarbons produced from the pyrolysis of various components and mixtures of MSW has not been investigated in this study but as reported in the literature, it is expected this unidentified gas consists of a wide variety of components.

Table 4.3: Melting points and boiling points of a range of hydrocarbons [114]

Hydrocarbon	Melting Point, °C	Boiling Point, °C	State in 40°C Tar Trap
Ethylene, C_2H_4	-103	-169	Gas
Methane, CH_4	-183	-164	
Ethane, C_2H_6	-183	-89	
Acetylene, C_2H_2	-84	-80	
Propane, C_3H_8	-190	-42	
Butane, C_4H_{10}	-138	-0.5	
Pentane, C_5H_{12}	-130	36	
Hexane, C_6H_{14}	-95	69	Liquid
Heptane, C_7H_{16}	-91	98	
Octane, C_8H_{18}	-57	125	

For the purpose of the mass balance shown in section 4.4.4, the mass of the gaseous products that were unidentified by the micro GC have been calculate as C_4H_{10} as this is the heaviest hydrocarbon likely to have been produced and will therefore give a maximum estimation of the total gaseous products produced. The errors associated with this assumption are discussed in section 4.8.3 where comparisons are made between these mass balance calculations and those for the unidentified gases assumed to be a lighter hydrocarbon.

4.4.3 LIQUID PRODUCTS

The liquid products have been calculated by difference with the assumption that any mass of the original sample not accounted for in the mass of gaseous or solid products has been converted to liquid products. Any errors associated with this assumption and this data are discussed in section 4.8.3. Figure 4.10 shows the moisture content of the raw sample, the tars measured in the tar trap system and the unidentified liquid products as calculated by difference. It has been assumed that the moisture lost from the sample was collected in the tar trap system. The mass of the tars collected in the tar trap system have therefore been calculated without the inclusion of the mass of the moisture from the raw sample. In order to avoid any errors of converting an unknown liquid from mass to litres, the liquid products and moisture content in Figure 4.10 are shown as a mass. Any errors involved in the measurement of solid and gaseous products are also included in the estimation of total liquid products.

The mass change of each part of the tar trap system was measured for the pyrolysis of paper, newspaper, cardboard and PET at 550 °C. Results for this are shown and discussed further in section 4.8.3.1. This data was not collected for all samples as the quantification of tars was not part of this study. As well as for ensuring minimal errors, this data can also be used to further understand the behaviour of liquid pyrolysis products within the pyrolysis reaction rig system. The mass of tars measured from pyrolysis of these samples is also shown in Figure 4.10.

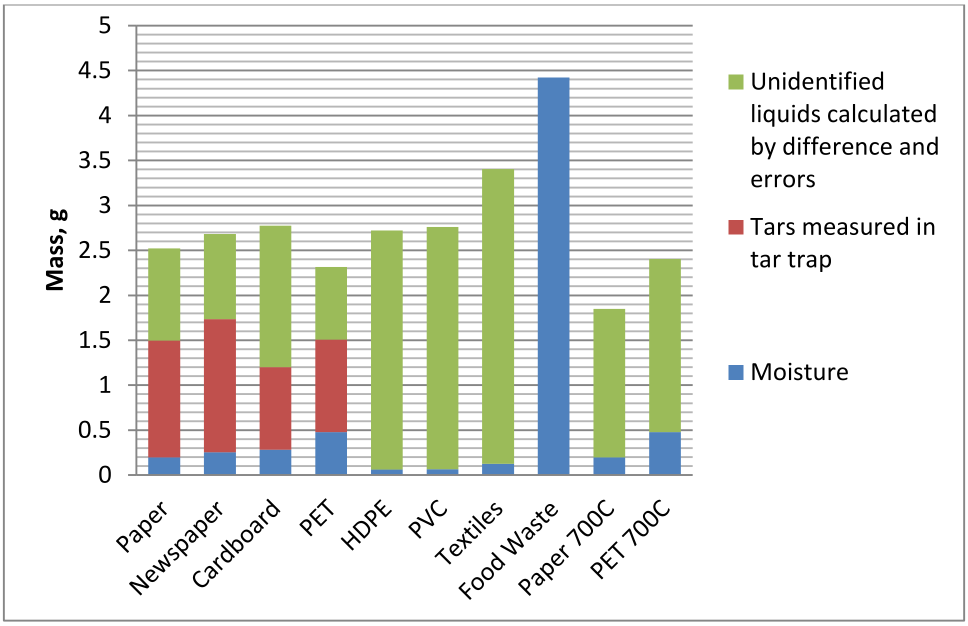


Figure 4.10: A graph of the moisture content from the raw sample and the mass of other liquid products from the pyrolysis of samples at 550 °C and of paper and PET at 700 °C.

It can be seen from Figure 4.10 that the majority of the liquid products are not due to the moisture content of the raw sample apart from for the food waste samples which had a very high moisture content of 88.5 %. The majority of liquid products are therefore tars and oils produced during the pyrolysis of samples.

As discussed above, the quantities of solid and liquid products are heavily dependent on the density of the tars produced by the pyrolysis of each sample as tars with a high viscosity could remain in the sample boat and be counted as solid products. Although the produced tars were not investigated during this study, apart from those in the tar trap for paper, newspaper, cardboard and PET, the visual appearances of tars were recorded in order to provide a greater understanding of the pyrolysis behaviour of each sample. Samples which produced higher density tars, such as HDPE and PVC, produced a higher mass of solid products and lower mass of liquid products. This is attributed to less tar being able to leave the sample boat and enter the tar trap system. For paper, newspaper and cardboard, the tars produced by pyrolysis were seen to have a lower density allowing the majority of these tars to enter the tar trap system and be measured as liquid products. However, it can be seen in Figure 4.10 that not all liquid products from these samples were measured in the tar trap system.

It can be seen that the majority of the mass of the liquids produced are not measured in the tar trap so must be elsewhere within the reaction rig system. As the reaction rig was design primarily for gas analysis, the ability to be able to collect and quantify all of the liquid products was not a high priority for the aim of this study. During experiments it was clear that a significant mass of tar collected within the reactor tube itself, outside of the sample boat. As the reactor tube was not removable from the furnace, the change in mass of this could not be measured. A small percentage of these unidentified liquid products will also be due to the errors in calculating this mass balance as the total liquid products were calculated by difference.

4.4.4 MASS BALANCE

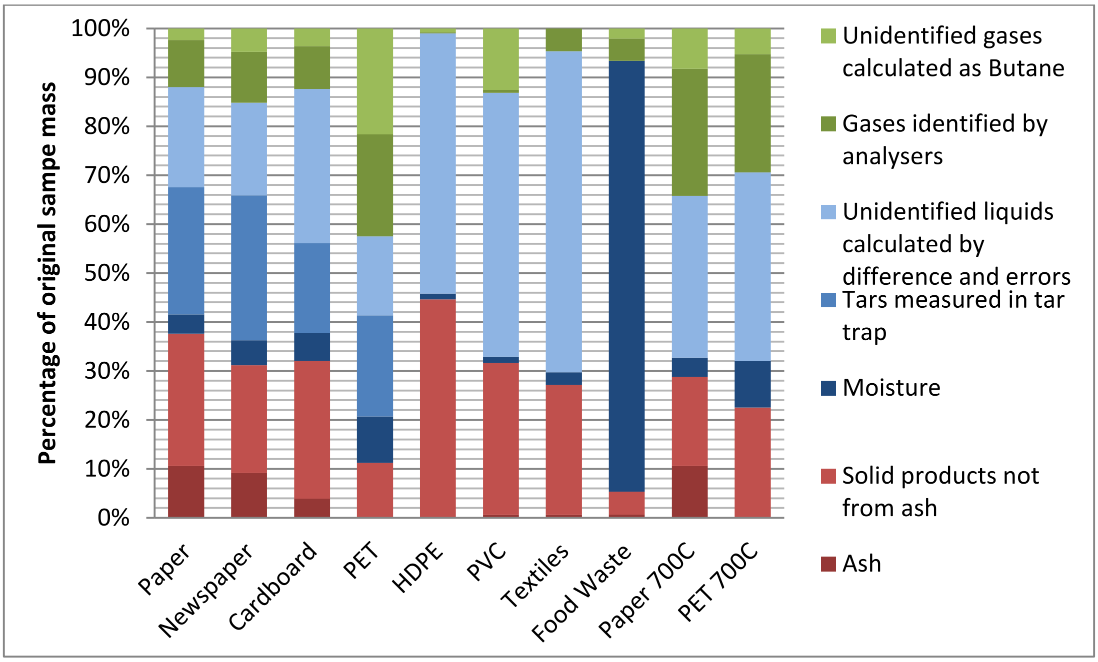


Figure 4.11: A graph of the complete mass balance for identified and unidentified solid, liquid and gaseous products for pyrolysis of samples at 550 °C and for paper and PET at 700 °C.

Figure 4.11 shows a complete mass balance to include all identified and unidentified solid, liquid and gaseous pyrolysis products for all samples at 550 °C and for paper and PET at 700 °C. The green sections of the graph show the gaseous products, the blue sections show the liquid products and the red sections show the solid products. For this mass balance the mass of unidentified gases has been calculated using the molecular mass of Butane. The mass of unidentified liquids has been calculated by difference, therefore values for this also contains any errors involved in calculations or in measuring the mass of each product for this mass balance as well as any errors introduced from assumptions made. As the mass of tar produced during pyrolysis was only measured for paper, newspaper, cardboard and PET any tar collected in the tar trap for the other samples is included in this graph as part of the ‘unidentified liquids calculated by difference and errors’ section. The ash content and moisture content of the raw sample has also been included as it is assumed the mass of these are included in the mass of solid and liquid products respectively. For those samples where mass of the tar collected in the tar trap was recorded, it has been assumed that the mass of moisture in the original samples was also collected in the tar trap system and the mass of the tars presented adjusted accordingly.

In a study into the pyrolysis products of uncoated writing and printing paper, Wu, et al found a gas yield at 350 °C of 10.46 % for non-hydrocarbons and 0.49 % for hydrocarbons [57]. At 664 °C, the gas yield for non-hydrocarbons was 79.1 % and hydrocarbons were 1.63 %. Data from this study found 9.58 % for identified gases, which include CH_4, C_2H_6 and C_3H_8 and 2.39 % for gases assumed to be hydrocarbons for pyrolysis of paper at 550 °C. Although values found in this study differ, they follow the same trend and show that the unidentified gases are most likely to be hydrocarbons. Wu et al [57] also found that the production of gases increases with temperature for the pyrolysis of paper. This increase is also shown in this study, although lower percentage of gas was produced. This is attributed to the larger sample size used in this study which, as found by Yang et al [97], leads to a increase in the solid products to the detriment of gaseous products.

Despite a lower accuracy in the measurement of the mass of the pyrolysis products in this study when compared to the high accuracy of data from TGA investigations, results presented here have been shown to give a good indication of the behaviours and trends of pyrolysis products. However, as discussed previously, it is suggested that the larger sample size used in this study provides a more realistic prediction of the behaviour of MSW components in a commercial scale rig where a considerably larger mass of waste would be pyrolysed. This is discussed further in section 5.1.1. The errors associated with this mass balance are discussed further in section 4.8.3.

4.5 GAS ANALYSIS

4.5.1 TYPICAL PYROLYSIS GAS ANALYSIS RESULTS

This subsection will demonstrate some typical gas analysis results from the rig in order to outline typical behaviour and hence allow for comparison with subsequent datasets. Figure 4.12 shows a graph of the gas analysis results for CO, CO_2 and O_2 for a typical pyrolysis run with 5 g paper pyrolysed at 550 °C for 20 minutes. The data was measured using the Rosemount NGA gas analyser described in section 3.2.3.1 using data collection methods described in section 3.5.3. All samples were pyrolysed for a residence time of 20 minutes. For all investigations, the percentage of CO produced had fallen below 0.05 % within this time and it can be assumed that there was negligible gas produced after this point.

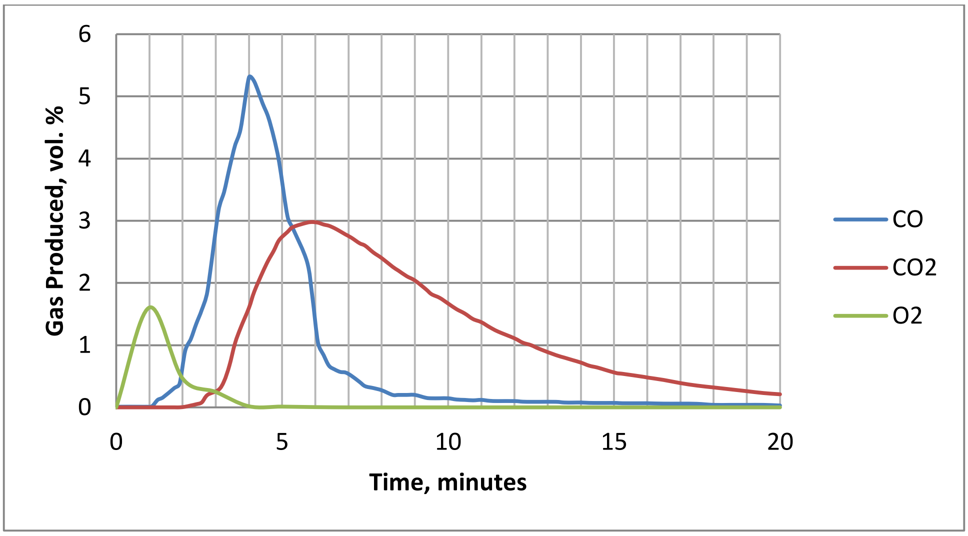


Figure 4.12: A graph showing the gas composition measured by the Rosemount analyser from the pyrolysis of 5 g paper at 550 °C for 20 minutes

It can be seen that the production of CO_2 produced a smooth curve showing a steady increase and decrease in volume percentage of the total flow rate. CO production was not quite as steady due to the more rapid rate of increase and decrease of the CO peak. This meant that the results for the production of CO were much more susceptible to error as a small error could make a greater difference than it would with the results for CO_2. The production of CO reached a peak of 5.3 % of the total flow rate at 4 minutes. It can be seen that there is an oxygen peak of 1.6 % at approximately 1 minute. This O_2 peak appears for all runs with a similar quantity and at a similar point in the run and is attributed to the O_2 introduced into the reaction rig when the sample boat is inserted. This is discussed further in section 4.8.4 along with the repeatability of laboratory experiments, comparisons between the micro GC and Rosemount analysers and a full discussion of errors.

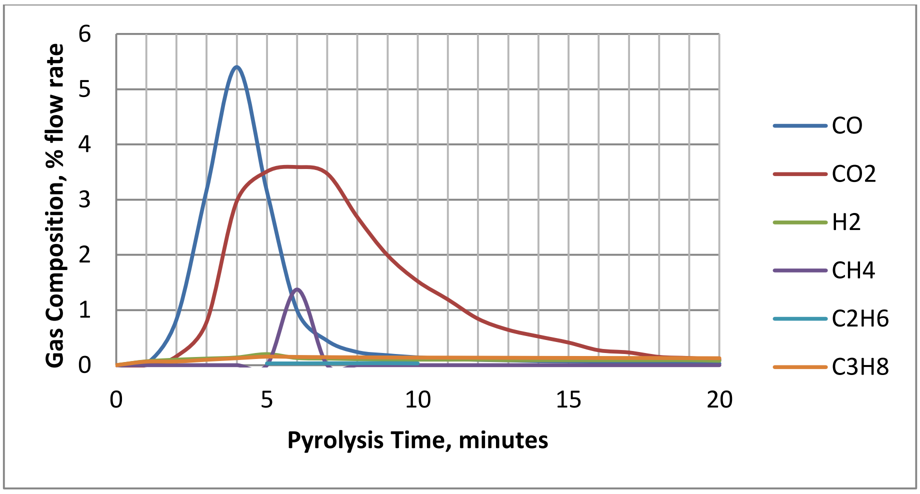


Figure 4.13: A graph showing the gas composition measured by the micro GC for the pyrolysis of 5 g of paper at 550 °C for 20 minutes

Figure 4.13 shows the gas composition measured by the micro GC analyser from the pyrolysis of 5 g of paper at 550 °C for 20 minutes. The micro GC could not analyse the gas continuously, hence it was set to record data every 3 minutes throughout the 20 minute pyrolysis run. Each run was then repeated twice with gas analysis data taken at different times in order to build up gas analysis data for each minute of the 20 minute run. This method is shown in Figure 4.36 in Section 4.8.4 where it is discussed further.

4.5.2 GAS COMPOSITION

Figure 4.14 shows a graph of the composition of the gas produced during pyrolysis for 20 minutes at 550 °C with a N_2 flow of 0.6 l/min, undertaken for 8 different fuels. The data was measured using the gas analysis hardware described in section 3.2.3. The gas analysis equipment measures the composition of the gas as a volume percentage of the total flow rate. This has been converted to litres using the assumptions discussed in section 4.8.44.4.

The unidentified gases have been calculated as the difference between the total gases produced and the sum of the gases that were identified by the analyser. The errors associated with these calculations along with the repeatability of results are discussed in section 4.8.4.

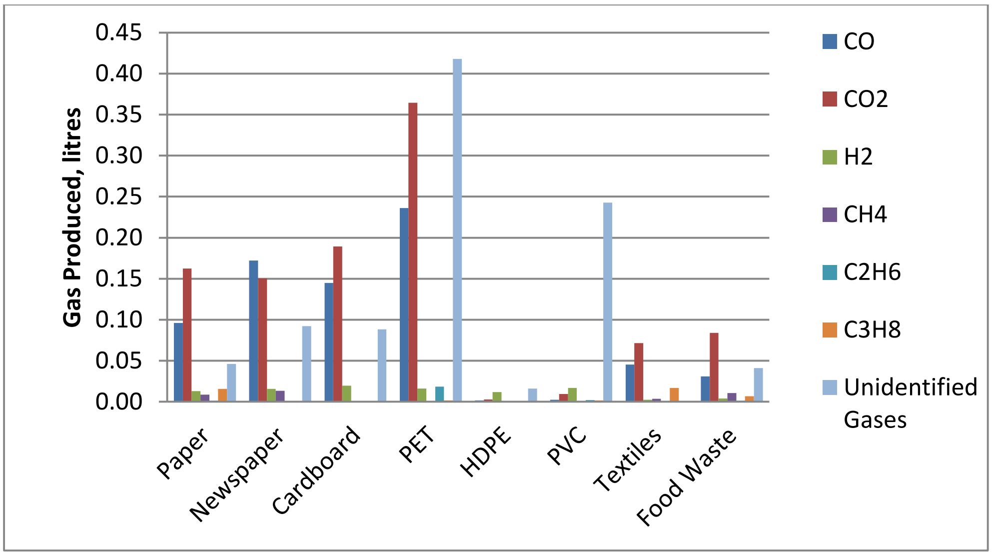


Figure 4.14: A graph of the composition of gas produced for each sample pyrolysed at 550 °C for 20 minutes

It can be seen that paper and cardboard produced similar levels of each gas compared to the other samples, although with slight variation for the production of CO, C_3H_8 and unidentified gases. The pyrolysis of newspaper produced a higher volume of CO than the pyrolysis of paper and cardboard. The composition of produced gas for PET was notably different to other plastics tested (HDPE and PVC). PET produced the highest volume of both CO and CO_2 where as HDPE and PVC produced the lowest with PVC producing a high volume of unidentified gases. The low production of gas from HDPE and the high production of unidentified gases from PVC are discussed in section 4.4.2.

In agreements with the findings presented herein, Wu et al [58] used TGA to investigate the pyrolysis of newspaper. At a pyrolysis temperature of 514 °C, the composition of the produced gas was found to be 0.32 % H_2, 5.29 % CO, 37.17 % CO_2 and 1.51% light hydrocarbons with 20.57 % H_2O. The relatively low volumes of H_2 and light hydrocarbons are comparable to those found in this study. However, a higher percentage of CO and lower percentage of CO_2 was detected in this study at 38 % and 33.9 % respectively. This could be attributed to the larger mass of waste used in this study and therefore the greater bed depth. As discussed in section 2.7.2, Phan et al [19] found that an increase in bed depth led to an increase in the production of CO. This is could also be attributed to the difference in heating rate between the two processes as TGA involves a slow heating rate and a significant volume of gas had already been produced from the sample pyrolysis at lower temperatures. In this study, the raw sample is subjected to a rapid heating rate as it is placed in to the pre-heated reactor tube with no previous pyrolysis occurring.

Ahmed et al [51] also found a relatively low volume of H_2 was produced from the pyrolysis of paper at 600 °C and the main gases produced were CO and CO_2. These are also stated as the main gases produced from the pyrolysis of mixed waste as reported by Lupa et al [33]. It has been reported that in some instances the production of CO_2 from pyrolysis will be greater than the production of CO; however above temperatures of approximately 750 °C, the production of CO becomes more favourable. This is attributed to the equilibrium shift of the water gas shift reaction, shown by Equation 5 in section 2.2. This was also reported by Tihay and Gillard [47]. The high volumes of CO_2 produced during pyrolysis in this study can therefore partly be attributed to the relatively low pyrolysis temperature. The effect of temperature on the composition of gas produced from pyrolysis is discussed further in section 4.5.6.

As well as the low pyrolysis temperature, the high volumes of CO_2 for the majority of samples can also be attributed to the O_2 present in the fuel. Although, ultimate analysis of fuels was not undertaken in this study, data is available from previous research for a wide range of MSW components; this can be found in Appendix I for MSW components similar to those used in this study [23, 43, 71, 77, 97]. Using this data the ratio of O/C of the raw components can be calculated and compared to the ratio of CO/CO2 produced during pyrolysis. This is shown in Figure 4.15.

It can be seen in Figure 4.15, that there is a correlation between the ratio of O/C in the fuel and the ratio of CO/CO_2 produced for paper, newspaper, cardboard and food waste samples. For these samples, it can be seen that a lower ratio of O/C leads to a higher ratio of CO/CO_2. During pyrolysis paper and cardboard produced similar quantities of both gases however newspaper produced a higher percentage of CO than CO_2. It can be seen that paper and cardboard have a similar ratio of O/C yet newspaper has a higher content of C therefore reducing the O/C ratio which leads to the production of CO being more favourable due to the limited availability of O. For plastic and textiles samples there is no correlation. This is attributed to the complex structures and hydrocarbons that are also present in these components. It can be seen that both the O/C ratio and the CO/CO_2 ratio for PET and textiles are the same. This is attributed to the 50 % polyester content of the fabric giving it similar composition to that of PET. HDPE has no oxygen present in the raw fuel, as found by Heikkinen et al [77] and produced relatively low volumes of both CO and CO_2. PVC also produced low quantities of both gases and was found to have a low oxygen content of 5.8 % [43].

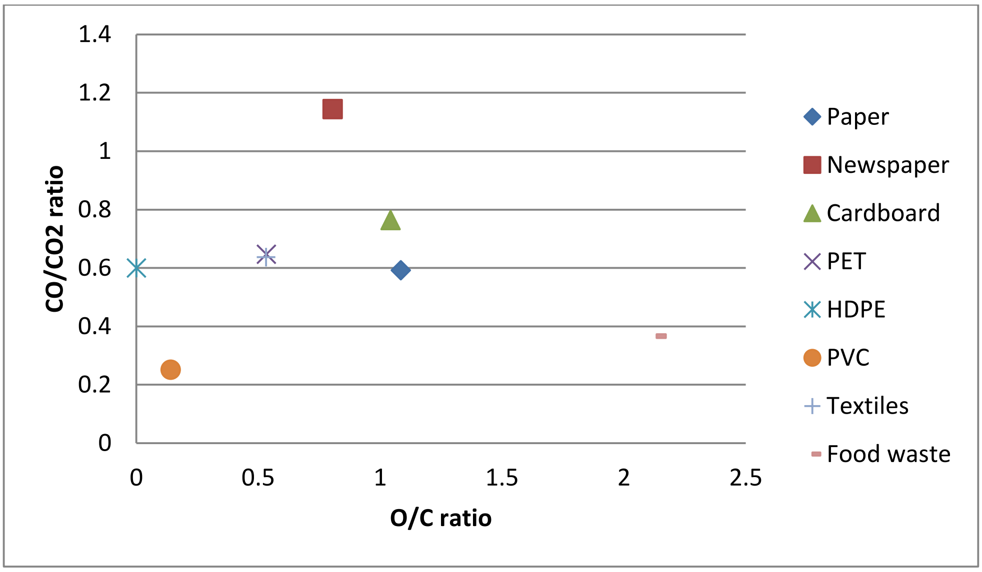


Figure 4.15: A graph of the relationship between the ratio of O/C of each component and the ratio of CO/CO_2 produced during pyrolysis.

4.5.3 HIGHER HEATING VALUE

Figure 4.16 shows the higher heating value (HHV) of the total gas produced for each sample pyrolysed for 20 minutes at 550 °C. This was calculated for the product gas using the HHV of the combustible gases; H_2, CH_4 and CO using the following equation [115, 116]:

$$\text{HHV (MJ/Nm}^3\text{)} = (\text{vol.\% } H_2) \times 12.75 + (\text{vol.\% } CH_4) \times 39.82 + (\text{vol.\% CO}) \times 12.63 \qquad \text{Equation 9}$$

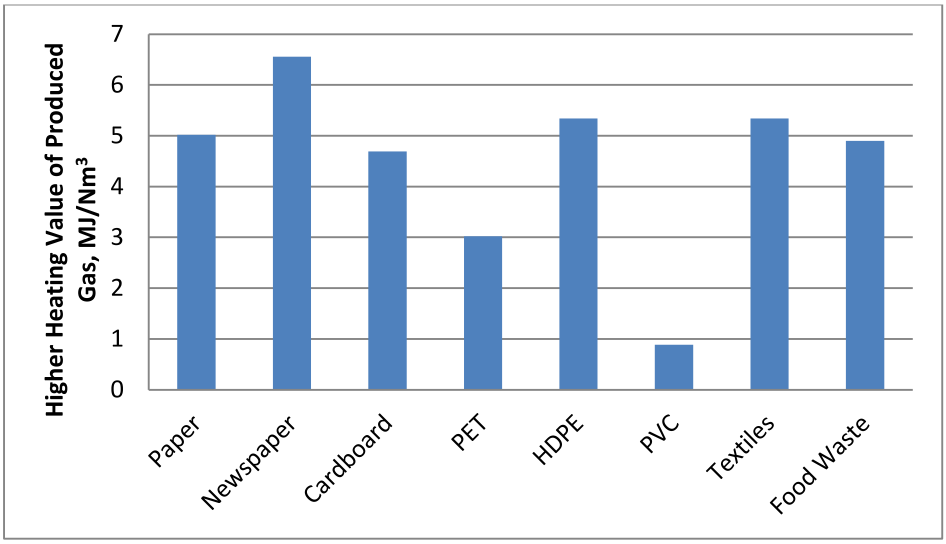


Figure 4.16: A graph of the Higher Heating Value of the produced gas for each sample pyrolysed for 20 minutes at 550 °C

It can be seen that the gas with the greatest HHV (based on the gas components measured) was produced from the pyrolysis of newspaper. This is due to the high volume of CO produced as shown in Figure 4.13. Although the pyrolysis of PET produced a higher volume of CO, a higher volume of unidentified gases were also produced which led to a significantly higher total volume of gas. This has led to a lower percentage of CO for PET in terms of the total measured gas produced and therefore a lower HHV. The gas produced from the pyrolysis of HDPE and textiles samples also has a relatively high HHV. For HDPE, this is attributed to the significantly low volume of total gas produced and the high percentage of this detected as H_2. The low volume of total gas produced from the pyrolysis of textiles and the high percentage of this that was detected as C_3H_8 was attributed to the high HHV for this sample. The low volumes of gas produced for both of these samples are discussed in section 4.4.2.

It can be seen that the lowest HHV calculated was for the pyrolysis of PVC. This is because the majority of the gases produced from the pyrolysis of PVC were not identified by the gas analysers so could not be included in the calculations of HHV. Therefore the value calculated here for the HHV of PVC may not fully represent the HHV of the gas produced from PVC. However, Zhou et al [75] found that the main gases produced from the pyrolysis of PVC are from dehydrochlorination due to the high content of hydrochloride and therefore this gas would be of limited use for energy production in EfW technologies. The HHV of the gas produced from samples is discussed further in section 5.2 were this data has been used to establish a mathematical model to predict the HHV of several waste mixes.

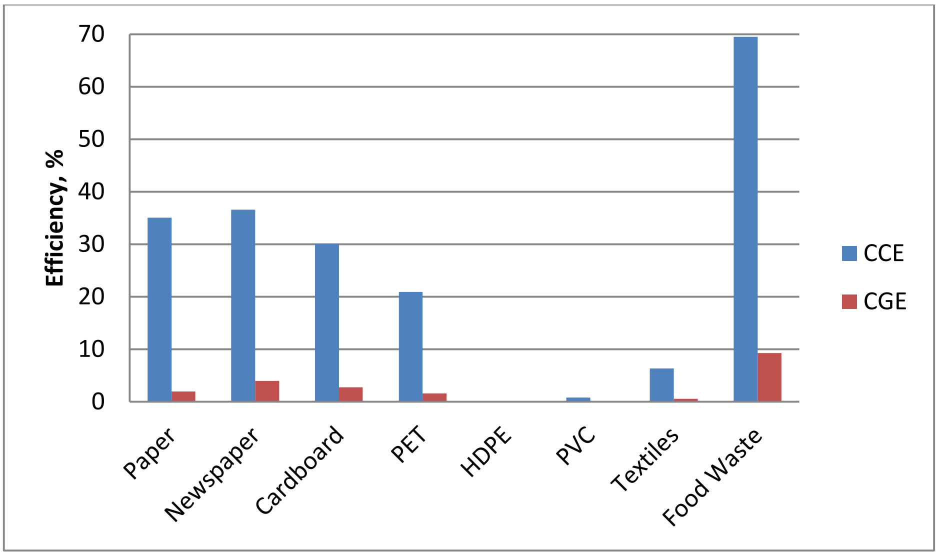
The values for HHV ranging from 0.8 – 6.56 MJ/Nm^3 for the gas produced from pyrolysis in this study is considerably lower than values found by previous research. Velghe et al achieved values of 13-20 MJ/Nm^3 from the pyrolysis of waste [44], Raveendran et al [40] and Chen et al [25] achieved values of 5-16 MJ/Nm^3 and 13-15 MJ/Nm^3 respectively from the pyrolysis of biomass. The HHV values reported by Velghe et al [44] were from the pyrolysis of mixed MSW in a semi-batch reactor at 550 °C. It was found that the residence time had a significant effect on the HHV of the produced gas with a longer residence time leading to a significantly lower HHV. The semi batch reactor would therefore produce a higher value of HHV for a longer time period due to the continuous feed of raw material. The lower values for HHV obtained in this study are therefore attributed to the longer residence time as well as this the low volumes of CO and H_2 produced in this study, leading to a lower HHV, have been attributed to the low pyrolysis temperature. This also has a significant effect on the HHV of the produced gas and is discussed further in section 5.2.

4.5.4 CARBON CONVERSION AND COLD GAS EFFICIENCY

Figure 4.17 shows the Carbon Conversion Efficiency (CCE) and the Cold Gas Efficiency (CGE) for each sample pyrolysed for 20 minutes at 550 °C. The CCE indicates the amount of carbon in the feed that was successfully converted into a carbon bearing gas such as CO, CO_2 and CH_4. The CGE determines the energy available in the product gas as a ratio of the energy in the original sample. The CCE and CGE were calculated using the following equations:

$$CCE = \frac{wt.\%\ carbon\ in\ produced\ gas\ (CO, CO_2, CH_4)}{wt.\%\ carbon\ content\ of\ dry\ feed} x100 \qquad \text{Equation 10}$$

$$CGE = \frac{wt.\%\ gas\ yield\ on\ dry\ feed\ basis\ x\ HHV\ of\ gas\ (\frac{MJ}{kg})}{CV\ of\ sample}\ x100 \qquad \text{Equation 11}$$



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4.5.5 EFFECT OF RESIDENCE TIME

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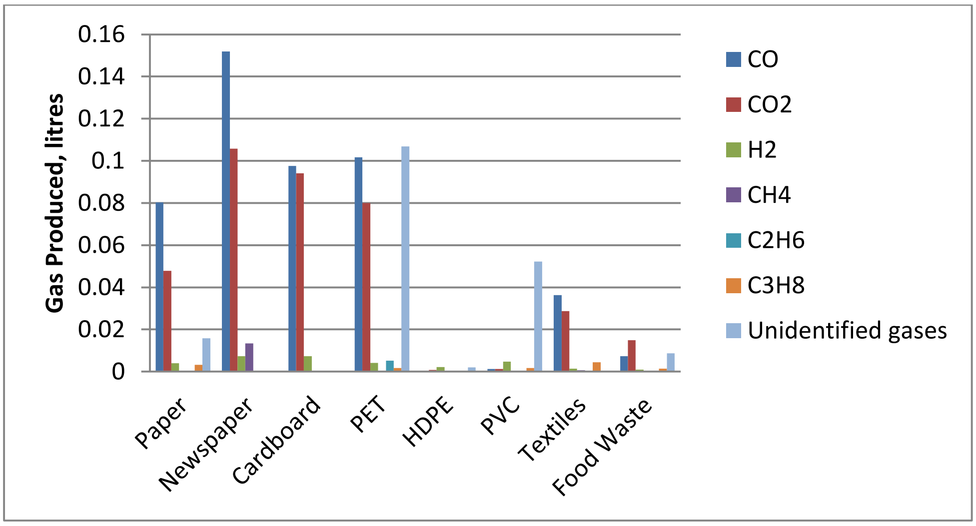

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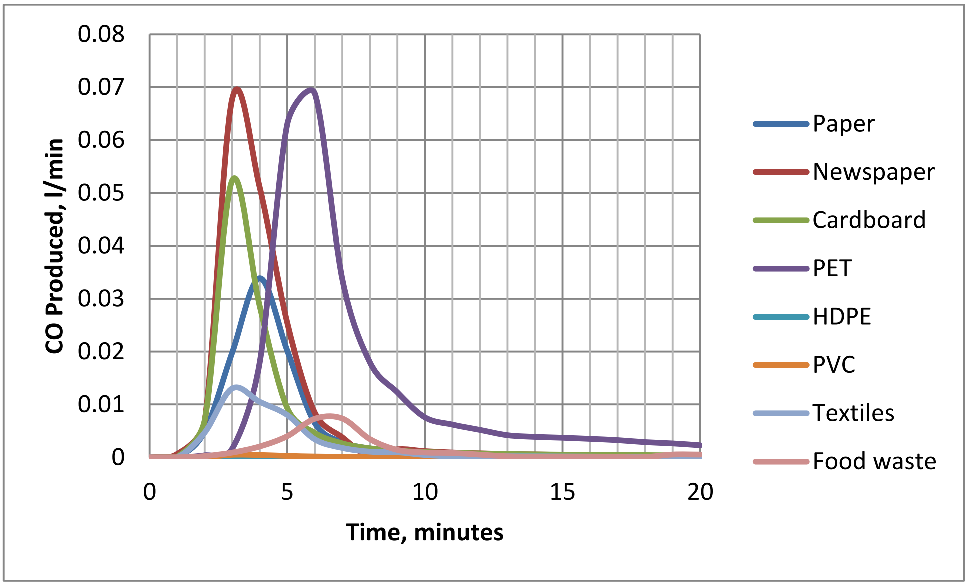

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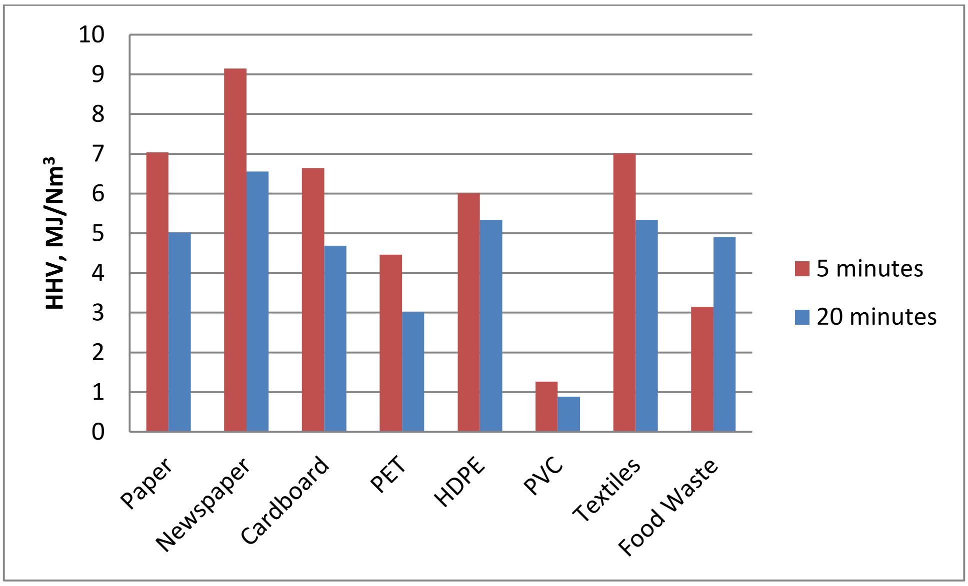

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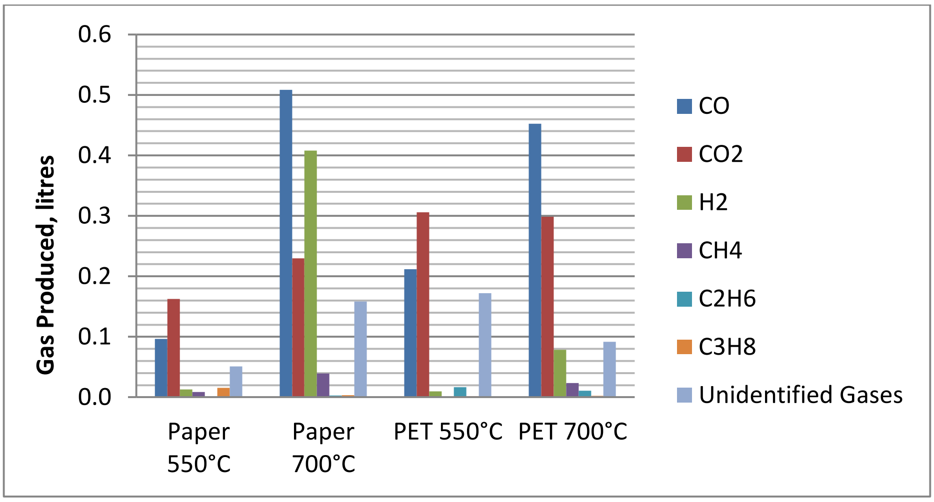
4.5.6 EFFECT OF TEMPERATURE

Pyrolysis



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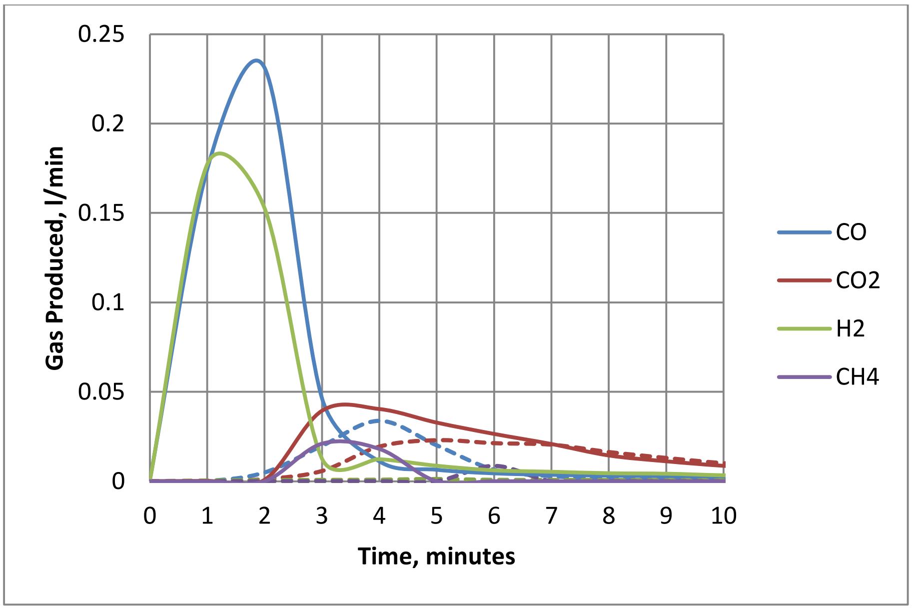

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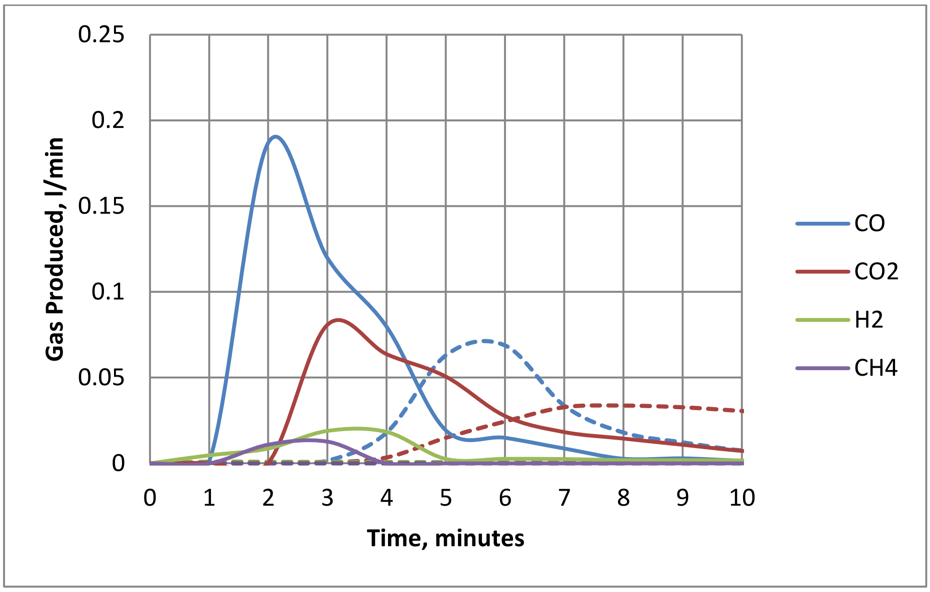

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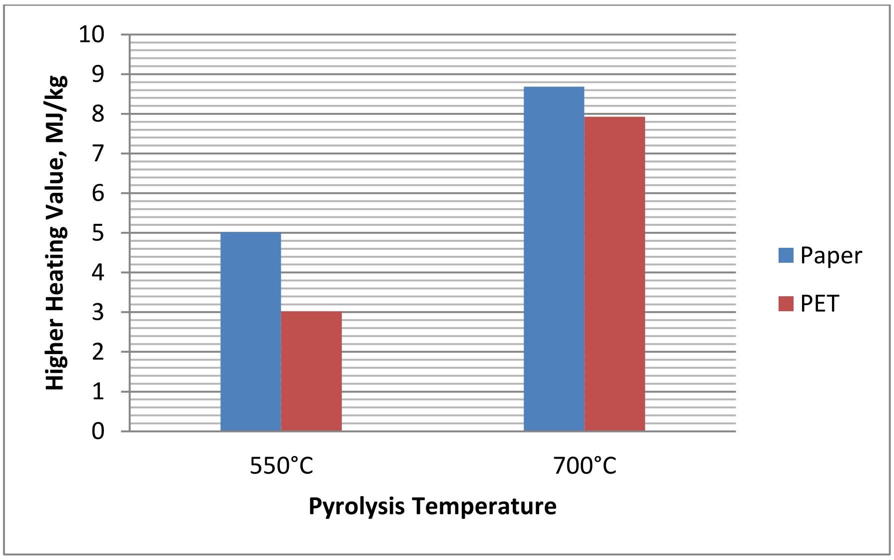


Figure

Figure

4.6 TESTING ON COMMERCIAL RIG 1: MICRO SCALE BATCH PYROLYSER

Details

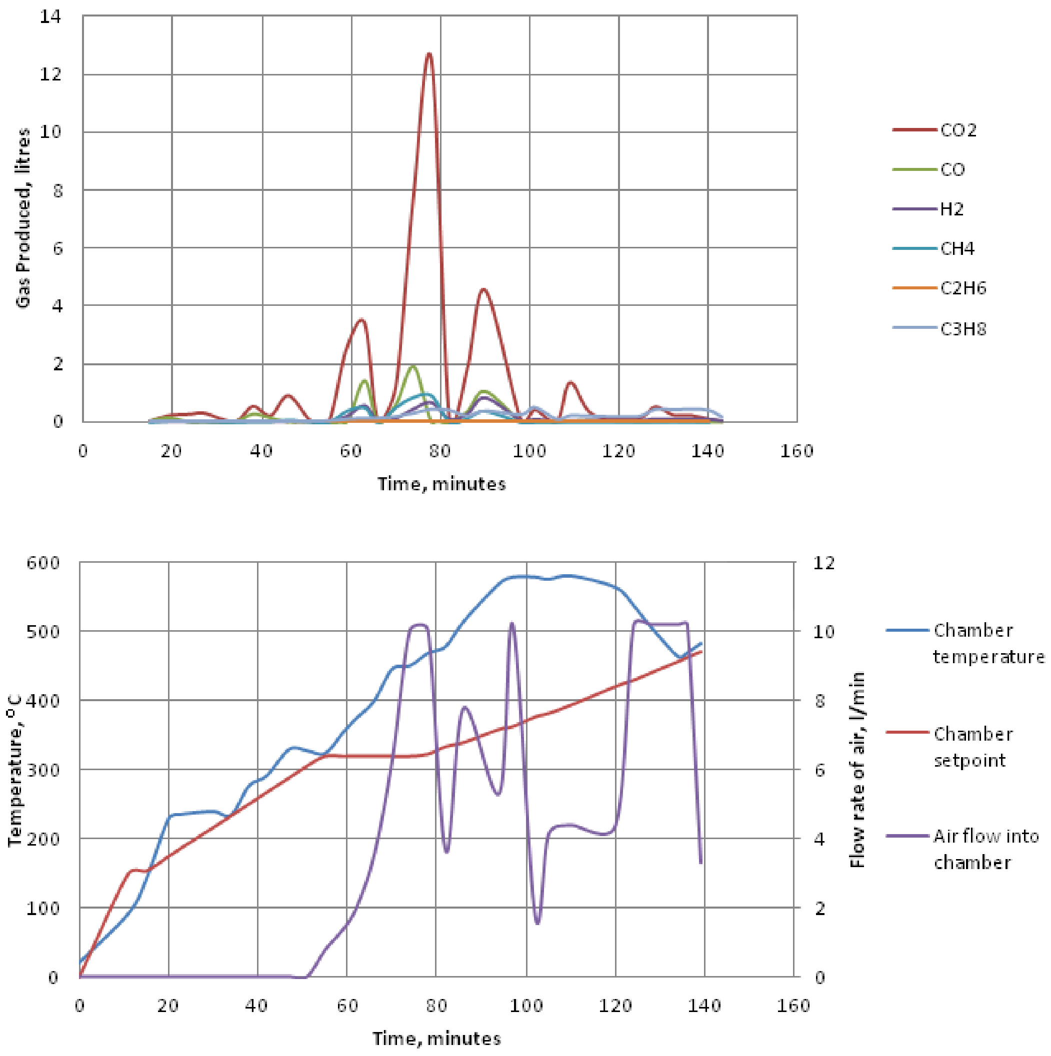
For tests with commercial rig 1, two waste mixes were used both with a total mass of 5 kg. These were:

- 100 % cardboard
- 66 % PET, 33 % cardboard

The

4.6.1 RUN 1

Figure



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4.6.2 RUN 2

Figure 4.26 shows the composition of the produced gas, the chamber temperature, set point temperature and the flow rate of the air introduced to the chamber for run 2 with a total fuel mass of 5 kg made up of 33 % cardboard and 66 % PET. As with Run 1, the first 50 minutes show the pyrolysis stage before air was introduced to the chamber. The production of CO_2 began once the temperature reaches approximately 230 °C. This was also seen in run 1 and can be attributed to pyrolysis of the cardboard. It can be seen that there were two distinctive time frames of gas production during the run, the first from approximately 50 – 85 minutes with a temperature increase from 230-380 °C and the second from approximately 90 – 150 minutes with a temperature range of 400-580 °C. After approximately 130 minutes the air flow to the chamber was increased for the final combustion phase to end the process. In a TGA study with PET by Çepelioğullar and Pütün, it was found that mass loss, and therefore pyrolysis reactions, began at 380-400 °C [52]. This first time frame of gas production from 50-85 minutes can therefore be attributed to the thermal degredation of the cardboard.

Comparisons between data for run 1 and run 2 for this time frame show the CO_2 peaks for run 2 are wider and have a lower maximum value, therefore showing a slower production of gas. The melting temperature for PET has been found to be approximately 165 °C [61]. The PET within the chamber is therefore likely to have melted around the cardboard and inhibited the release of gas until a temperature high enough for the thermal degredation of PET is reached.

It can be seen that there were two main time frames where the chamber temperature exceeds the chamber set point temperature. These time frames of 50-80 minutes and 105-150 minutes coincide with the time frames discussed above of maximum gas production. It can be seen that a higher temperature of above 440 °C is needed before the second stage of exothermic reactions occur. This is attributed to the complex structure of PET requiring a higher temperature for thermal degradation.

Comparisons can also be made with laboratory data for the pyrolysis of cardboard and of PET in the laboratory scale reaction rig. It was found, as shown in Figure 4.14, that the pyrolysis of PET produced a significantly higher volume of CO at 0.24 litres compared to 0.15 litres from the pyrolysis of cardboard. During pyrolysis of cardboard and PET in commercial rig 1, it can be seen that a significantly higher volume of CO was produced from the addition of PET when compared to run 1. The low volumes of H_2, CH_4, C_2H_6 and C_3H_8 detected during pyrolysis on commercial rig 1 are also comparable with volumes detected during pyrolysis in laboratory investigations. Further comparisons and discussion of laboratory data and results from tests at commercial rig 1 can be found in section 5.2.3 where an empirical model based on laboratory results is used to aid comparison of the pyrolysis of mixed MSW.

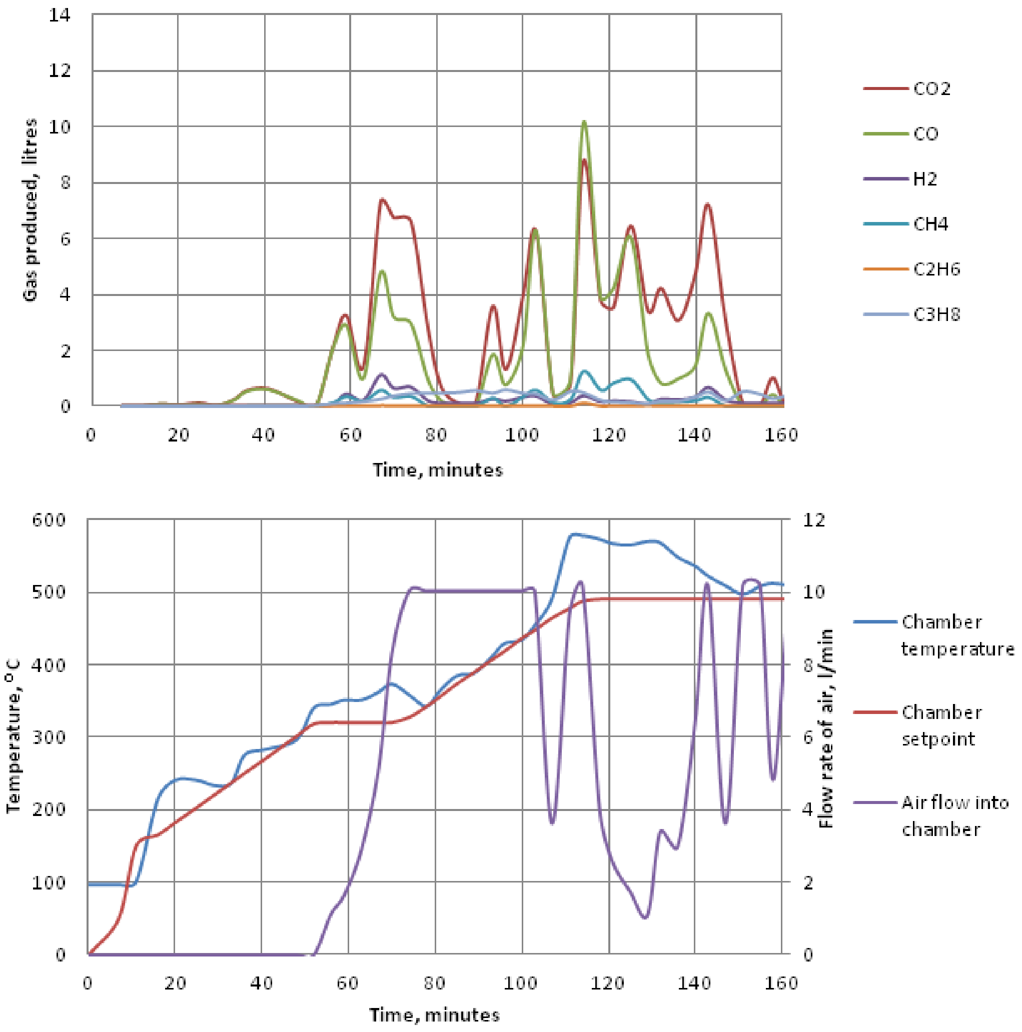

Figure 4.26: Graphs of the composition of the produced gas and the chamber temperature, set point and air flow in during run 2 on commercial rig 1

4.7 TESTING AT COMMERCIAL RIG 2: SMALL SCALE SEMI-BATCH PYROLYSER

Details of commercial rig 2 can be found in section 1.4.2 and the testing methods can be found in section 3.6.2. Further discussion of these results and comparisons with laboratory data can be found in section 5.2.4 with discussion of errors in section 4.8.6. Full numerical values are given in tabulated form in Appendix X. For tests with commercial rig 2, one waste mix was used based on the typical composition of MSW. The components of this mix were:

Paper	30 %
Cardboard	40 %

Plastic*	20 %
Textiles	10 %

*The plastic waste used in this study was made up of a mixture of PET, PVC and HDPE.

Figure 4.27 shows the composition of the gas measured by the micro GC at the point at which it leaves the pyrolysis chamber. This data is an average of 5 readings taken whilst the rig was under stable operation at 550 °C. Data set 1 shows the gas composition as found by the micro GC. Data set 2 shows the gas composition with the air discounted from the results as calculated using the percentage of oxygen present in the output gas. As any air leaks within the tar trap and gas analysis system were checked and minimised, it is assumed this air leak entered the gas before the tar trap equipment.

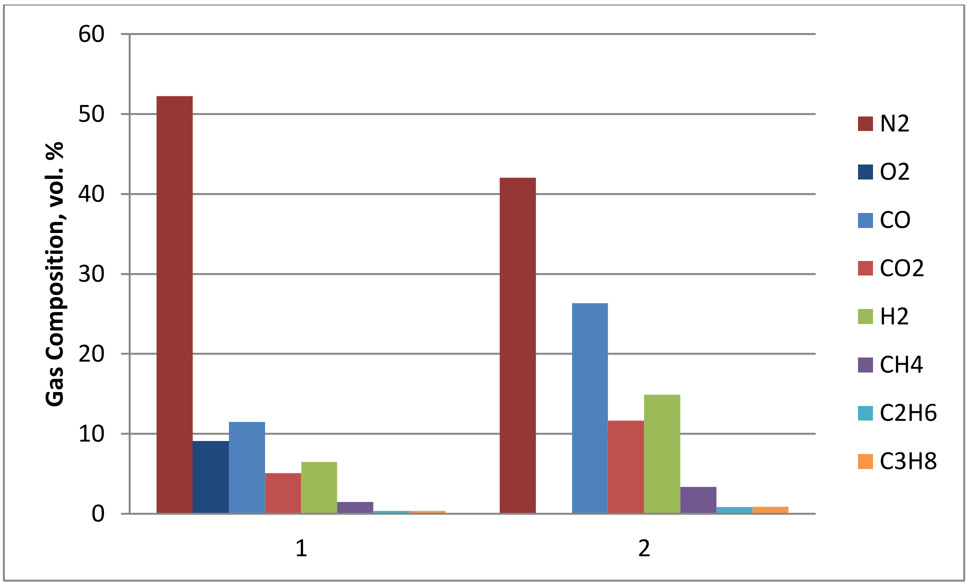

Figure 4.27: A graph showing the composition of the gas leaving the pyrolysis chamber for 1) As recorded by micro GC and 2) With air discounted from data

However, there is still a significant percentage of N_2 present in data set 2 once the air has been discounted. As found in previous research, the N_2 content of uncoated paper, cardboard, plastics and textiles is approximately 0 – 0.4 % [22, 28, 39, 41, 43, 62, 66, 75, 77], this is shown in Appendix I. The majority of N_2 in the product gas is therefore not due to N_2 present in the fuel. It is therefore assumed that the majority of this came from air flow into the pyrolysis chamber and was not consumed in pyrolysis reactions. Although it is known that a gas was introduced into the chamber during pyrolysis, the composition or quantity is unknown.

The composition of gas produced from commercial rig 2 can be compared to the gas produced from the individual components of waste during laboratory investigations as shown in Figure 4.14 and discussed in section 4.5.2. For all individual components used in the waste mix for commercial rig 2, the main gases produced are CO and CO_2. This is also true for the gas produced from commercial rig 2, however a significantly higher percentage of CO was produced compared to CO_2 which was not shown in laboratory studies for pyrolysis of 20 minutes.

The composition of the gas produced from commercial rig 2 shows significant similarities with the composition of the gas produced from the pyrolysis of paper in laboratory investigations at a higher temperature of 700 °C as shown in Figure 4.21. The main components of the gas produced from the pyrolysis of paper at 700 °C were found to be 43.0 % CO, 34.3 % H_2 and 19.3 % CO_2 as a percentage of the total indentified gases compared to 45.4 % CO, 25.7 % H_2, 25.7 % CO_2, as found from commercial rig 2. Both processes produced lower values of CH_4, C_2H_6 and C_3H_8. It can therefore be assumed that the temperature of the pyrolysis chamber in commercial rig 2 is higher than 550 °C during stable operation and at a temperature of approximately 700 °C. This is discussed further along with further comparisons between laboratory and commercial rig data in section 5.2.4.

4.8 DATA REPEATABILITY AND SOURCES OF ERRORS

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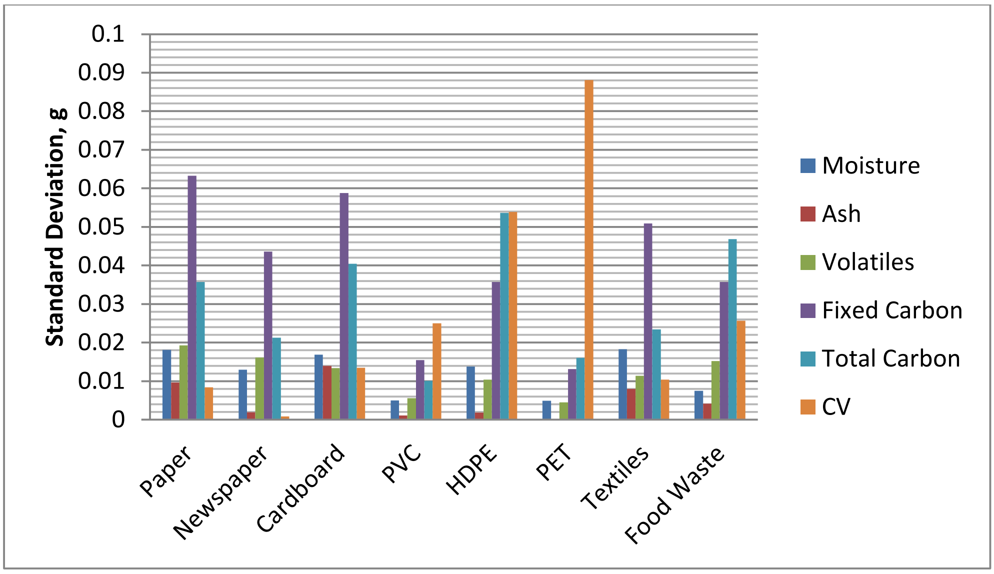
4.8.1 CHARACTERISATION OF MSW FUEL SAMPLES



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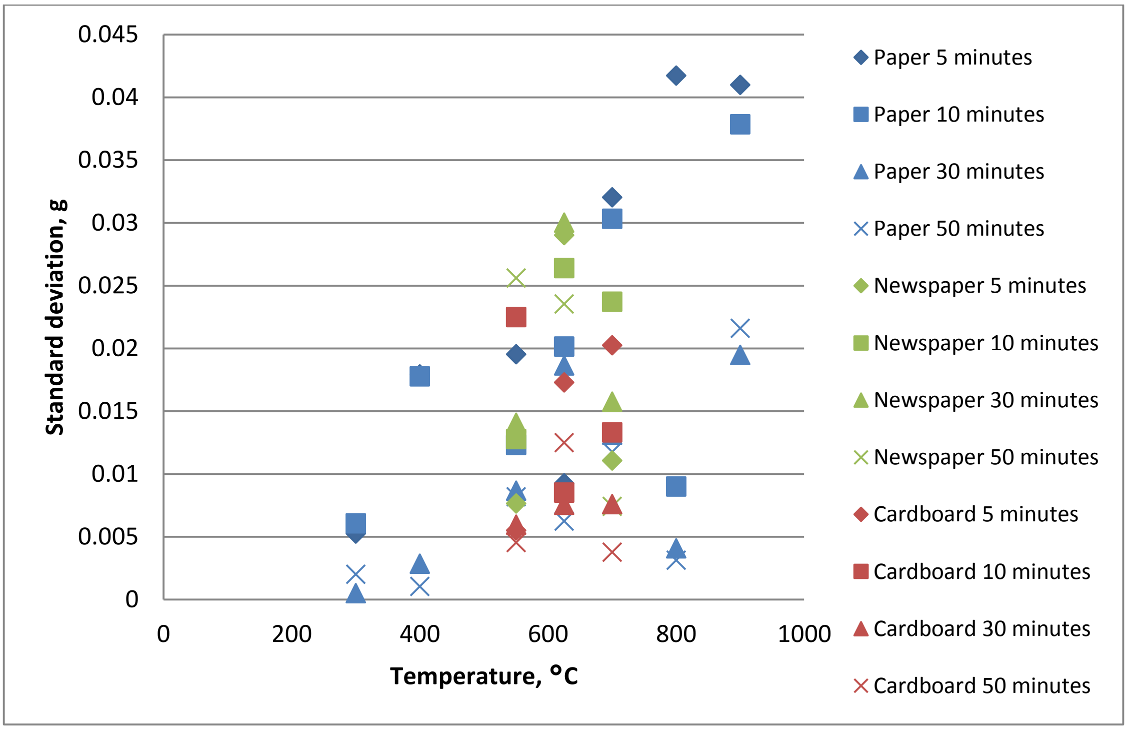
4.8.2 MASS LOSS



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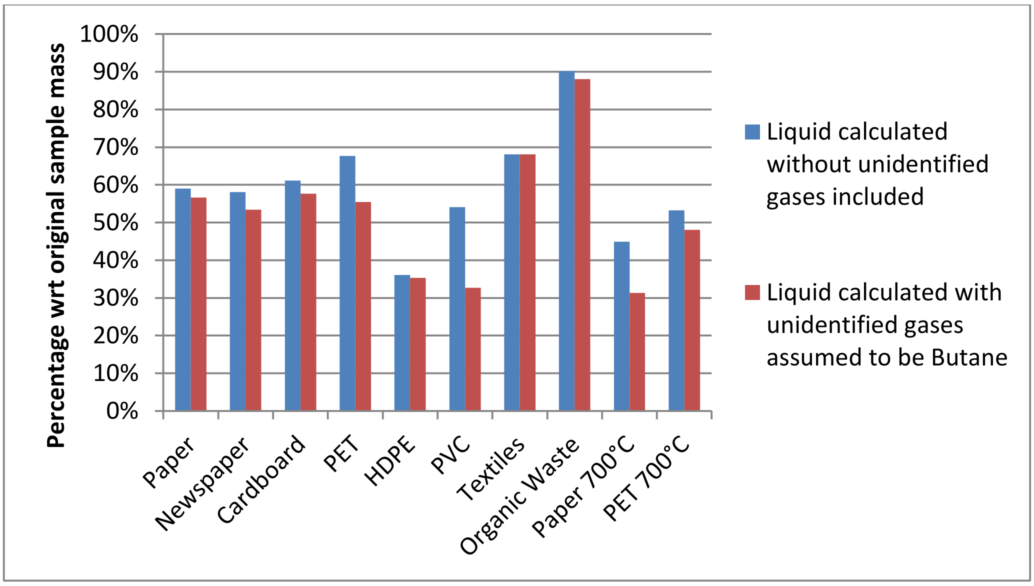
4.8.3 PYROLYSIS PRODUCTS

As

It can be seen that for the majority of samples there is only a small change in the percentage of the total liquid products. For PVC, the inclusion of the unidentified gases decreases the percentage of the liquid products. This is due to a large percentage of the gaseous products for PVC being unidentified gases. This also occurs for paper pyrolysed at 700 °C. The assumption that any unidentified gases have a molecular mass similar to butane is therefore adequate for the estimation of pyrolysis products, although with a lower accuracy for products from PVC and paper at 700 °C. The pyrolysis reaction rig used in this study was primarily designed for analysis of the gaseous pyrolysis products. A secondary aim was to estimate the liquid products produce. It has been shown that the reaction rig can be used to estimate the pyrolysis products although for greater accuracy in quantification of these products, adjustments would need to be made to the laboratory instrumentation in order to collect and measure the produced tars with a higher accuracy.



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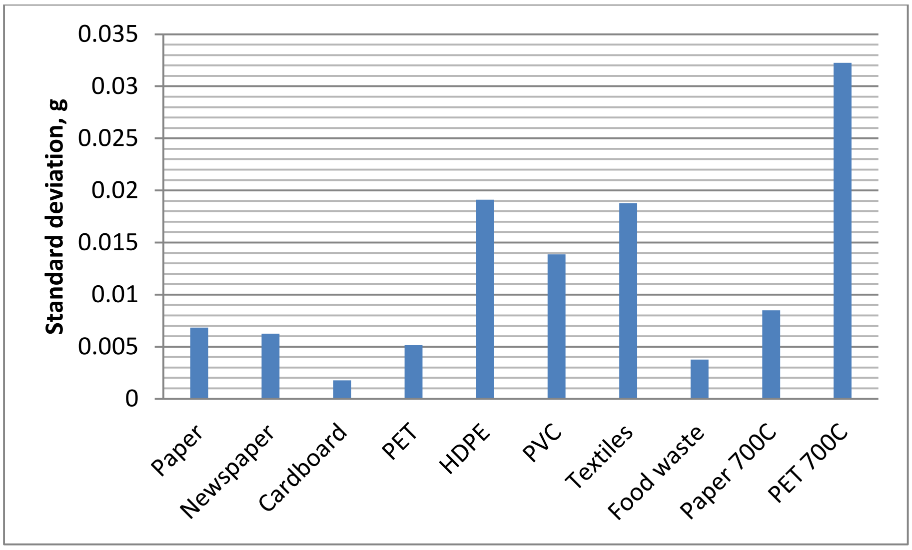

Figure

4.8.3.1 TAR TRAP SYSTEM

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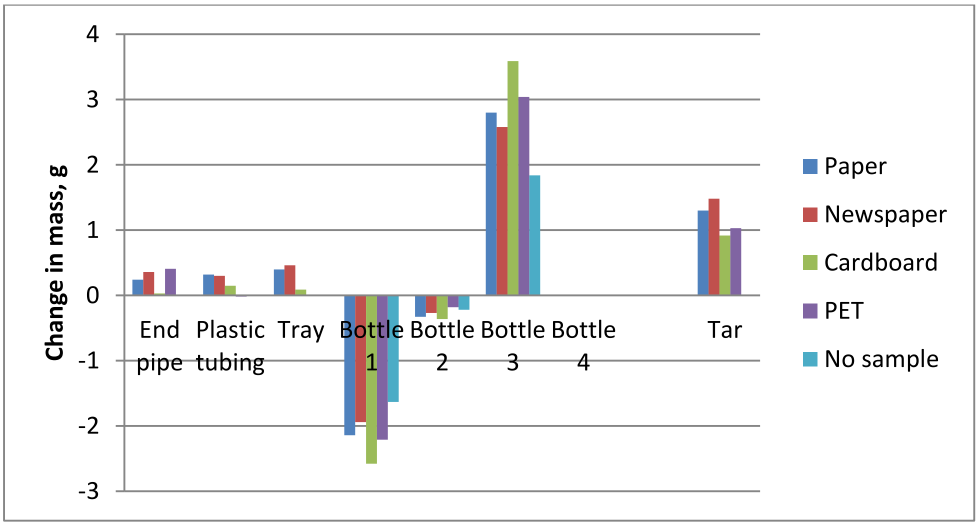

Figure

4.8.4 GAS ANALYSIS

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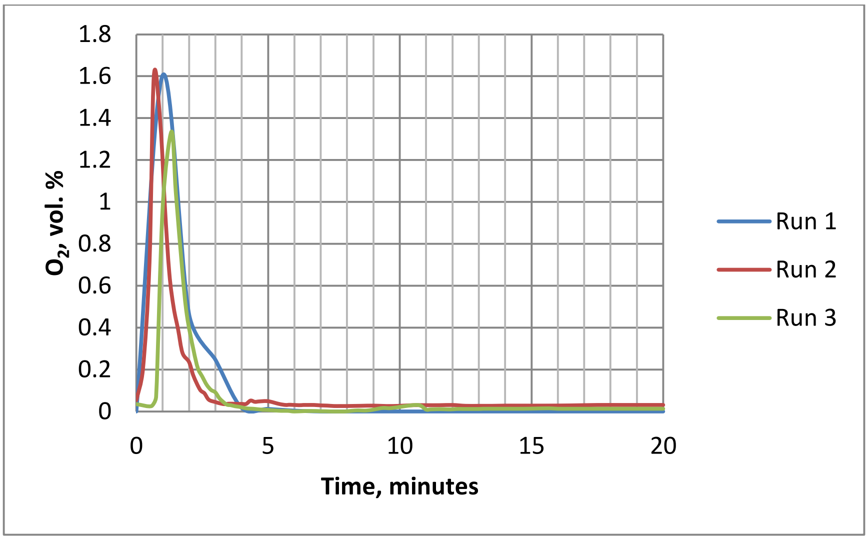

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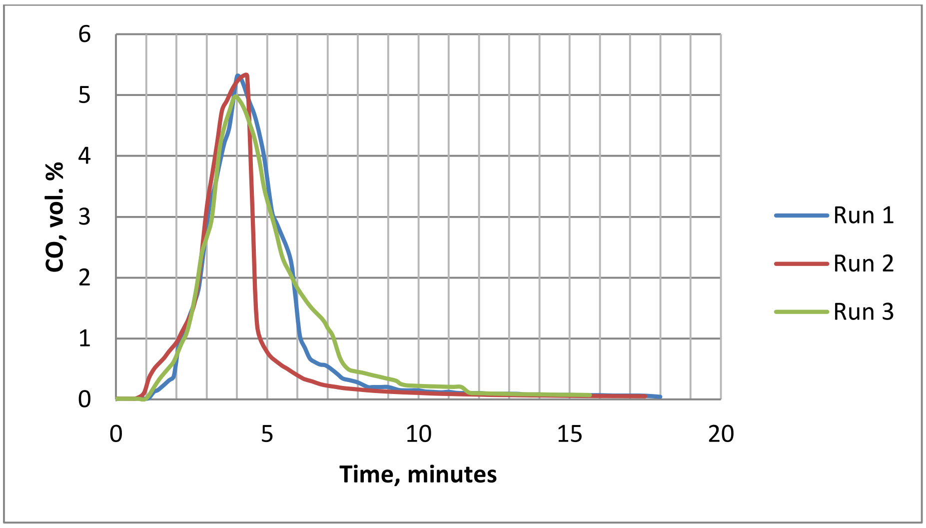

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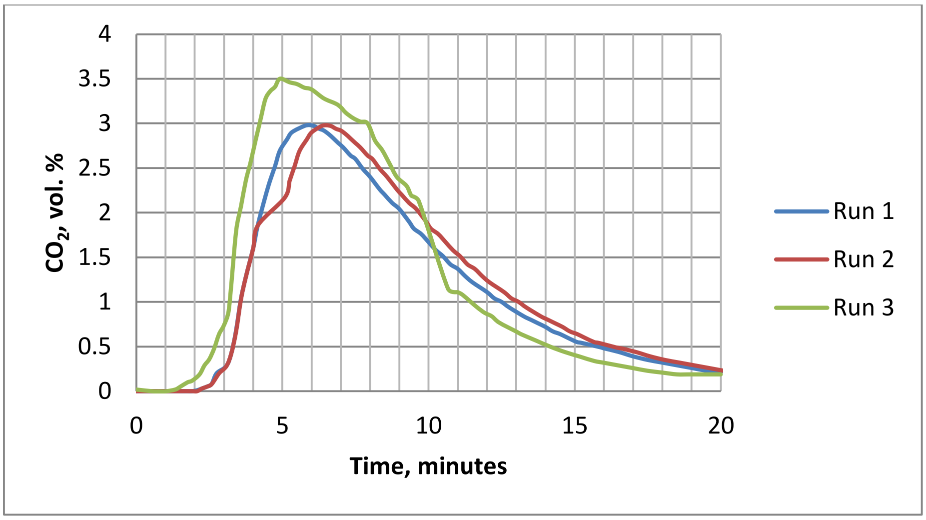

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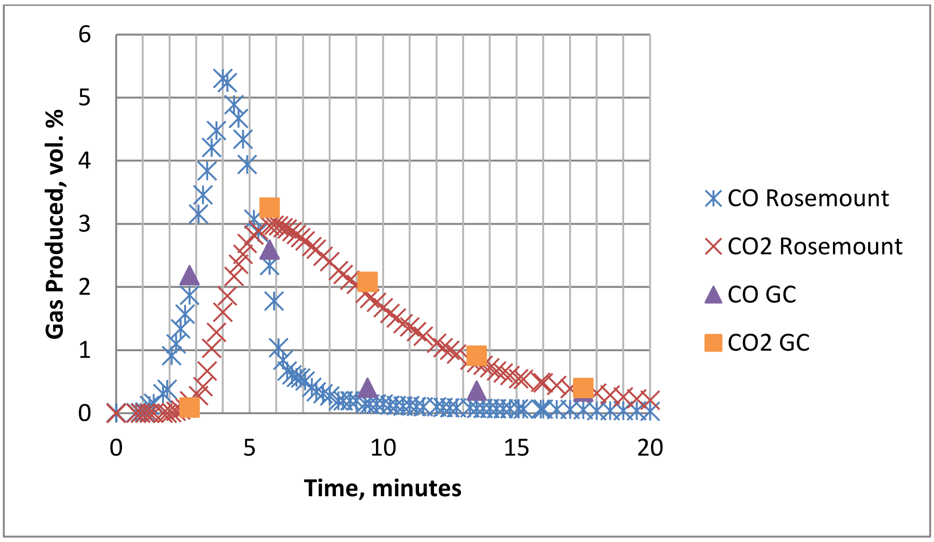

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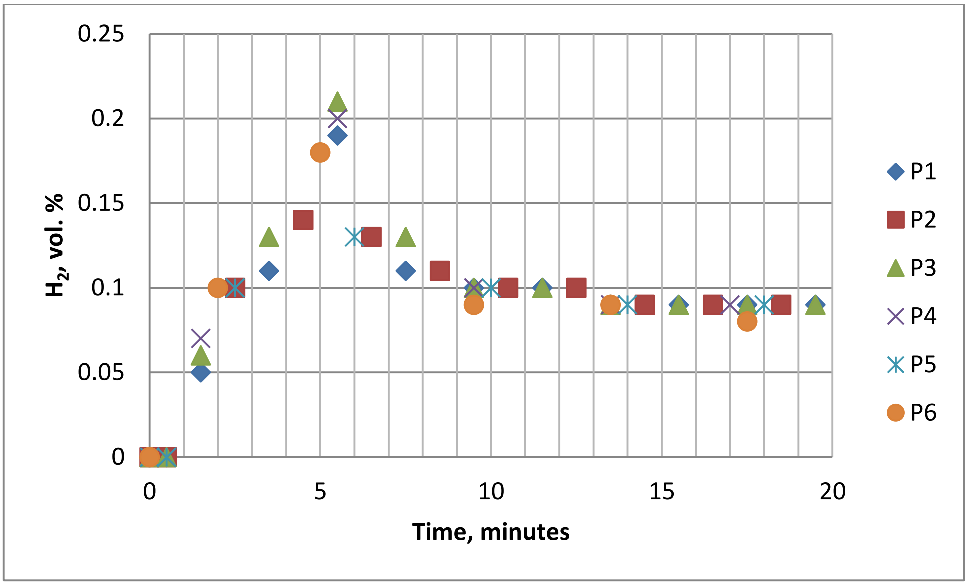

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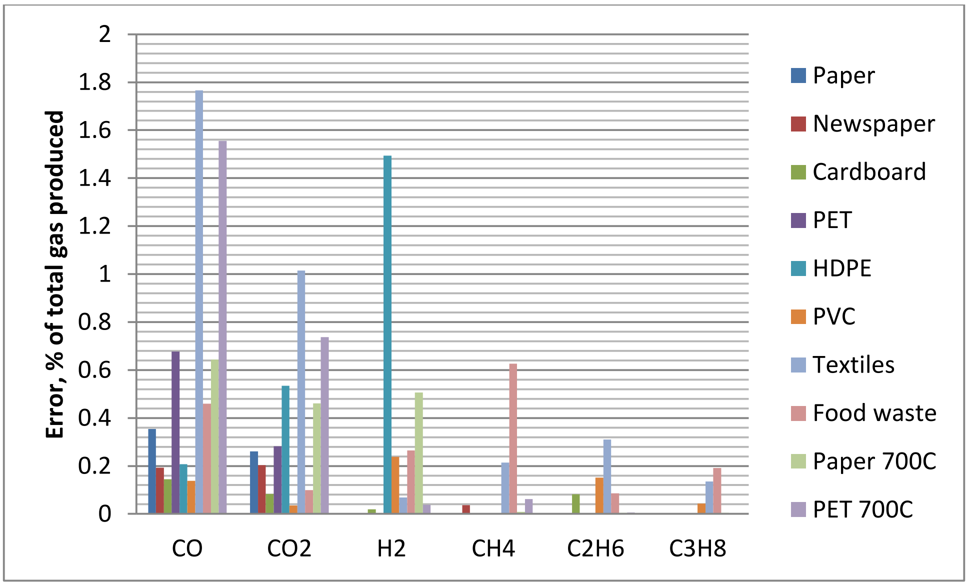

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4.8.5 TESTING ON COMMERCIAL RIGS

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4.8.5.1 TESTING ON COMMERCIAL RIG 1: MICRO SCALE BATCH PYROLYSER

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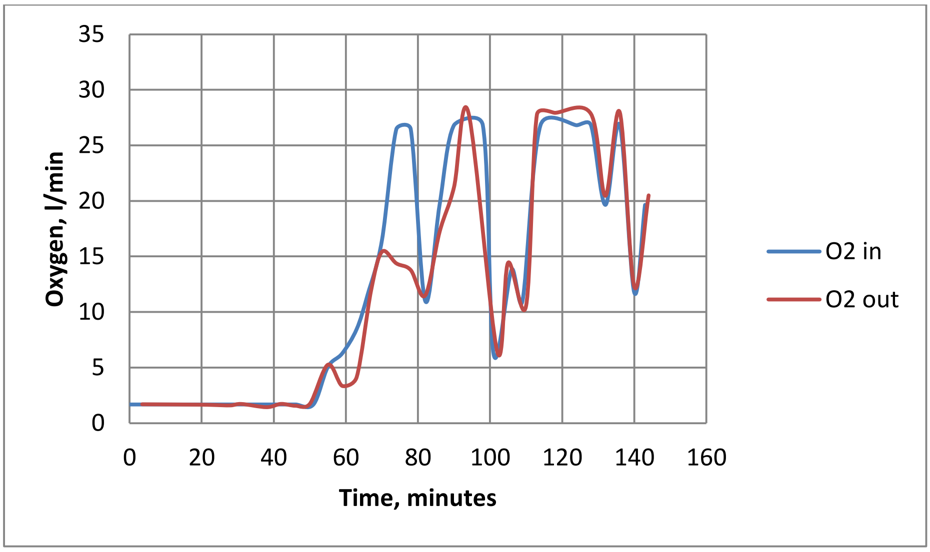

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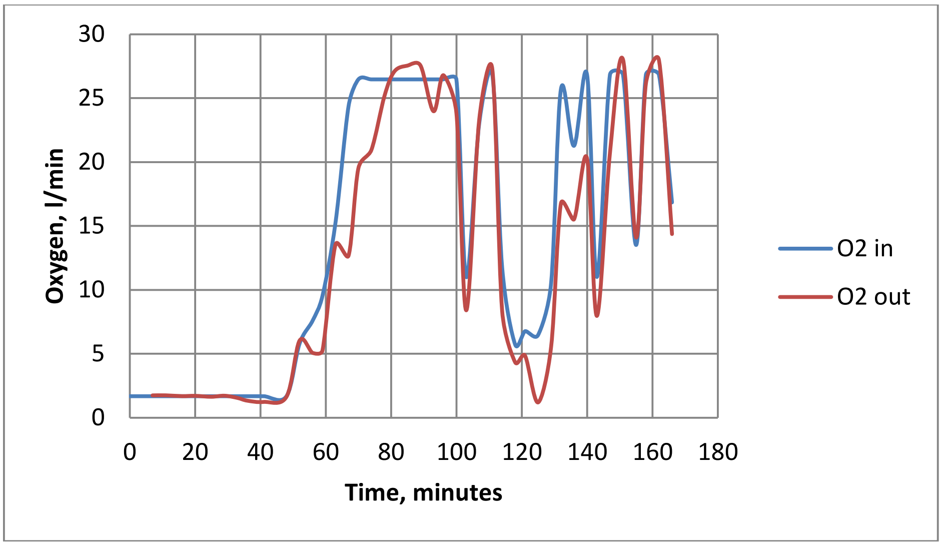

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4.8.6 TESTING ON COMMERCIAL RIG 2: SMALL SCALE SEMI-BATCH PYROLYSER

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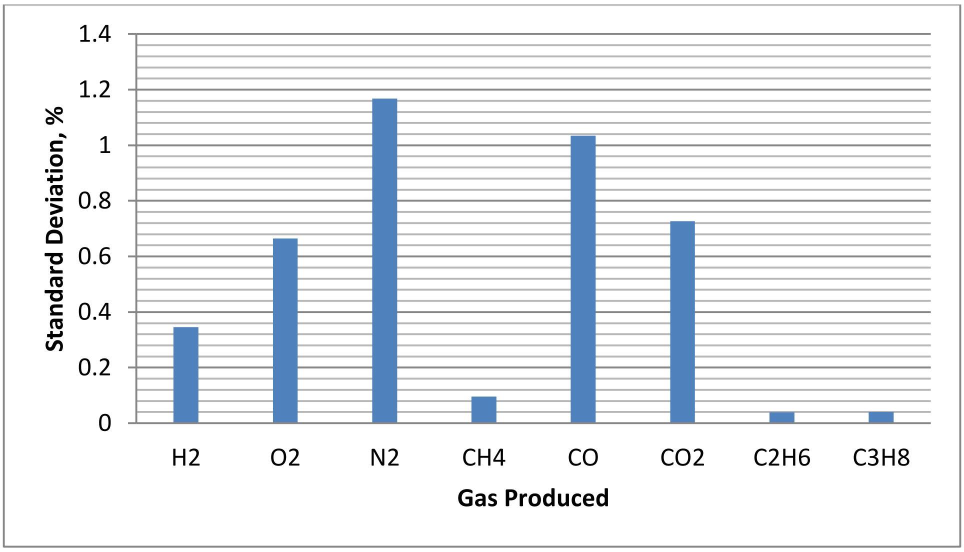

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4.9 SUMMARY

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CHAPTER 5 MATHEMATICAL MODELLING

5.1 MODELLING MASS LOSS

From

Exponential equations were calculated, based on the trends in laboratory data, to enable prediction of the percentage of sample mass remaining for pyrolysis at any point *100–abx+a* Equation 122, where y is the percentage of sample mass remaining and x is the pyrolysis time in minutes. The values calculated for *a* and *b* for each sample at each temperature are shown in Table 5.1.

$$y = (100 - a)b^x + a \qquad \text{Equation 12}$$

Table 5.1: Values of *a* and *b* calculated for charcoal and paper at 300-900 °C and newspaper and cardboard at 550, 625 and 700 °C

Temperature, °C	Charcoal		Paper		Newspaper		Cardboard	
	a	b	a	b	a	b	a	b
300	93.40	0.68	92.70	0.70	-	-	-	-
400	92.10	0.83	61.40	0.85	-	-	-	-
500	89.10	0.79	38.60	0.79	-	-	-	-
550	87.90	0.79	35.90	0.76	30.90	0.66	30.74	0.66
600	87.10	0.74	33.90	0.66	-	-	-	-
625	84.80	0.81	32.10	0.65	26.70	0.71	24.70	0.68
700	80.80	0.81	30.20	0.65	23.90	0.69	20.70	0.62
800	77.80	0.74	23.80	0.71	-	-	-	-
900	76.90	0.75	22.60	0.73	-	-	-	-

It can be seen in Figure 5.1 that, for charcoal samples, there is a sigmoid relationship between the values for *a* and the pyrolysis temperature. It is assumed that there is a similar sigmoid relationship between these values for paper, newspaper and cardboard samples although the full sigmoid relationship is not shown within the range of data collected. This is because paper, newspaper and cardboard have a lower reaction temperature for pyrolysis than charcoal.

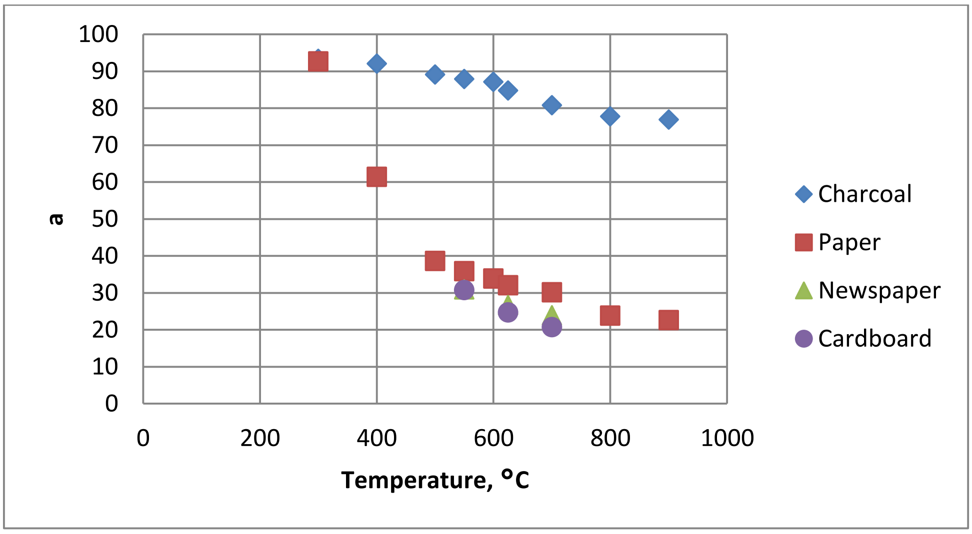


Figure 5.1: A graph of the a values calculated for each sample against the pyrolysis temperate

The equation of a standard sigmoid function, as described by McDowall et al [117], is:

$$a = \frac{A_1}{1+e^{A_2(z-A_3)}} + A_4 \qquad \text{Equation 13}$$

Where:

a = the coefficient of Equation 12

z= the pyrolysis temperature, °C

A_1 = the range in *a* (value of *a* at the top plateau – value of *a* at the bottom plateau

A_2 = the gain coefficient

A_3 = the value of z at the midpoint (also the point of maximum gain)

A_4 = the value of a at the bottom plateau

Using this, an equation for a for each of the samples has been established as shown in $a = \frac{20}{1+e^{0.008(z-610)}} + 75$ Equation 14$a = \frac{90}{1+e^{0.011(z-395)}} + 22$ Equation 15$a = \frac{85}{1+e^{0.013(z-410)}} + 21$ Equation 16 and$a = \frac{93}{1+e^{0.01(z-390)}} + 15$ Equation 17.

For charcoal:

$$a = \frac{20}{1+e^{0.008(z-610)}} + 75 \qquad \text{Equation 14}$$

For paper:

$$a = \frac{90}{1+e^{0.011(z-395)}} + 22 \qquad \text{Equation 15}$$

For newspaper:

$$a = \frac{85}{1+e^{0.013(z-410)}} + 21 \qquad \text{Equation 16}$$

For cardboard:

$$a = \frac{93}{1+e^{0.01(z-390)}} + 15 \qquad \text{Equation 17}$$

$100-abx+a$ Equation 12 with values calculated for a using $a = \frac{20}{1+e^{0.008(z-610)}} + 75$ Equation 14$a = \frac{90}{1+e^{0.011(z-395)}} + 22$ Equation 15$a = \frac{85}{1+e^{0.013(z-410)}} + 21$

$931+e0.01(z-390)+15$ Equation 17. As the value of *b* did not change significantly for each temperature, an average was taken for each sample.

$100–abx+a$ Equation 12 gives an equation modelling the change in the percentage of the sample mass remaining after pyrolysis with a change in pyrolysis time and temperature as shown for each sample in the equations below.

For charcoal:

$$y = \left(175 - \frac{20}{1+e^{0.008(z-610)}}\right)0.77^{x} + \frac{20}{1+e^{0.008(z-610)}} + 75 \qquad \text{Equation 18}$$

For paper:

$$y = \left(122 - \frac{90}{1+e^{0.011(z-395)}}\right)0.7^{x} + \frac{90}{1+e^{0.011(z-395)}} + 22 \qquad \text{Equation 19}$$

For newspaper:

$$y = \left(121 - \frac{85}{1+e^{0.013(z-410)}}\right)0.67^{x} + \frac{85}{1+e^{0.013(z-410)}} + 21 \qquad \text{Equation 20}$$

For cardboard:

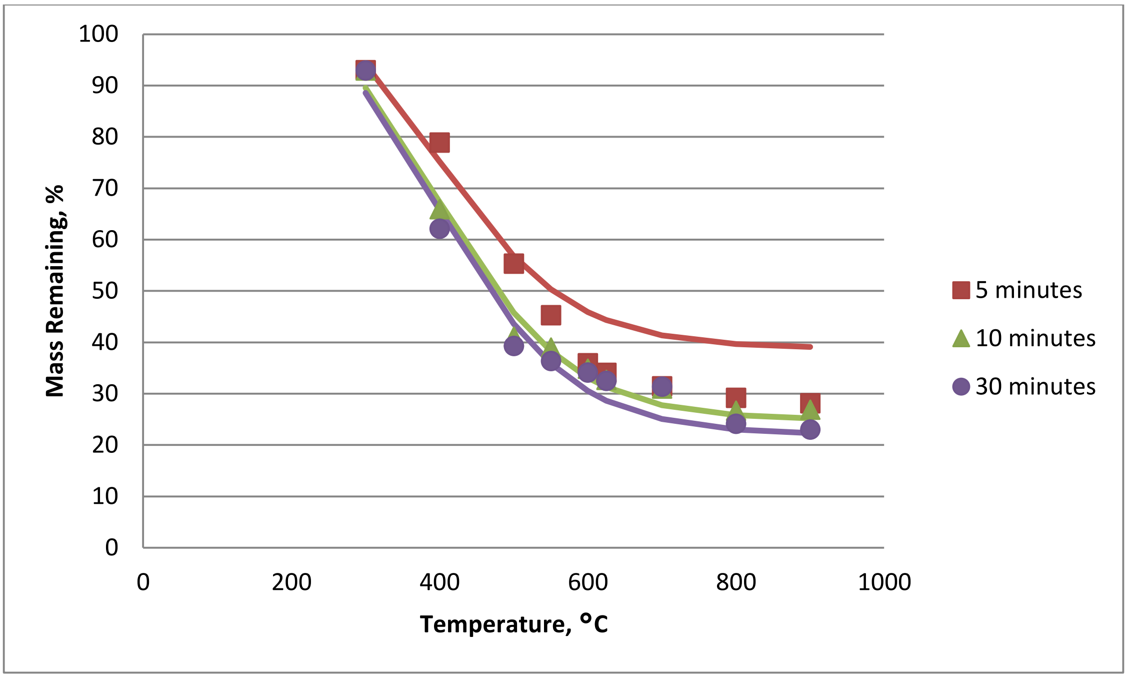
$$y = \left(115 - \frac{93}{1+e^{0.01(z-390)}}\right)0.7^{x} + \frac{93}{1+e^{0.01(z-390)}} + 15 \qquad \text{Equation 21}$$

Where

x= the pyrolysis time (minutes)

z=the pyrolysis temperature (°C)

Figures



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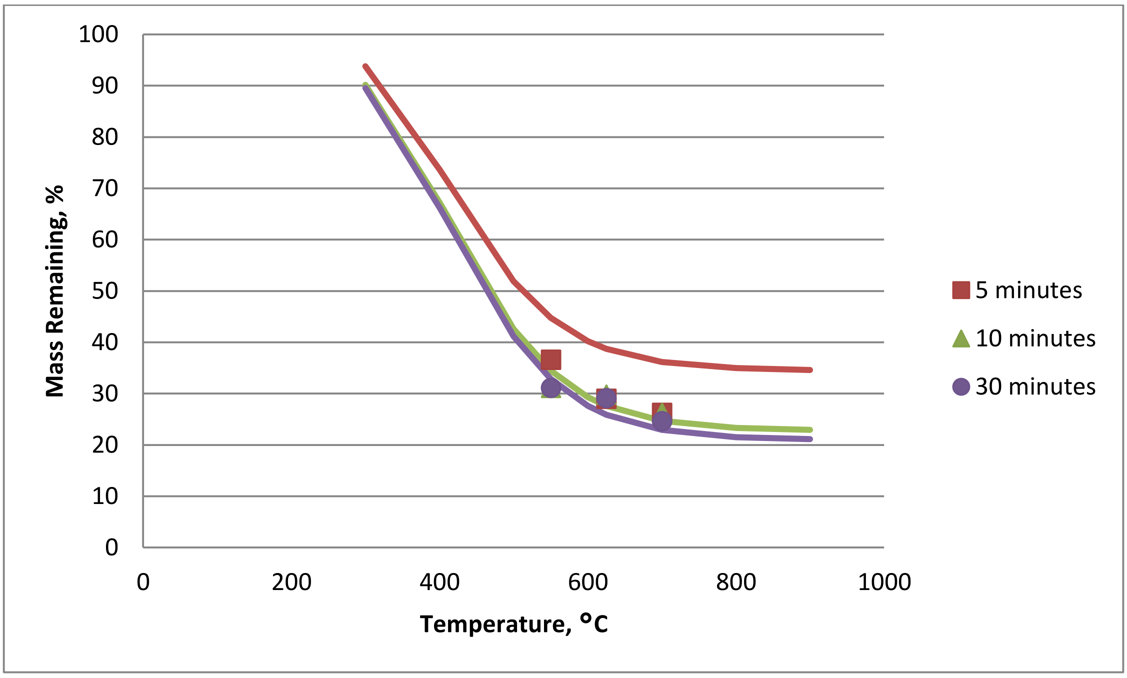

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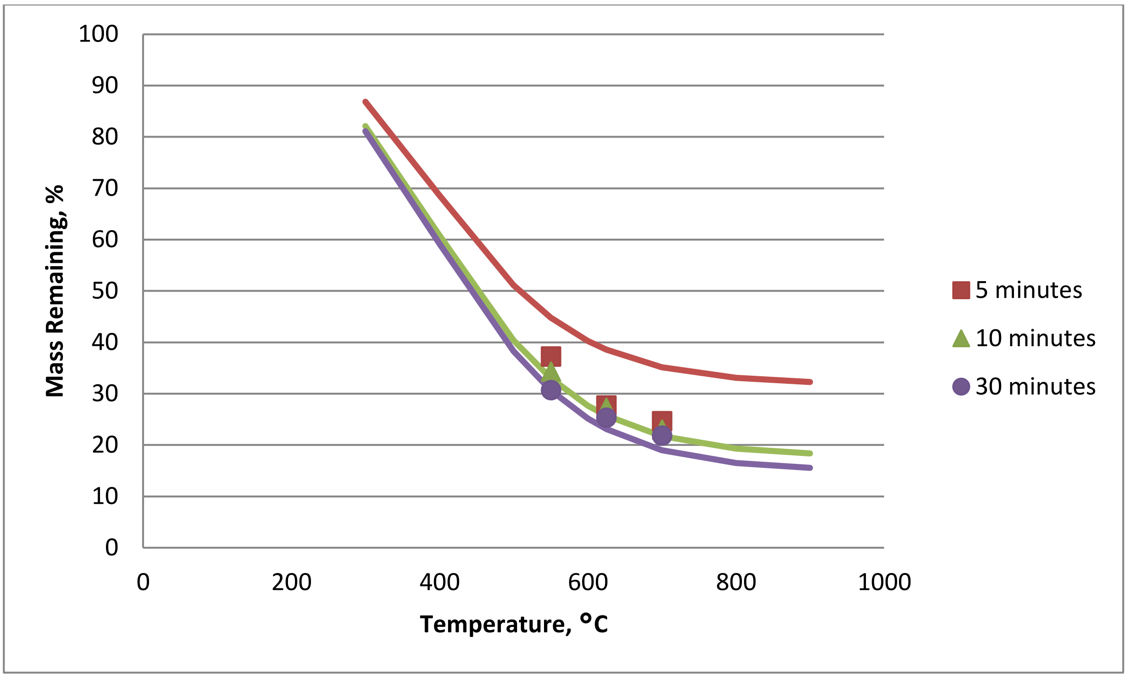
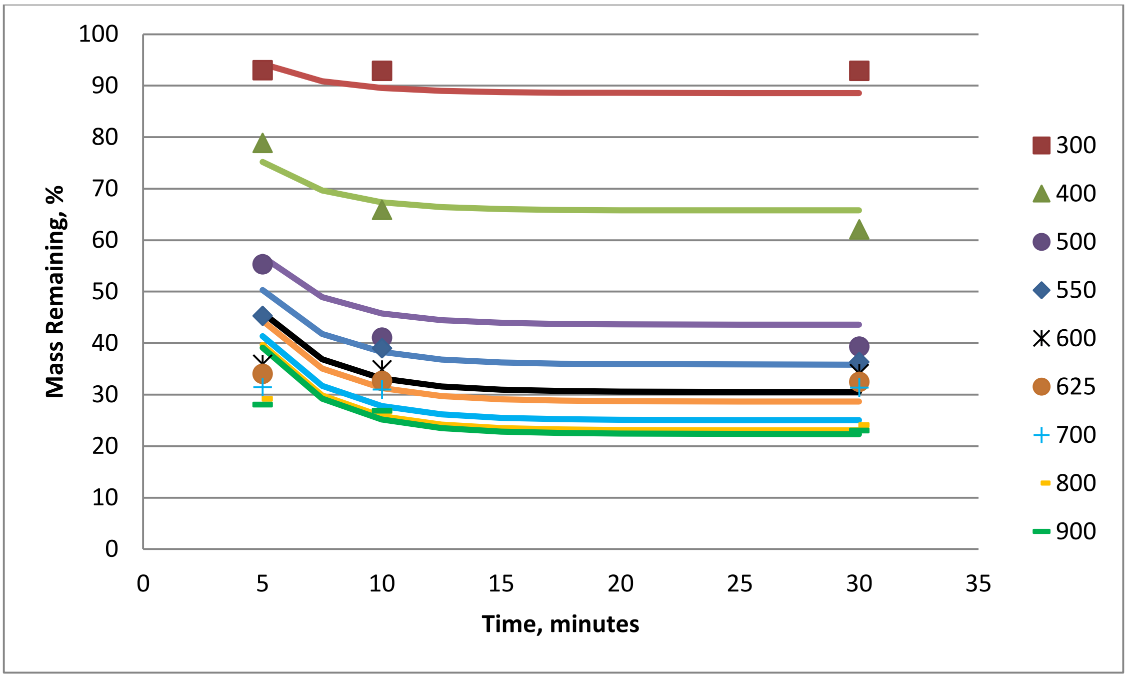

100
90
80
70
60
50
40
30
20
10
0
Mass Remaining, %
0
200
400
600
800
1000
Temperature, °C
5 minutes
10 minutes
30 minutes

Figure



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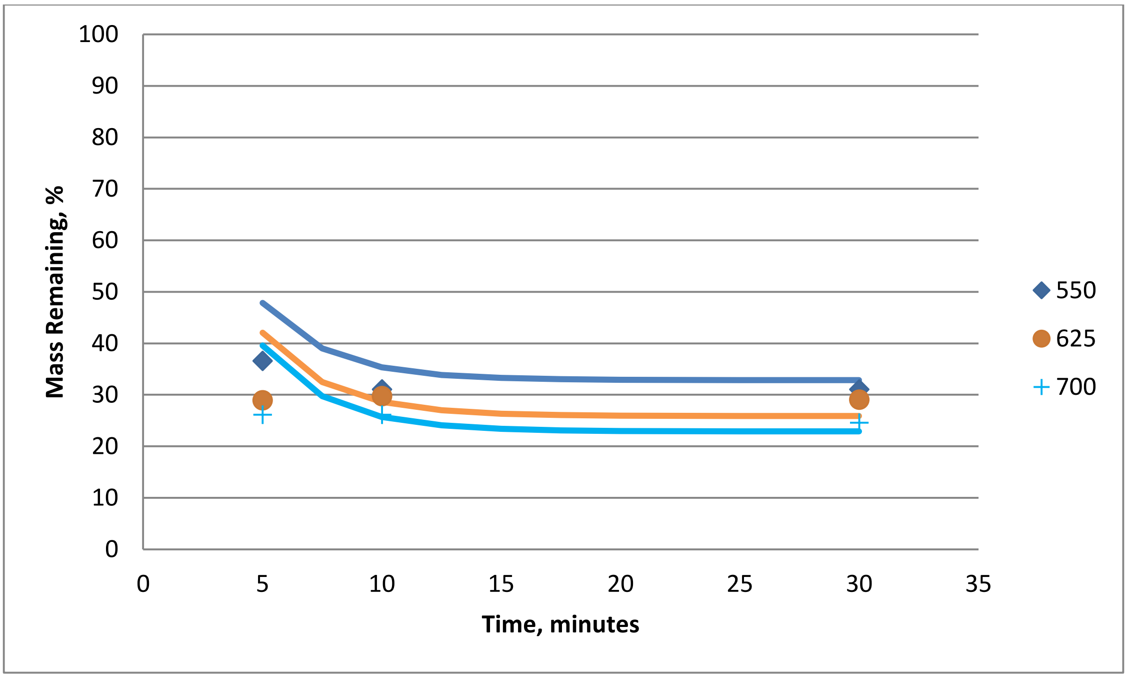

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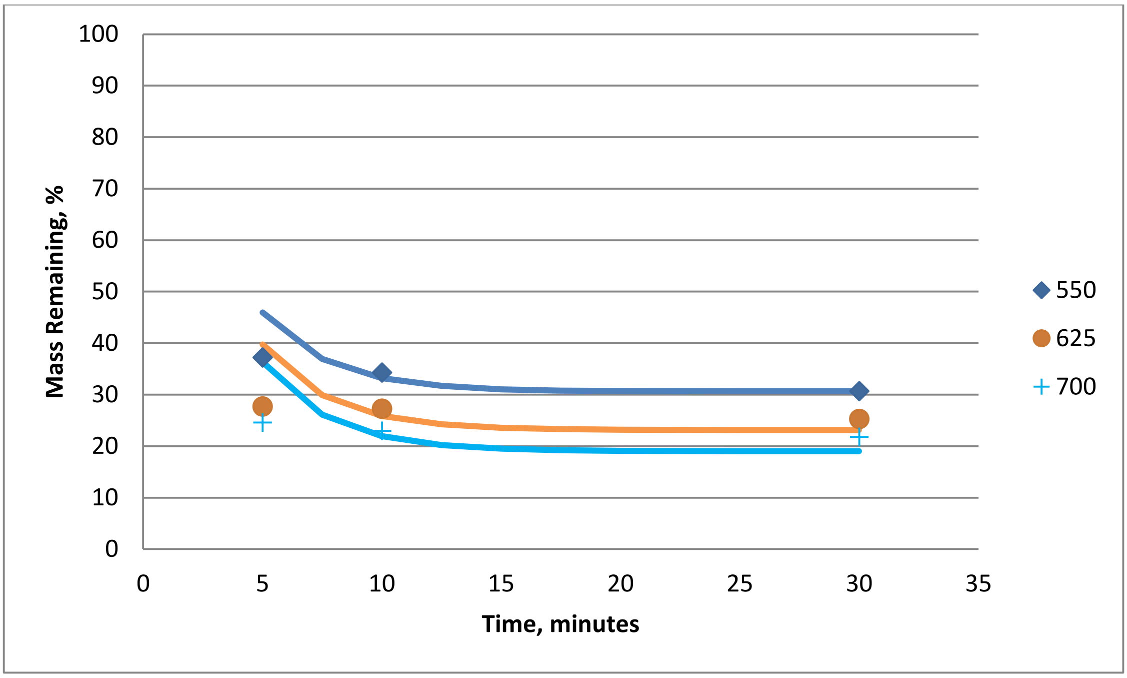
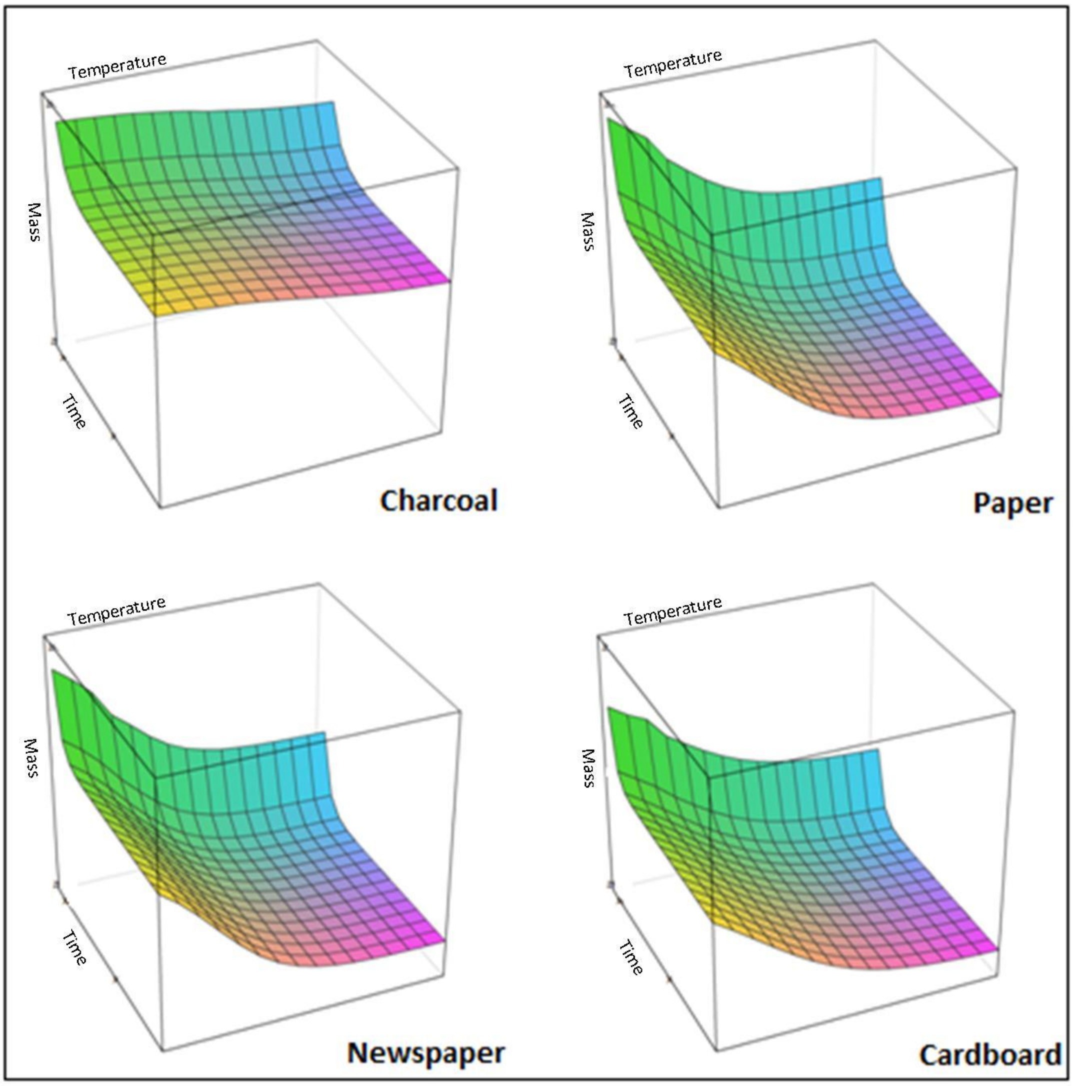


Mass Remaining, %
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
Time, minutes
550
625
700

Figure

A



Figure

For charcoal and paper, the model is based on lab data for the full range of 300-900 °C from 0-50 minutes. For newspaper and cardboard the model has been extrapolated for temperatures from 300-550 °C and from 700-900 °C with the assumption that these samples would follow the same trend as paper samples.

5.1.1 COMPARISONS OF MODEL WITH THERMOGRAVIMETRIC ANALYSIS

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Figure

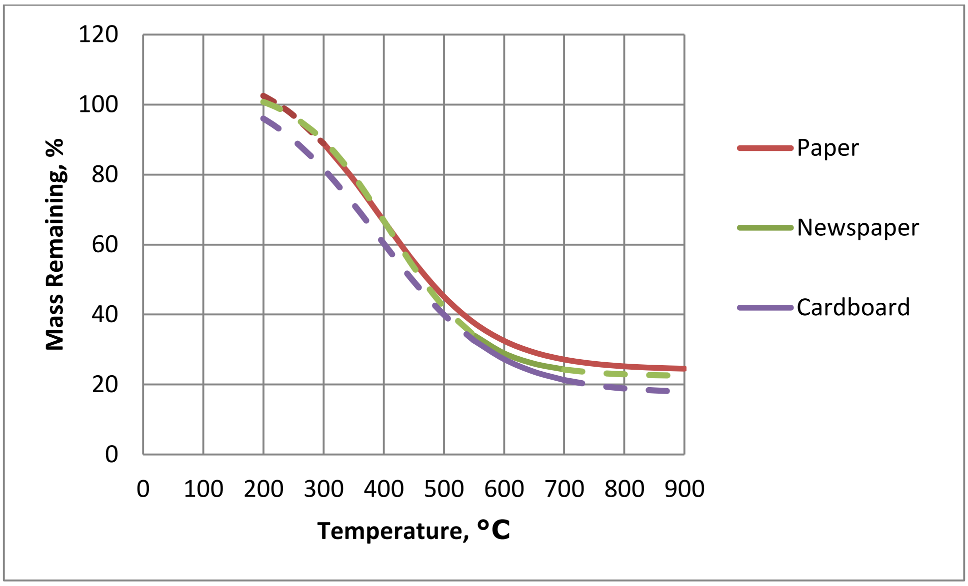

Figure 5.9: The percentage of sample mass remaining for paper, newspaper and cardboard $122-901+e0.011z-3950.7x+901+e0.011(z-395)+22$ Equation 19, 20 and 21.

An increase in the pyrolysis temperature above 900 °C is not expected to have a significant effect on the mass loss as Figure 5.9 shows the reduction of mass for all samples plateaus after approximately 800-900 °C. At temperatures below 300 °C, the mass reduction of samples is expected to deviate from the sigmoid trend shown. An initial mass loss at approximately 100 °C would be expected due to moisture content, following this no further mass loss would be expected until the initial temperature of thermal degradation for each MSW component is reached. This has been predicted using Equations 19, 20 and 21 as the temperature at which the mass remaining of the sample falls below 100%. The initial thermal degradation temperature has been predicted as approximately 225 °C for paper, 220 °C for newspaper and 165 °C for cardboard.

The initial temperature for the thermal degradation of paper is comparable to that of 230 °C reported by Chen et al [23]. Other authors have reported similar temperatures ranging from 240 °C to 260 °C for the pyrolysis of paper [39, 43, 55, 75]. For newspaper, the initial thermal degradation temperature is comparable to a temperature of 206 °C found by Wu et al [58] and a temperature of 240 °C reported by Sorum et al [43]. The thermal degradation of cardboard in this study has been predicted to begin at a lower temperature than that for paper or newspaper. This was confirmed by Yang et al [97] who reported a temperature of approximately 140 °C using TGA tests. Yang et al also studied the thermal degradation of cardboard using a sample mass of 150-200 g in a laboratory scale pyrolyser and found an increase in mass of the sample led to an increase in the temperature needed for thermal degradation to begin. The initial temperature for the thermal degradation of 200 g of cardboard in the laboratory scale pyrolyser was found to be approximately 240 °C.

Figure 5.10 shows data from the study by Yang et al [97] showing comparisons between TGA and packed-bed pyrolyser results for the mass loss of contaminated wood, cardboard and textiles. It can be seen that there is a significant difference between the thermal degradation of samples in TGA tests compared with samples in the packed-bed pyrolyser. This slower reduction in mass when compared with TGA confirms the findings in this study and the sigmoid trend for the change in mass with a change in pyrolysis temperature. The sample size of 5 g used in this study is between that of 13 mg used by Yang et al for TGA tests and that of 150 g used for tests in the packed-bed pyrolyser. The temperature of initial thermal degradation of cardboard for this study is also within the temperature range found for both investigations by Yang et al [97].

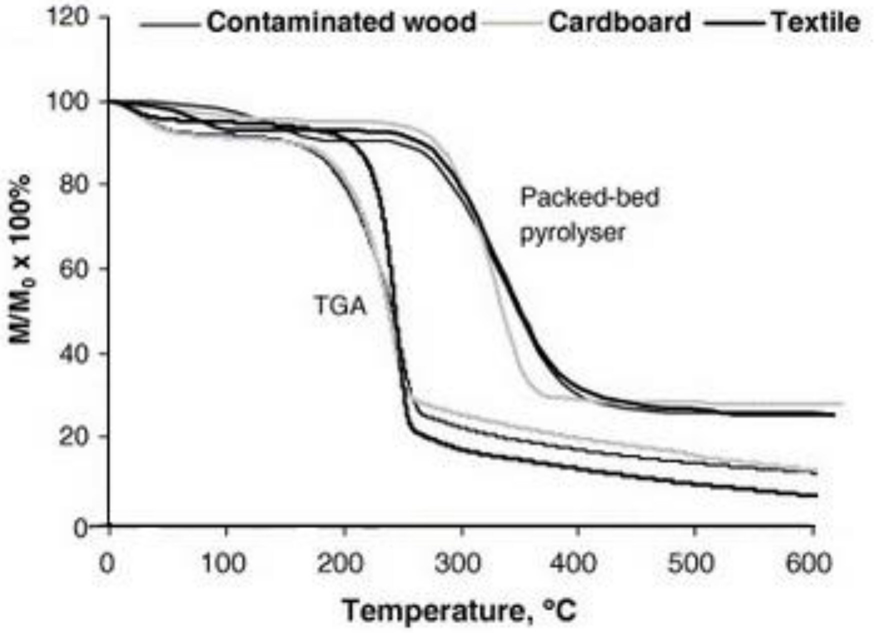

Figure 5.10: Comparison of TGA and packed-bed pyrolyser results for mass loss of contaminated wood, cardboard and textile as found by Yang et al [97].

It can be seen in Figure 5.10 that after a temperature of approximately 400 °C there is little further mass loss from the pyrolysis of cardboard in the packed bed pyrolyser. Figure 5.9 shows that in this study, this did not occur until temperatures of approximately 700 °C. In this study, a different sample was pyrolysed at each temperature as opposed to both studies by Yang et al, wherein the same sample was used and heated slowly up to the maximum temperature. The difference in the trend of thermal degradation in this study compared to the trends reported by Yang et al is therefore attributed to the procedural difference. The thermal degradation models developed in this study can be used to predict the reduction in mass of pyrolysis processes where raw waste is introduced into a pre-heated chamber, such as in commercial rig 2, the small scale semi-batch pyrolyser. The data reported by Yang et al from investigations using the packed bed reactor with a slow heating rate would be most suitable for predicting the mass reduction of a pyrolysis process where raw waste is introduced before the pyrolysis chamber is heated, such as in commercial rig 1, the micro-scale batch pyrolyser.

5.2 MODELLING THE HHV OF PRODUCED GAS

An empirical model has been created using Microsoft Excel to predict the composition and HHV of the gas produced from pyrolysis at 550 °C for any mixed MSW composed of the most common materials (i.e. paper, newspaper, cardboard, PET, HDPE, PVC, textiles and food waste based on the laboratory results found in this study. This model will be referred to as Model 1. For each individual MSW component, the model has been set up to calculate the volumetric flow rate of CO, CO_2, H_2, CH_4, C_2H_6 and C_3H_8 produced by 5 kg of solid reactant, as well as the total gas produced. From this, the HHV has been calculated. This can be scaled up to give gas data for any mass of each MSW component. The volumes of each gas produced from the pyrolysis of each component are then summed to give the total litres of each gas for the specified mix of MSW. The model is based on laboratory data for a pyrolysis time of 20 minutes. As a larger mass of waste would need a longer residence time, the residence time of the model has been set to a percentage of the time needed for complete pyrolysis (i.e. for the production of CO to fall below 0.05 %).

Several assumptions have been made in creating this model, including:

- Each individual MSW component is not affected by the presence of other MSW components in the pyrolysis of mixed MSW.
- Each individual MSW component is the same as tested in laboratory investigations when comparing to other MSW mixtures.
- The mass and shape of the sample does not affect pyrolysis, i.e. there is a uniform temperature profile throughout the mass of the MSW. This is unrealistic in a larger scale commercial rig as the surface of the mass of MSW would heat up quicker than the centre of the mass of MSW.
- The pyrolysis temperature is 550 °C.
- The pyrolysis residence time long enough for the completion of pyrolysis reactions. The model is based on the residence time of 20 minutes as used in laboratory investigations. However, as the residence time would be considerably longer for a larger mass of waste, this should be taken as the point at which the production of CO falls below 0.05 %.

Model 1 has been used to predict the effect of each MSW component on the composition, HHV and total gas produced from pyrolysis at 550 °C for a residence time allowing complete pyrolysis. This is shown in section 5.2.1. Model 1 has also been used to predict the composition, quantity and HHV of the gas produced from pyrolysis at 550 °C for four mixed MSW samples as shown in Table 5.2. MSW Mix 1 has an equal mass of each MSW component, MSW Mix 2 is based on the typical composition of MSW in Wales as shown in section 5.2.2 [11], MSW Mix 3 is the composition of MSW tested in commercial rig 1 and MSW Mix 4 is the composition of MSW tested in commercial rig 2. MSW Mix 2 and 4 are both based on typical compositions of MSW. MSW Mix 3 was used to investigate the effect of the pyrolysis of mixed waste using 2 MSW components. Predictions for MSW Mix 2 and 4 are compared to data from commercial rig 1 and commercial rig 2 in section 5.2.3 and section 5.2.4 respectively.

Table 5.2: Composition of MSW mixes used for Model 1

	Mass of waste, %			
MSW Component	MSW Mix 1	MSW Mix 2	MSW Mix 3	MSW Mix 4
Paper	12.4	13.6	-	30.0
Newspaper	12.4	-	-	-
Cardboard	12.4	13.6	33.3	40.0

PET	12.4	5.0	66.6	6.6
HDPE	12.4	5.0	-	6.6
PVC	12.4	9.2	-	6.6
Textiles	12.4	7.0	-	10.0
Food Waste	12.4	46.2	-	-
Total	5.0	5.0	5.0	5.0

5.2.1 THE EFFECT OF EACH MSW COMPONENT ON PYROLYSIS OF MIXED WASTE SAMPLES

As discussed previously, the heterogeneous nature of MSW provides a significant challenge for EfW technologies. Establishing the effect of a change in composition, and specifically the effect of each individual component on the pyrolysis of MSW mixtures is therefore of great importance. Model 1 has been used to establish the effect that each individual MSW component has on the gas produced by pyrolysis of simulated mixed MSW samples. Firstly Model 1 was set with each component having an equal mass of 12.4 %. This will be referred to as ‘MSW Mix 1’. Following this seven of the components in MSW Mix 1 were set to an equal mass and one component set to double the mass of the other components, (i.e. 11 % and 22 % respectively). These values have been calculated with the total mass of all components remaining the same at 5 kg in order to allow for comparisons with the commercial rigs 1 and 2 in sections 5.2.3 and 5.2.4 respectively.

Figure 5.11 shows the composition of the produced gas from pyrolysis of each waste mix as predicted using Model 1 for pyrolysis at 550 °C. It can be seen that doubling the mass of PET produces the highest volume of both CO and CO_2, whereas doubling the volume of PVC produces the highest volume of H_2. Doubling the mass of paper or cardboard has no significant effect on the composition of produced gas when compared to the gas composition produced from MSW Mix 1 however, doubling the mass of newspaper leads to a small increase in the production of CO.

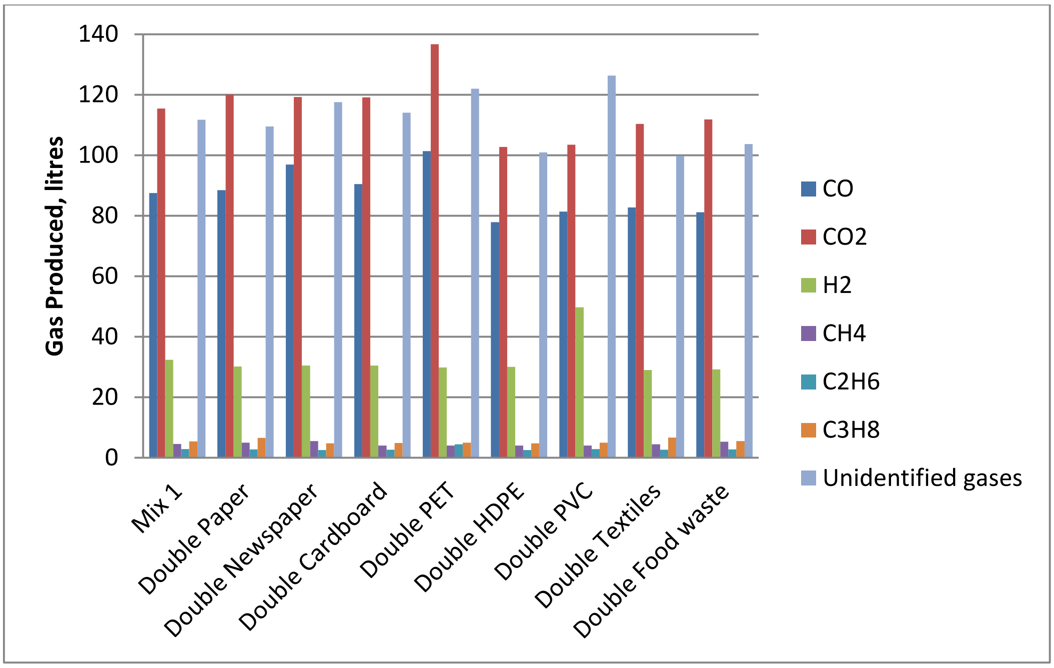

Figure 5.11: A graph to show the composition of gas produced from each waste mix as predicted using Model 1 for pyrolysis at 550 °C

Figure 5.12 shows the cumulative HHV of the produced gas as predicted using Model 1 for each waste mix. It can be seen that doubling the mass of HDPE has negligible effect on the HHV of the produced gas; this is due to the very low quantity of gas produced from HDPE samples, as found in section 4.4.2. Doubling the mass of newspaper causes the greatest increase in HHV, followed by cardboard and paper. This is due to the high quantity of CO produced by the pyrolysis of newspaper as mentioned above. An increase in the mass of PET causes a significant reduction in the HHV of the produced gas. This is due to the high quantity of total gas produced by the pyrolysis of PET but low quantities of H_2 and CH_4. For a residence time allowing 40 % of complete pyrolysis, doubling the mass of PVC causes a decrease in the HHV, although after this time an increasingly higher HHV is obtained. This is due to the production of CH_4. It can be seen in Figure 5.12 that all waste mixes reached a peak HHV at approximately 20-30 % of the total residence time and the residence time of pyrolysis has a significant effect on the HHV of the produced gas.

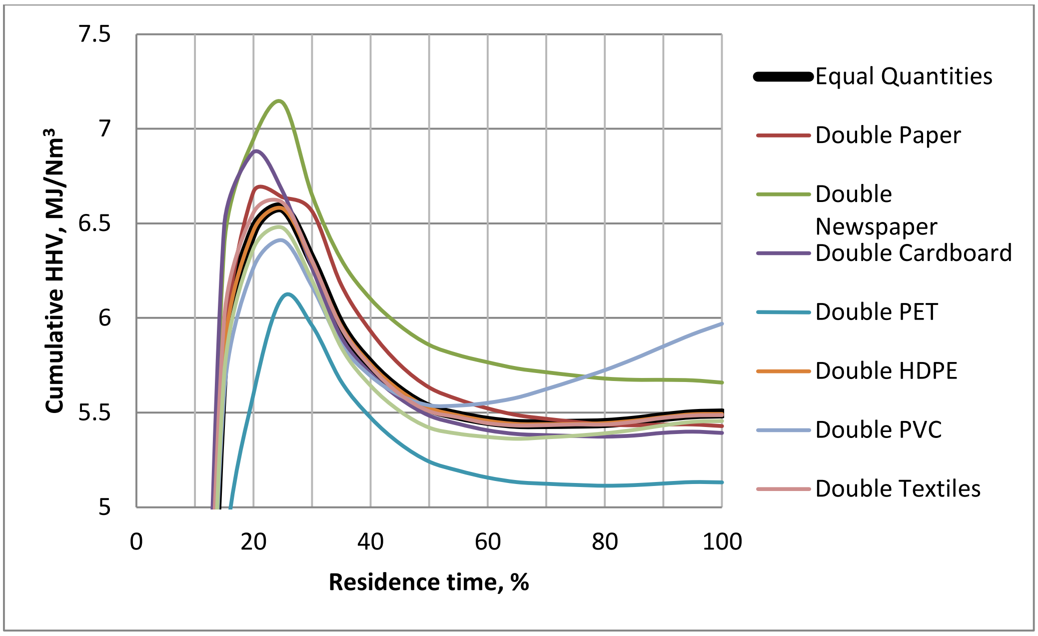

Figure 5.12: A graph to show the change in the cumulative HHV of the produced gas with pyrolysis residence time

Figure 5.13 shows the cumulative gas produced for each of the MSW mixes as predicted by Model 1 for pyrolysis at 550 °C for a residence time allowing complete pyrolysis. It can be seen that doubling the mass of paper, newspaper or cardboard only has a small effect on the total litres of gas produced. Doubling the mass of HDPE lowers the total gas produced although this component had negligible effect on the HHV of the produced gas. It can be seen that the greatest increase in gas produced is for the MSW mix with double the mass of PET however, as discussed above, doubling the mass of PET causes a significant reduction in the HHV of the produced gas. The increase in gas production is due to the unidentified gases produced during the pyrolysis of PET leading to a higher quantity of gas produced yet no increase in HHV as unidentified gases have not been taken into account in calculations of HHV. If these unidentified gases are hydrocarbons then this could increase the HHV of the produced gas and therefore significantly change the trend shown in Figure 5.12. Pyrolysis of PVC also produced a high quantity of unidentified gases. Therefore, the predictions of HHV using Model 1 for waste mixes which include PET and PVC have a lower level of accuracy than predictions for other waste mixes without these components.

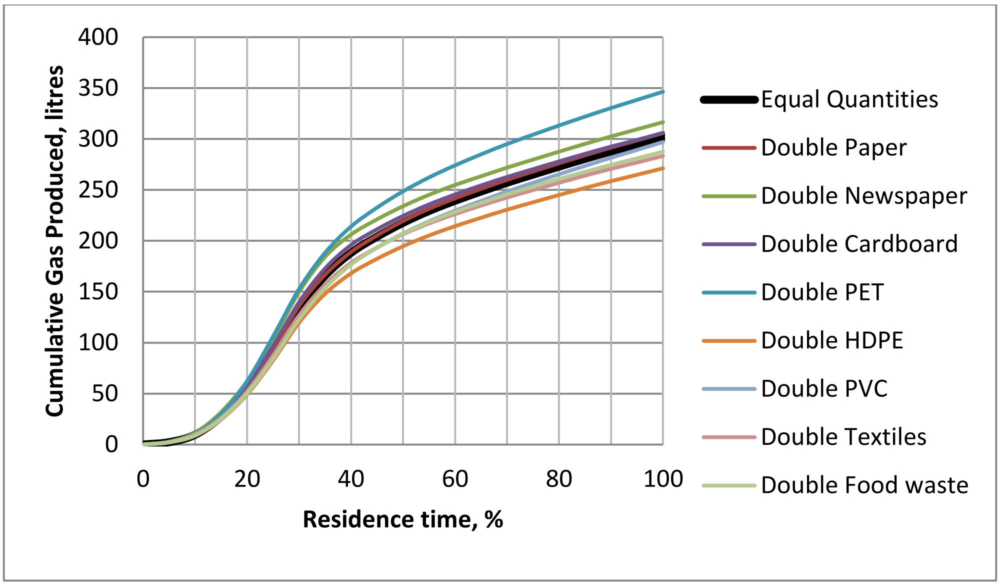

Figure 5.13: A graph of the cumulative gas produced for each MSW mix as predicted by Model 1 for a pyrolysis time of 20 minutes at 550°C.

The effect of each component of MSW on the pyrolysis of mixed waste is an important consideration for both the design and operation of EfW technologies and in case of a change in the composition of the waste used as fuel. Model 1 can be used either to predict the effects of a change in MSW composition on the produced gas or to predict the MSW composition needed to produce a gas with a particular HHV, volume or composition. For example, if a process required the litres of CO produced to be maximised, PET should be added to the waste mix, if the litres of H_2 is to be maximised, PVC should be added. For an increased HHV, a higher mass of newspaper could be added and for a higher total volume of gas produced, PET should be added. The limitations of this model are discussed in section 5.3.2.

5.2.2 MODELLING THE HHV OF THE GAS PRODUCED FROM FOUR MSW MIXES

Figure 5.14 shows the predicted composition of produced gas from pyrolysis of the four waste mixes shown in **Error! Reference source not found.** at 550 °C. MSW Mix 1 consists of an equal mass of all components, MSW Mix 2 and 4 are based on the typical composition of MSW and MSW Mix 3 was the waste mixture pyrolysed during run 2 on commercial rig 1 in order to investigate the co-pyrolysis of 2 MSW components.

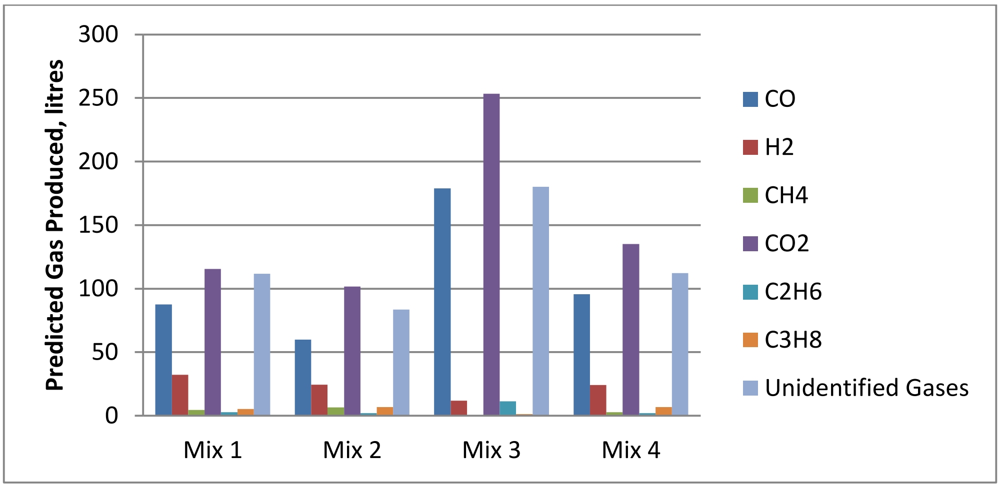

Figure 5.14: Predicted gas composition for four MSW mixes using Model 1

It can be seen that MSW Mix 3 produces the highest volumes of CO, CO_2 and C_2H_6 and the lowest volumes of H_2, CH_4 and C_3H_8. This is due to the high mass of PET which led to a high volume of CO_2; this was confirmed in a study by Dimitrov et al [63]. The high volume of gas produced during the pyrolysis of PET was confirmed in a study by Cepeliogullar et al [52]. MSW Mix 3 is also predicted to produce a high volume of unidentified gases; this is also attributed to the high content of PET.

The gas produced from pyrolysis of MSW Mix 1 and 2 is very similar, although a lower quantity of CO was produced by pyrolysis of MSW Mix 2. The lower quantity of CO is due to both the higher mass of food waste in MSW Mix 2 and the absence of newspaper in the mix. The composition of gas produced by MSW Mix 3 and MSW Mix 4 are discussed further in section 5.2.3 and 5.2.4 respectively where they are compared to the composition of the gas produced by commercial rigs 1 and 2.

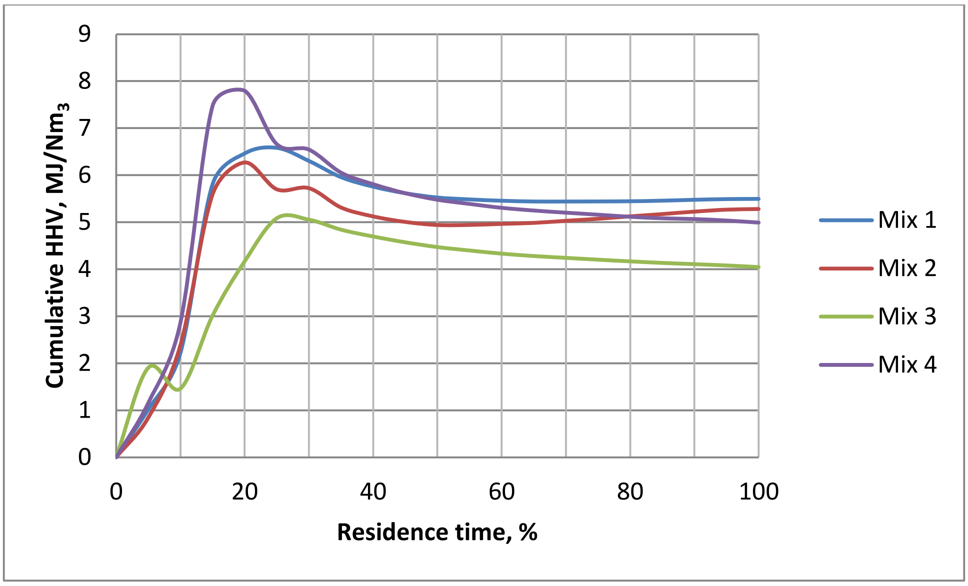

Figure 5.15: Predicted cumulative HHV of gas produced from pyrolysis of four MSW mixes using Model 1

Figure 5.15 shows the predicted cumulative HHV of the gas produced from pyrolysis of the four waste mixes. It can be seen that MSW Mixes 2 and 4 follow a similar trend. This is because both mixes are based on the typical composition of MSW with MSW Mix 2 based on the typical composition of MSW in Wales, 2010 [11] and Mix 4 a simplified version of typical MSW composition made up of fewer MSW components. However, MSW Mix 2 is predicted to produce a gas with a lower HHV; this is due to the 2.31 kg of food waste included in MSW Mix 2 which has been shown to lower the HHV of the produced gas. This is due to a high moisture content of food waste and therefore the low volume of gases produced. If food waste is taken out of MSW Mix 2, the percentage of the other components with regards to the total mass of the waste mix is very similar to MSW Mix 4. For both MSW Mix 2 and 4, two peaks in the HHV can be seen. The first peak from approximately 15-25 % of the total residence time is due to the peak production of CO. The small peak at approximately 30 % for both mixes is when the production of CH_4 begins. The first peak is mostly due to the higher mass of paper and cardboard, both of which show a CO peak at approximately 4 minutes (20 % of the residence time) as shown by Figure 4.19 in section 4.5.5. The CH_4 peak at approximately 30 % is due to the paper which shows a peak in CH_4 at 6 minutes (30 % of the residence time) and both MSW Mix 2 and 4 include a high mass of paper.

It can also be seen that there are 2 peaks in the HHV for MSW Mix 3. The first peak, at approximately 5 % of the residence time, is due to the peak production of H_2 from both the cardboard and the PET. The second peak at approximately 25 – 30 % is due to the peak production of CO from both the cardboard and the PET.

Figure 5.16 shows the cumulative gas produced from pyrolysis of the four MSW mixes as predicted using Model 1. It can be seen that MSW Mix 3 produces a significantly higher volume of gas. This is due to the higher PET content which leads to a higher volume of gas produced as discussed above and shown in **Error! Reference source not found.**. As with HHV, the total gas produced from MSW Mix 2 is lower than the total gas produced from MSW Mix 4. This is due to the higher mass of paper, cardboard and PET in Mix 4 which all increase the volume of gas produced as shown in **Error! Reference source not found.** and a much higher mass of food waste in MSW Mix 2 which decreases the volume of gas produced.

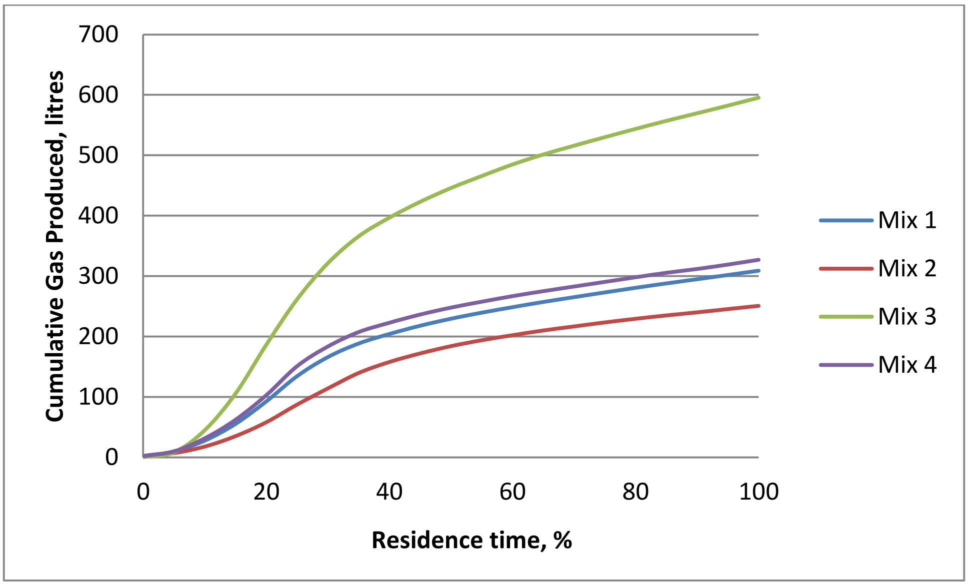

Figure 5.16: Predicted cumulative gas produced from pyrolysis of four MSW mixes using Model 1

As discussed above, the effect of a change in MSW composition on the gas produced during pyrolysis is an important factor in the design and operation of EfW technologies. Model 1 developed in this study can be used to predict the volume, HHV and composition of the gas produced from any mixture of MSW that is comprised of the components investigated in this study. The validity and reliability of this model is discussed in section 5.3.2.

5.2.3 COMPARISON WITH COMMERCIAL RIG 1: MICRO-SCALE BATCH PYROLYSER

During tests at commercial rig 1, data was recorded for a waste mix of 66 % PET and 33 % cardboard for a total MSW mass of 5 kg. Results for these tests are shown in section 4.8.5.1. The waste mix tested in run 2 for commercial rig 1 is the same as MSW Mix 3 shown above. As discussed in section 4.8.5.1, comparisons between tests on commercial rig 1 and laboratory data are difficult due to both the high volume of air introduced to the commercial rig and also the change in temperature. There are 2 points which allow for the most accurate comparison to laboratory data where the inlet air flow was at a minimum, although still significant, and where the temperature of the pyrolysis chamber was the same as that in laboratory investigations. The first point is from 50-60 minutes as this has the lowest air flow in of approximately 8-45 l/min, and point two is from 120-140 minutes where the chamber temperature is 500-600 °C and the air flow is relatively low at approximately 30-50 l/min. The instantaneous compositions of the gas produced at these points are shown in Figure 5.17. This is compared to Figure 5.18 which shows the instantaneous composition of gas produced for the same waste mixed as predicted using Model 1 based on laboratory data.

It can be seen that for both investigations the predominant gases produced are CO and CO_2 with a longer run time favouring the production of CO_2 over CO. For tests on commercial rig 1, a significant volume of the CO_2 produced is attributed to the combustion reactions due to the air flow into the chamber as well as O_2 in the fuel, whereas any CO_2 produced in laboratory studies is due to O_2 within the fuel. Comparatively low volumes of H_2, CH_4, C_2H_6 and C_3H_8 were found for both investigations.

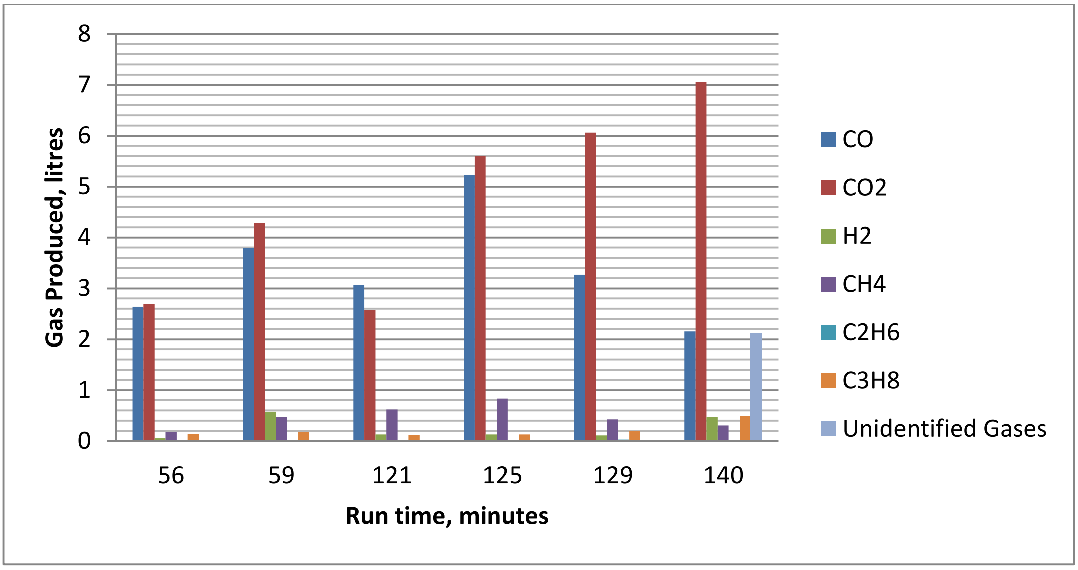

Figure 5.17: Composition of instantaneous gas produced for specified run time with commercial rig 1, run 2

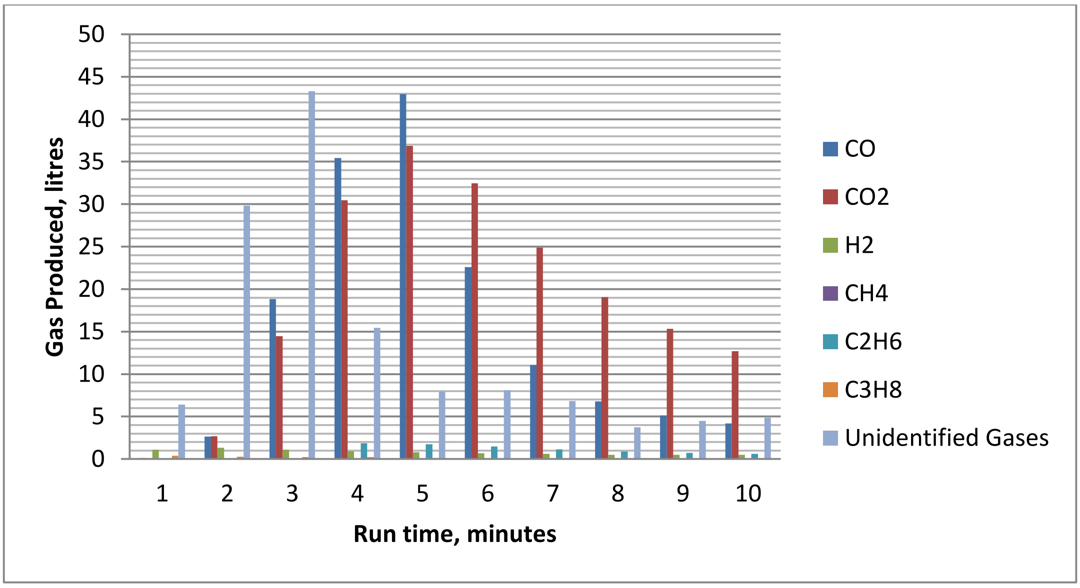

Figure 5.18: Composition of instantaneous gas produced for specified run time as predicted by Model 1

It can be seen that there is a significantly lower quantity of unidentified gases detected in the gas from commercial rig 1, which as discussed previously have been assumed to be hydrocarbons. This is attributed to the use of a freezer to collect tars from the produced gas during investigations on commercial rig 1, which would have condensed and therefore collected the majority of the hydrocarbons produced. A freezer was not used in laboratory investigations as the produced gas had already cooled to below 40 °C as it entered the tar trap system. Inside the freezer, the produced gas was cooled to approximately -18 °C and passed through the tar trap system. As well as collecting tars, this would have led to the condensation of some of the produced light hydrocarbons and their collection in the tar trap system and as such would not have reached the gas analysis instrumentation. The significantly lower heating rate of the waste in commercial rig 1 compared to that in the laboratory reaction rig could also have a significant effect on the production of hydrocarbons. In commercial rig 1, the pyrolysis chamber does not reach a temperature of 550 °C until after 100 minutes. In laboratory investigations the waste was inserted into a pre-heated chamber that had already reached 550 °C. Previous research has shown that a higher temperature increases the production of light hydrocarbons [58, 69].

It can also be seen in Figure 5.18, that the instantaneous volumes of gases as predicted by Model 1 were generally much higher than the volumes from commercial rig 1, shown in Figure 5.17. This is especially true for the CO and CO_2 production in laboratory data from 3-7 minutes as these times correspond with the times of the peak production of CO and CO_2. This can also be attributed to the slower increase in temperature in commercial rig 1. The lower temperature and slower increase rate leads to slower reactions and therefore a slower production of gas. The gas in commercial rig 1 is produced over a long residence time of 166 minutes. In laboratory investigations, the gas was produced over 20 minutes. The mass of the waste in commercial rig 1 is also a significant factor. The 5 g waste sample used in laboratory studies had a low depth and high surface area when placed in the sample boat. This allows for rapid heat transfer throughout the sample. The 5 kg waste testing in commercial rig one had a significantly larger depth and significantly lower surface area. This would lead to a lower rate of heat transfer and therefore a lower rate of pyrolysis and gasification reactions and gas production.

The total gas produced from 5 kg of waste in commercial rig 1 for run 2 was 3154 litres. This figure includes the volume of CO, CO_2, H_2, CH_4, C_2H_6, C_3H_8 and unidentified gases produced. Using Model 1 the total gas produced for the same 5 kg of waste is predicted to be significantly lower at 595 litres. This is attributed to the inlet air flow in commercial rig 1 as the addition of O_2 promotes further gas production.

Comparisons between predictions from Model 1 and data from gas analysis tests on commercial rig 1 have shown some similarities in the composition of the produced gas. Both methods showed the main gases of pyrolysis of the waste mix to be CO_2 and CO with lower quantities of H_2, CH_4, C_2H_6 and C_3H_8. However, as discussed in section 4.8.5.1, the larger mass of the waste, slower heating rate, longer residence time and the addition of air in commercial rig 1 compared to that in laboratory studies have shown some significant differences in results.

It has been found that the lower heating rate along with the varied temperature profile expected in the larger mass of the waste used in commercial rig caused by the larger depth and lower percentage of surface area compared to laboratory studies has inhibited the thermal degradation of the waste and therefore the production of gas. This led to a significantly longer residence time and lower instantaneous volume of gas produced compared to that predicted in Model 1 which was based on a residence time of 20 minutes.

The addition of air into the pyrolysis chamber of commercial rig 1 also caused significant problems in comparisons with the model created based on pyrolysis without the addition of excess O_2. This led to the production of CO_2 becoming more favourable as the air flow was increased and also increased the volume of the total gas produced compared to that predicted by model 1. The limitations of Model 1 are discussed further in section 5.3.2,

5.2.4 COMPARISON WITH COMMERCIAL RIG 2: SMALL SCALE SEMI-BATCH PYROLYSER

During tests at commercial rig 2, data was recorded for the gas produced from a waste mix of 30 % paper, 40% cardboard, 20 % plastics and 10 % textiles for a total MSW mass of 5 kg. This is the same as MSW Mix 4 shown above. Data for the tests at commercial rig 2 for this waste mix are shown and discussed in section 4.8.6. Data predicted using Model 1 has been compared to the results shown in data set 2 in Figure 4.27 with the air discounted from the produced gas as discussed in section 4.8.6.

Data for the composition of the gas produced from commercial rig 2 has been compared to the instantaneous gas composition predicted for the same waste mix using Model 1. It was found that the gas composition was most similar for a pyrolysis run time of 3 minutes (15 % of the total residence time). Both of these gas compositions are shown in Figure 5.19. The similarities with this short run time are likely attributed to the continuous feed of waste into the top of the pyrolysis chamber for commercial rig 2 during stable operation. As seen in laboratory investigations, the pyrolysis reactions of waste below the surface was slightly inhibited by the waste on the surface. In commercial rig 2, there was a continuous feed of raw waste on the surface of waste in the pyrolysis chamber. Therefore, at any given time during stable operation, the waste on the surface would be in the first few minutes of pyrolysis. However, the feed in rate of the waste for commercial rig 2 for this run is not known. To investigate this further, this would need to be recorded. The mass of the waste in commercial rig 2 will be at different stages of pyrolysis throughout the pyrolysis chamber due to both the temperature profile across the chamber and the residence time that the waste has been in the chamber.

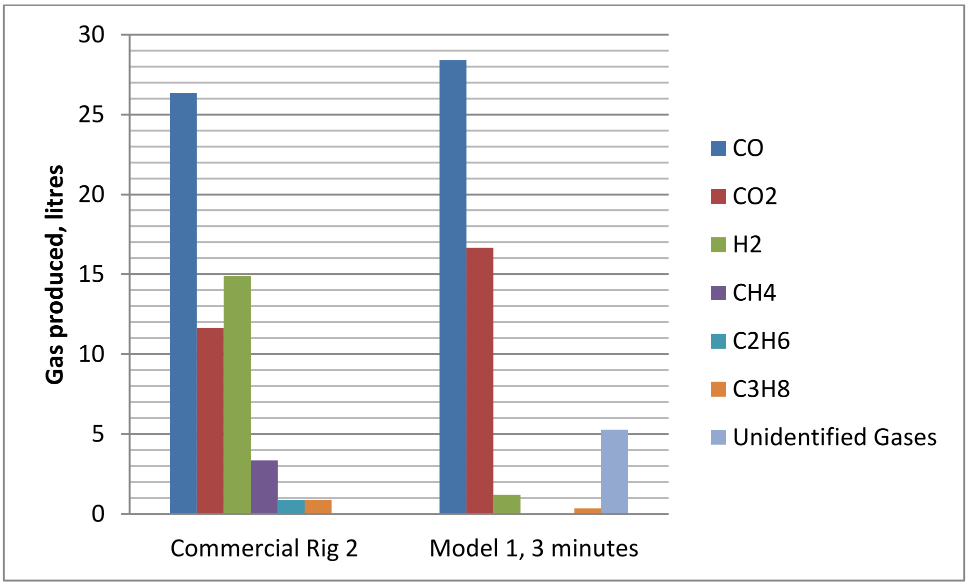

Figure 5.19: Instantaneous gas composition from commercial rig 2 during stable operation and as predicted by model 1 for a pyrolysis run time of 3 minutes

It can be seen that for both the commercial rig and the model, the main gas produced is CO; however the model predicts a higher volume of CO_2 and a significantly lower volume of H_2. The model also predicts a lower volume of CH_4 although this is due to the run time as the production of CH_4, as predicted by the model, begins at a run time of 4 minutes and reaches a peak in production at approximately 6 minutes.

The exact temperature of the pyrolysis chamber of commercial rig 2 during the stable operation of this run is not known however it was suggested by the process developer that the temperature could reach a maximum of approximately 700 °C. The laboratory data shown in Figure 4.21 in section 4.5.6 for paper and PET samples pyrolysed at 700 °C show significantly higher volumes of CO, H_2 and CH_4 produced compared with paper and PET samples pyrolysed at 550 °C. It is therefore suggested that the temperature of the pyrolysis chamber of commercial rig 2 was higher than 550 °C. The higher volumes of CO produced by commercial rig 2 could also partly be attributed to an increase in bed depth compared to laboratory investigations. It was found by Phan et al [19], that an increase in bed depth resulted in an increase in the production of CO.

The pyrolysis process during laboratory investigations has more similarities with the pyrolysis process of commercial rig 2 than that of commercial rig 1. As discussed above the lower temperature, low heating rate and excess air in commercial rig 1 caused a significant difference in comparisons of results. In commercial rig 2, the waste is subjected to a rapid heating rate as it is introduced into the top of the pre-heated pyrolysis chamber. This is similar to the process used in laboratory investigations. It is suggest that if the temperature of the pyrolysis chamber in commercial rig 2 was established, along with the composition and quantity of any gases introduced to the pyrolysis chamber, Model 1 would have the potential to predict the composition and quantities of the gases produced with a higher accuracy.

5.3 VALIDITY AND RELIABILITY OF EMPIRICAL MODELS

5.3.1 MASS LOSS MODEL

The aim of this model was to estimate the behaviour of fuel samples during pyrolysis in a commercial scale rig, which would have a pyrolysis time greater than 10 minutes. Therefore, the accuracy of the model from 10 to 30 minutes has been prioritised over the accuracy from 0 to 5 minutes. Figure 5.20 shows the percentage of errors between laboratory data and data calculated using the above equations.

It can be seen that data for 10 and 30 minutes has a higher accuracy than data for a pyrolysis time of 5 minutes. This is partly due to the prioritisation given to the accuracy of data at 10 and 30 minute when developing the model although it is also attributed to the loss of volatiles and moisture from the sample causing a significant mass loss within the first few minutes of pyrolysis, therefore an error in timing of just a few seconds would cause a greater error in measuring the mass of the sample. The cooling of the sample after pyrolysis before the sample boat and sample mass was recorded also had a significant effect on the accuracy of laboratory data which would have the greatest affect for data for 5 minutes. The sample could not be cooled instantly so some mass loss may have continued once the sample had been removed from the furnace.

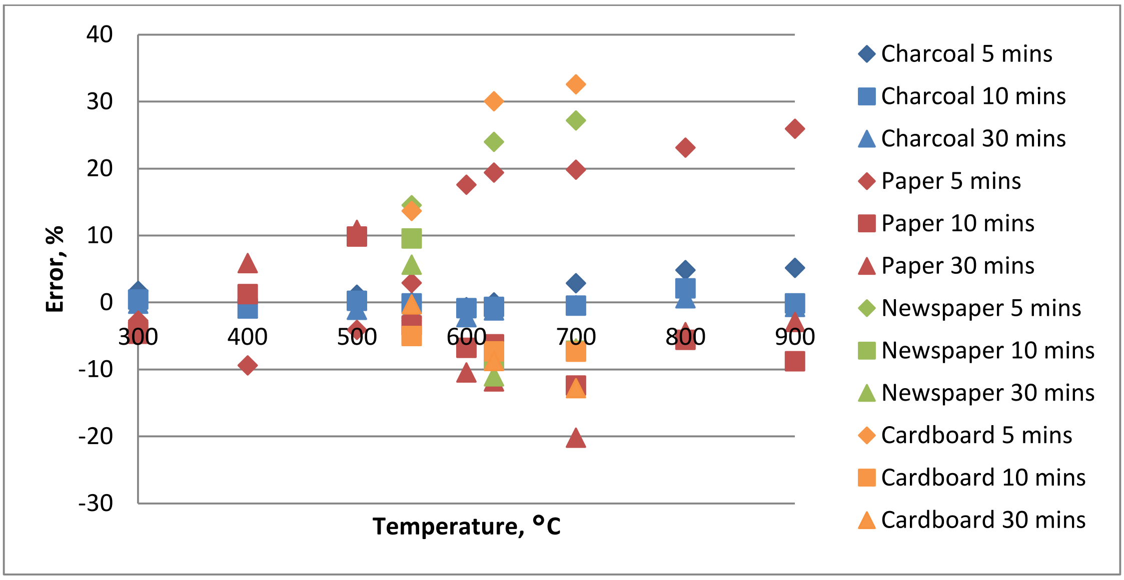

Figure 5.20: A graph to show the percentage of error between the laboratory data and calculated data for the mass remaining of samples during pyrolysis

This model was created with the aim of ensuring an error of below 10 % for all results for 10 and 30 minutes. This was achieved for all data expect paper samples pyrolysed at 500 °C, 700 °C and 900 °C. As discussed in section 4.8.2, it could be seen during laboratory experiments that there were greater errors involved in the cooling of paper samples after pyrolysis than for cardboard or newspaper as the paper sample would often ignite during removal from the furnace before the sample boat could be made air tight and the sample left to cool. This was due to thin layers of partially-pyrolysed paper, some of which ignited as the sample came into contact with air. This did not occur with charcoal samples as the sample was more compact. It can be seen that there is a higher accuracy in the loss of mass predicted for charcoal samples which is attributed to this.

The greater errors shown for paper in Figure 5.20 compared to newspaper and cardboard are also because there are more data points from laboratory data to compare with the mathematical model where as for newspaper and cardboard data was only established for three temperatures. It can also be seen that the percentage of error increases as the temperature increases, this is due to the lower mass remaining at higher temperature so therefore a smaller difference in mass from laboratory data and from calculated data will lead to a higher percentage of error.

As discussed in section 5.1.1, it can be seen by the comparisons with TGA data that the mass of waste has a significant effect on the behaviour of the fuel during pyrolysis as found by Yang et al [23]. TGA is a more accurate way of measuring the mass loss of a sample during pyrolysis; however pyrolysis of a larger sample size as used in this investigation gives a more realistic indication of how paper would behave during pyrolysis in a commercial scale rig. The aim of the models established in this investigation is not to provide exact data but to estimate and predict the behaviour of samples during pyrolysis on a much larger scale. This is especially useful for EfW processes, for which mass reduction, as well as energy production, is of high importance.

5.3.2 HHV MODEL

Model 1 developed in this study can be used to predict the effect of a change in mass of each of the components investigated as part of a mixed MSW fuel. The total volume, HHV and composition of the produced gas can be estimated for pyrolysis at 550°C for a range of residence times. The model has shown good comparisons with the composition of gases produced in commercial rig 2 although significant differences in the volumes of gas produced in commercial rig 1.

Several limitations of Model 1 have been identified. A difference in the pyrolysis conditions from that studied in laboratory investigations can cause significant challenges in comparison of model predictions with data from other pyrolysis rigs. It is suggested that model predictions are therefore most accurate for pyrolysis processes with a high heating rate up to 550°C without the addition of excess O_2.

The unidentified gases detected during the pyrolysis of several MSW components, especially PET and PVC, although assumed to be hydrocarbons, have not been identified. Without identification, the effect of these gases on the HHV of the produced gas is unknown and therefore so too is the effect on HHV predictions using Model 1.

A low gas yield was found in this study from the pyrolysis of HDPE, PVC and textiles. This was lower than that reported in other studies [66, 69]. This could partly be attributed to the challenges presented in comparison between data from TGA test and that from laboratory scale pyrolysers as discussed in section 5.1.1. This could also be partly attributed to the thick tar produced during laboratory investigations that may have inhibited the progression of the produced gas through the tar trap to the gas analysis instrumentation. If the low gas yields are due to inaccuracies in laboratory data, the predictions of Model 1 for waste mixtures including these components would also contain inaccuracies.

A 5 g mass of waste is unlikely to pyrolysis in exactly the same way as a much larger mass of waste. A change in the temperature profile throughout a larger mass of waste could have a significant effect on the gas produced as shown in comparisons with commercial rig 1. Model 1 is based on laboratory data from the pyrolysis of 5 g samples and any predictions using this model are made using the assumption that pyrolysis behaviour of the mass of waste is the same as that of a 5 g sample.

5.4 SUMMARY

Empirical models have been developed based on laboratory data from the laboratory scale pyrolysis reaction rig found in this study. The first models have been developed with the aim of predicting the mass reduction behaviours of MSW components during pyrolysis for temperatures ranging from 300 °C to 900 °C for a residence time of 0-50 minutes. The reduction of mass was found to change exponentially with a change in residence time and sigmoidally with a change in pyrolysis temperature.

Data was extrapolated for pyrolysis temperatures below 300 °C and show good comparisons with previous research using TGA methods for the temperatures at which thermal degradation began for each component. However, it has been established that the larger mass of waste used in laboratory studies did not follow the same trend in terms of mass reduction during pyrolysis as that shown in TGA tests. This was attributed to the variation in temperature profile throughout the larger mass which reduced the rate of pyrolysis reactions and inhibited gas production causing a slower reduction in mass. This was also found by Yang et al [97]. This has shown that mass reduction predictions based on TGA tests are unrealistic when predicting the behaviour of a larger mass of waste such as that in commercial scale rigs. Although the 5 g mass of waste used in this study is also significantly smaller than that in commercial rigs, it is significantly larger than that used in TGA tests. Results presented in this study can therefore provide an estimation of the effect of a larger mass. It is suggested that a mass of waste larger than 5 g would follow the same trend and have a slower mass reduction rate due to the increased variation in temperature throughout the increase mass.

An empirical model was also developed based on laboratory data with the aim of predicting the composition, HHV and volume of the gas produced from pyrolysis at 550 °C for any composition of MSW that is based on the components investigated in this study. This model was used to predict the composition and quantities of the gas produced from the pyrolysis of a range of waste mixes as well as to establish the effect of each individual MSW component on the gas produced. It was found that the addition of newspaper to a waste mix led to the highest HHV an increased volume of gas produced. This model could be especially useful for predicting the composition of MSW needed to for a variety of optimum conditions i.e. to maximise HHV or the production of a specific gas.

There were significant challenges in the comparison of model predictions with data from both commercial rig 1 and commercial rig 2. This is due to fundamental differences in pyrolysis process for both commercial rigs and laboratory investigations. However, it was found that the composition of gas as predicted using Model 1 was similar to the composition of gas analysed from both commercial rigs. Comparisons with predictions from Model 1 and data from commercial rig 2 suggested that commercial rig 2 was operating at a temperature higher than 550 °C.

Comparisons between model predictions and data from commercial rig 1 were difficult due to the lower pyrolysis temperature, slow heating rate and the introduction of a high flow rate of air. Extending the parameters of Model 1 to include the effect of a range of pyrolysis temperatures on MSW components as well as the effect of post-pyrolysis gasification would allow for much closer comparison between model predictions and data recorded from commercial rig 1. Conclusions of this study along with other recommendations for future work can be found in Chapter 6.

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

Overall it has been shown that the laboratory scale pyrolysis reaction rig developed and used in this study can be employed to predict the behaviour of larger scale commercial pyrolysis systems. Data showed good repeatability and the results found using the laboratory scale pyrolysis reaction rig are comparable with findings in published literature. As with many other research activities in this area, there is a substantial challenge in gaining a fully-closed mass balance on the reactions, especially when it comes to quantifying the liquid fraction evolved during the pyrolysis of plastics. It was found that these components produced high molecular weight tars, a high percentage of which remained in either the sample boat or the reactor tube after pyrolysis and were then either measured as solid product or could not be quantified. Despite the low accuracy in the precise quantification of these products, these results can still give a reliable estimate and indication of the products produced from the pyrolysis of single MSW components.

The majority of mass loss was found to occur within the first 5-10 minutes of pyrolysis with a loss of up to 70 % at 550 °C and up to 77 % at 700 °C for paper, newspaper and cardboard. A change in temperature had a greater effect on mass loss than pyrolysis residence time with a higher temperature leading to a higher loss in mass. For paper, newspaper and cardboard a temperature increase from 300-700 °C had the greatest effect on mass loss decreasing the mass remaining in the sample boat from approximately 90 % to less than 30%. The solid, liquid and gaseous pyrolysis products were found to vary significantly with different MSW components as well as with an increase in pyrolysis temperature. As expected, the raw potato used for the food waste component of MSW produced the highest volume of liquids at 88% due to the high moisture content of the raw sample. Paper, newspaper and cardboard behaved similarly with solid, liquid and gas fractions of approximately 33, 53 and 13 % respectively. The products from the plastic components varied greatly with PET producing the highest percentage of gaseous products at 42 %, HDPE the highest solid products at 45 % and textiles the second highest volume of liquid products at 68 %. An increase in pyrolysis temperature to 700 °C increased the gaseous products from paper to 34 % to the detriment of the liquid and solid yields. Pyrolysis of PET at 700 °C led to a decrease in gaseous products to 29 % and an increase in solid products and small increase in liquid products. The decrease in gaseous products was attributed to the decrease in the production of hydrocarbons at higher temperatures as found by Mastral et al [69].

The composition of gas produced from pyrolysis varied greatly with each component. Paper, newspaper and cardboard gave similar results although a higher volume of CO was produced by the pyrolysis of newspaper. This was attributed to the higher quantity of O_2 present in newspaper. Pyrolysis of plastics led to a more varied composition of gas. The pyrolysis of PET produced the highest volume of CO whereas HDPE and PVC produced the lowest volumes of CO, CO_2, and CH_4 as well as low volumes of H_2 and C_3H_8. The pyrolysis of PVC also produced the highest volume of unidentified gases which have been attributed to hydrocarbons not identified by the gas analysers used in this study. An increase in pyrolysis temperature increased the production of CO and H_2 from both paper and PET. The pyrolysis residence time also had a significant effect on the composition and quantity of the produced gas and therefore, a significant effect on the HHV. This has highlighted the importance of establishing the process residence time when comparing data.

The mass loss models developed in this study can be used to predict the mass remaining after pyrolysis for a residence time of 0-50 minutes and a temperature of 300-900 °C for paper, newspaper and cardboard. From extrapolation of laboratory data it was found that the initial reaction temperature for paper was approximately 225-250 °C with lower temperatures predicted for newspaper and cardboard. Data from this study is comparable to results found by TGA in published literature. An empirical model was also developed to predict the effect of a change in the composition of MSW on the pyrolysis gas. Using this, it was found that an increase in the mass of paper or cardboard had a similar effect on the gas composition and a slightly higher volume of CO could be achieved by increasing the mass of newspaper. Doubling the mass of PET led to the greatest increase in the volume of CO and CO_2 produced, whereas doubling the mass of PVC increased the volume of H_2. The highest HHV was found to be from a waste mix with double the mass of newspaper due to the higher volume of CO produced. The lowest peak HHV was found to be from a waste mix with double the mass of PET due to the higher volume of total gas produced but lower quantities of H_2 and CH_4.

The composition of gas produced from a waste mix of PET and cardboard in commercial rig 1 was similar to that from 100 % cardboard for the first 100 minutes although a higher volume of CO was produced from the addition of PET. After 100 minutes the production of gas from cardboard was minimal yet the addition of PET in run 2 led to a second stage of reactions from 100-160 minutes with further production of CO and CO_2. This has been attributed to PET requiring a higher temperature for thermal degradation. From 60

– 130 minutes in run 1 the chamber temperature was approximately 200 °C higher than the set point temperature due to exothermic reactions. The addition of PET led to fewer exothermic reactions with an increase in chamber temperature above the set point of approximately 80 °C from 110-150 minutes this is attributed to the very high carbon content and low oxygen content of PET. The composition of gas produced from commercial rig 2 had high volumes of CO and H_2, as well as high volumes of O_2 and N_2 which was been attributed to unreacted air passing through the rig. The precise temperature of the pyrolysis chamber could not be measured although through comparisons with laboratory data it has been estimated at approximately 700 °C due to the high volumes of CO and H_2.

It is suggested that a small scale laboratory pyrolyser of less than 100 g provides a more realistic approach for comparisons with larger scale pyrolysis than TGA. The use of TGA provides more accurate data for single components of MSW, however the laboratory reaction rig used in this study could be more accurate for establishing the behaviour of more heterogeneous materials, such as mixed MSW.

To utilise the gas produced from commercial rig 1 for the production of energy a higher pyrolysis temperature is required to increase the volumes of CO and H_2 and therefore the HHV of the gas. A lower volume of air should be introduced into the pyrolysis chamber to increase the production of CO and decrease the production of CO_2. In order to maximise the available heat energy from the rig, the mass of PET in the waste should be minimised as this has been shown to inhibit exothermic reactions during pyrolysis. The gas produced from commercial rig 2 would be suitable for energy production due to the high percentage of CO and H_2. However, improvements are needed to deal with the production of tars to enable stable operation of the rig for a longer period of time. This problem could be overcome by reducing the mass of plastics, especially HDPE and PVC, in the waste stream.

6.2 RECOMMENDATIONS FOR FUTURE WORK

- The effect of an increase in temperature on the pyrolysis of components investigated in this study should be established and Model 1 extended to allow the prediction of gas composition, HHV and total volume of gas for a range of temperatures and residence times. This would allow the optimum pyrolysis temperature and residence time for a given composition of MSW to be estimated.

- For greater accuracy of future work, a continuous H2 analyser should be used and the volume of the output gas should be measured. As well as this, an improved method for cooling the sample once it has been removed from the furnace would improve the accuracy of mass loss data.
- Further research is needed into the pyrolysis behaviours of the plastic components of MSW and especially their behaviour during the pyrolysis of mixed waste.
- Further investigation is needed to establish the effect of the mass of the waste, its depth and surface areas on the temperature profile throughout the mass and on pyrolysis behaviours.
- To allow for closer comparisons between laboratory data and the performance of commercial rig 1, the effect of heating rate and post-pyrolysis gasification should be investigated.
- To allow for closer comparisons between laboratory data and the performance of commercial rig 2, the chamber temperature, waste feed in rate and the type and quantity of the gas introduced into the pyrolysis chamber needs to be established

6.2.1 RECOMMENDATIONS FOR COMMERCIAL RIG 1

Following the findings of this study, it has been established that commercial rig 1 has great potential for both the reduction of waste and the production of heat energy. Further research is needed to establish the effect of mixed MSW on the exothermic reactions of pyrolysis and the effect of interactions between components. In order for the produced gas to be utilised for energy production, the production of CO, H_2 or CH_4 must be increased. This could be achieved through an increase in the pyrolysis temperature, a lower volume of air introduced to the pyrolysis chamber or the addition of newspaper to the MSW mix.

6.2.2 RECOMMENDATIONS FOR COMMERCIAL RIG 2

The gas produced from commercial rig 2 under stable conditions had high volumes of CO and H_2 and therefore has the potential to be utilised for energy production. However, improvements are needed in order to solve significant problems allowing for stable operation of the rig for a longer period of time. This would allow for a higher efficiency of the performance of the rig and a longer period of time for optimum gas production. The most significant problem was due to blockages from the thick tars produced during pyrolysis. To overcome this, the mass of the plastic fractions in the waste could be reduced. Alternatively, the rig could be adapted to collect these tars to prevent pipe blockages.

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Appendix I: Ultimate Analysis, Proximate Analysis and CV of MSW Components as found in Published Literature

Sample	Proximate Analysis (wt%)				Ultimate Analysis (wt%)					CV MJ/kg	Reference
	VM	FC	Ash	Moisture	C	H	O	N	S/Cl		
Paper	10.56	11.2	10.56	3.92						12.9	This study
Newspaper	9.14	11.48	9.14	5.09						15.49	This study
Cardboard	3.93	15.19	3.93	5.65						16.2	This study
PET	0	9.53	0	9.53						44.15	This study
HDPE	0.08	0.35	0.08	1.2						46.3	This study
PVC	0.58	10.59	0.58	1.33						46.2	This study
Textiles	0.54	11.65	0.54	2.54						28.1	This study
Food waste	0.65	0.96	0.65	88.5						16.5	This study
Paper	79.3	10.0	10.7		45.1	5.3	48.9	0.4			[23]
Recycled paper	73.6	6.2	20.2							13.6	[43]
Glossy paper	67.3	4.7	28.0		45.6	4.8	49.4	0.1	0.1	10.4	[43]
Coated paper			27.7	0.9	30.5	4.6	37.7	2.9	1.5/1.5	12.2	[59]
Glossy paper	70.7	4.5	24.8	3.8	41.9	5.3	52.6	0.1	0.02/0.093	10.4	[39]
Glossy paper	65.4	6.9	27.7	6.5	26.5	3.4	42.3	0.0	0.04/0.04	11.9	[77]
Glossy paper	70.6	4.5	24.8		31.5	4.0	64.4	0.1	<0.02		[72]
Paper cup	52.0	46.0	2.0	0.0	46.7	6.7	44.4	2.1	0.0	20.1	[55]
Tissue paper	90.5	9.0	0.5		45.2	6.1	48.3	0.3	0.11/0	17.3	[75]
Paper sludge (dried)	53.1	1.2	45.7	2.5	23.8	3.3	26.8	0.1	0.16/0.06	6.2	[77]
Newspaper	88.5	10.5	1.0		52.1	5.9	41.9	0.1	0.0	19.3	[43]
Newspaper	85.9	10.7	3.5		44.7	5.8	49.4	0.1	<0.02		[72]
Cardboard	79.1	10.0	10.9	5.4	40.0	4.6	45.6	0.3	0.34/0.33	13.7	[77]
Cardboard					39.5	5.8	44.3	0.2	0.3		[41]
Cardboard	84.7	6.9	8.4		48.6	6.2	45.0	0.1	0.1	16.9	[43]
Cardboard	80.4	11.2	5.7	2.7	41.7	6.4	43.5			15.7	[97]
PET					62.0	4.2	33.2	0.1	0.3		[41]

Sample	Proximate Analysis (wt%)				Ultimate Analysis (wt%)					CV MJ/kg	Reference
	VM	FC	Ash	Moisture	C	H	O	N	S/Cl		
PET	86.8	13.2	0.0	0.6	62.5	4.2	33.3	0.0	0.0	22.1	[77]
HDPE	98.6	0.0	1.4	0.0	83.7	15.5	0.0	0.0	0.0	42.2	[77]
HDPE	100.0	0.0	0.0		86.1	13.0	0.9			46.4	[43]
HDPE	99.9	0.0	0.1	0.0	83.3	13.9	2.5	0.2	0.1	47.6	[66]
PVC	91.0	9.0	1.0		38.0	5.0	0.0	0.0	0/57	19.2	[28]
PVC	94.8	4.8	0.4		41.4	5.3	5.8	0.0	0.03/47.7	22.8	[43]
PVC	94.9	5.1	0.0		38.3	4.5	0.0	0.2			[23]
PVC	94.8	5.2	0.0	0.7	42.5	6.2	0.0	0.0	0/51.31	22.3	[77]
PVC	94.9	5.1	0.0		38.3	4.5	0.0	0.2	0.61/56.35	20.8	[75]
PVC			0.0		38.4	4.8		0.0	1.4		[81]
Polyethylene	100.0	0.0	0.0	1.1	85.7	13.9	0.0	0.0	0.0		[77]
Polyethylene	100.0	0.0	0.0		86.0	14.0	0.0	0.0	0.0	40.5	[28]
Polyethylene			0.0		85.3	14.7		0.0	0.0		[81]
PP	97.9	0.2	2.0	0.2						41.0	[77]
Polypropylene	100.0	0.0	0.0		86.0	14.0	0.0	0.0	0.0	43.4	[28]
LDPE	10.0	0.0	0.0		85.7	14.2	0.1	0.1	0.0	46.6	[43]
Polystyrene	99.0	1.0	0.0		92.0	8.0	0.0	0.0	0.0	44.5	[28]
Polyester Fabric	88.6	10.9	0.5		62.2	4.1	33.1	0.3			[23]
Textiles	89.0	6.9	0.5	3.6	43.3	6.2	46.5			16.0	[97]
Cotton				<0.1	45.5	6.6		0.3	<0.1		[81]
Polyester				<0.1	62.6	4.6		0.4	<0.1		[81]
Vegetable waste					29.9	4.2	63.8	2.0	0.1		[71]
Coffee waste	76.7	16.8	6.6	10.7	51.3	6.8	38.6	3.0	0.21/0.055	19.8	[39]
Orange peel	76.5	20.6	2.9		48.4	5.9	43.7	1.4			[23]
Chinese cabbage	67.6	22.5	9.9		47.5	5.9	41.9	4.1			[23]

Appendix II: Isopropanol Safety Data Sheet

Product Overview:

- Isopropanol (IPA) is one of the most widely used solvents in the world; also used as a chemical intermediate. See Product Uses.
- IPA exposure is possible in both industrial and consumer applications. Occupational exposure limits have been established to control the allowable amount of exposure in workplace settings. Consumer exposure, generally infrequent and short in duration, is also highly dependent upon the conditions under which IPA is used. See Exposure Potential.
- IPA does not cause adverse health or environmental effects at levels typically found in the workplace or in the environment.
- Flammable with high vapor pressure; use good ventilation and avoid all ignition sources. See Physical Hazard Information.

Product Description:

IPA is a colorless, flammable liquid with a characteristic alcohol / acetone-like odor.[3] It mixes completely with most solvents, including water. One well-known yet relatively small use for IPA is “rubbing alcohol,” which is a mixture of IPA and water and can be purchased in many pharmacies and grocery stores

Product Uses

The largest use for IPA is as a solvent. The second largest use is as a chemical intermediate. IPA is also found in many everyday products such as paints, inks, general-purpose cleaners, disinfectants, room sprays and windshield deicing agents.

IPA produced by Dow is commonly used in nitrocellulose-based lacquers and thinners for wood finishing, in adhesives, pharmaceuticals, cosmetics and toiletries, disinfectants, rubbing compounds, and lithography. It is also used as an ingredient in cleaners and polishers, as a chemical intermediate, and as a dehydrating agent and extractant.

Exposure Potential

Based on the uses for IPA, the public could be exposed through:

- Workplace exposure – Exposure can occur either in an IPA manufacturing facility or through the evaporation of IPA in various industrial and consumer product applications. Generally, personnel exposures in IPA manufacturing facilities are low because the process, storage and handling operations are enclosed. Less is known about customer workplace exposures, but a study done by the U.S. Environmental Protection Agency (EPA) in 1997 showed that the highest occupational exposures to IPA occurred in the printing industry. In the EPA survey of the printing industry, the highest 8-hour time-weighted average (TWA) exposure was 161 ppm. The U.S. Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) is 400 ppm (980 mg/m^3) (8-hour TWA). The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs®) are: 200 ppm (8-hour TWA) and 400 ppm for short-term exposure limit (STEL)[5].
- Consumer exposure to products containing IPA – This category of exposure is highly variable depending on the products used and the conditions under which they are used. Exposure of the majority of consumers to IPA is likely to be infrequent and of short duration. Exposure could occur through use of IPA in personal care items or in lacquers and thinners. The estimate prepared by the U.S. EPA in 1997 was on the order of grams/person for each use.
- Environmental releases – Fugitive emissions (loss of IPA through evaporation from manufacturing facilities) were estimated at 1.5% of the total U.S. production in 1976, and 3.3%

in the Netherlands from 1974-1979. However, care must be exercised to minimize environmental releases due to IPA's flammability, which is one of its largest risks.

- Large release – Industrial spills or releases are infrequent and often controlled. A spill poses a significant flammability issue. Emergency response personnel generally respond with a controlled burn that limits over-exposure or uncontrolled burning. The combustion products are carbon monoxide (CO), carbon dioxide (CO_2) and water (H_2O).

Health Information

Under usual conditions of exposure, IPA is quickly converted to acetone once taken into the body. Acetone is naturally present in virtually every organ and tissue in the human body as a result of metabolic processes.

Toxicology studies have shown that IPA poses a low health hazard and does not cause adverse health or environmental effects at levels typically found in the workplace or the environment.[7] Overexposure to IPA can cause irritation to the eyes, nose and throat, and may produce central nervous system depression.[8] These effects are typically mild and end shortly after exposure is terminated, not showing any permanent adverse health effects. In coordination, confusion, hypotension, hypothermia, circulatory collapse, respiratory arrest and death may follow a longer duration or higher levels. Swallowing small amounts is not likely to cause injury; however swallowing larger amounts may cause serious injury, and even death.[9]

Chronic, prolonged or repeated overexposure to IPA has produced adverse liver effects and kidney effects and/or tumors in male rats. Such effects are believed to be species-specific, however, and unlikely to occur in humans.

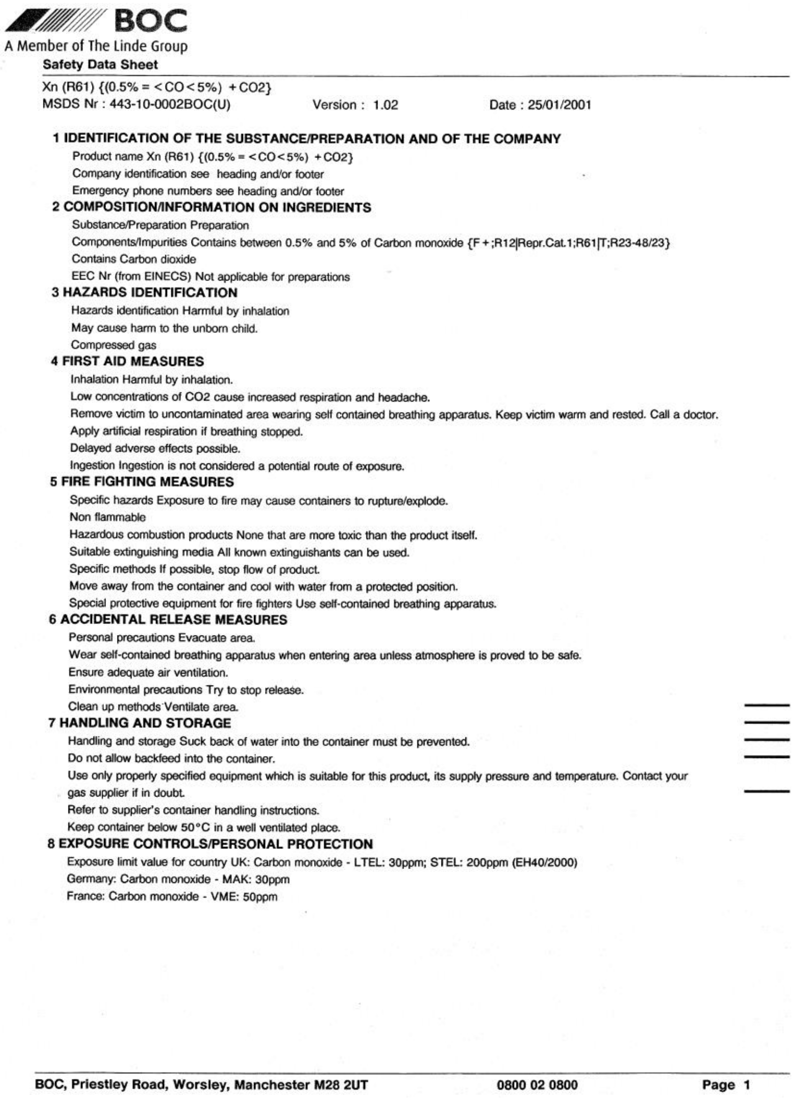
Environmental Information

Public and wildlife exposure through environmental releases is limited because IPA rapidly biodegrades in water and undergoes photo-oxidation relatively rapidly in the atmosphere. IPA is not expected to persist in soil due to its rapid evaporation, and has a low potential to bio-accumulate in aquatic organisms. IPA studies show low toxicity to aquatic organisms and micro-organisms, and toward plant germination and growth.

Physical Hazard Information

IPA is a flammable material and should be handled only with adequate ventilation and in areas where ignition sources have been removed (e.g., matches and unprotected light switches).

Appendix III: Calibration Gas Safety Data Sheets



BOC
A Member of The Linde Group

Safety Data Sheet

Xn (R61) {(0.5% = <CO<5%) +CO2}
MSDS Nr : 443-10-0002BOC(U) Version : 1.02 Date : 25/01/2001

1 IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY

Product name Xn (R61) {(0.5% = <CO<5%) +CO2}

Company identification see heading and/or footer

Emergency phone numbers see heading and/or footer

2 COMPOSITION/INFORMATION ON INGREDIENTS

Substance/Preparation Preparation

Components/Impurities Contains between 0.5% and 5% of Carbon monoxide {F+;R12|Repr.Cat.1;R61|T;R23-48/23}

Contains Carbon dioxide

EEC Nr (from EINECS) Not applicable for preparations

3 HAZARDS IDENTIFICATION

Hazards identification Harmful by inhalation

May cause harm to the unborn child.

Compressed gas

4 FIRST AID MEASURES

Inhalation Harmful by inhalation.

Low concentrations of CO2 cause increased respiration and headache.

Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor.

Apply artificial respiration if breathing stopped.

Delayed adverse effects possible.

Ingestion Ingestion is not considered a potential route of exposure.

5 FIRE FIGHTING MEASURES

Specific hazards Exposure to fire may cause containers to rupture/explode.

Non flammable

Hazardous combustion products None that are more toxic than the product itself.

Suitable extinguishing media All known extinguishants can be used.

Specific methods If possible, stop flow of product.

Move away from the container and cool with water from a protected position.

Special protective equipment for fire fighters Use self-contained breathing apparatus.

6 ACCIDENTAL RELEASE MEASURES

Personal precautions Evacuate area.

Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe.

Ensure adequate air ventilation.

Environmental precautions Try to stop release.

Clean up methods Ventilate area.

7 HANDLING AND STORAGE

Handling and storage Suck back of water into the container must be prevented.

Do not allow backfeed into the container.

Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Contact your gas supplier if in doubt.

Refer to supplier's container handling instructions.

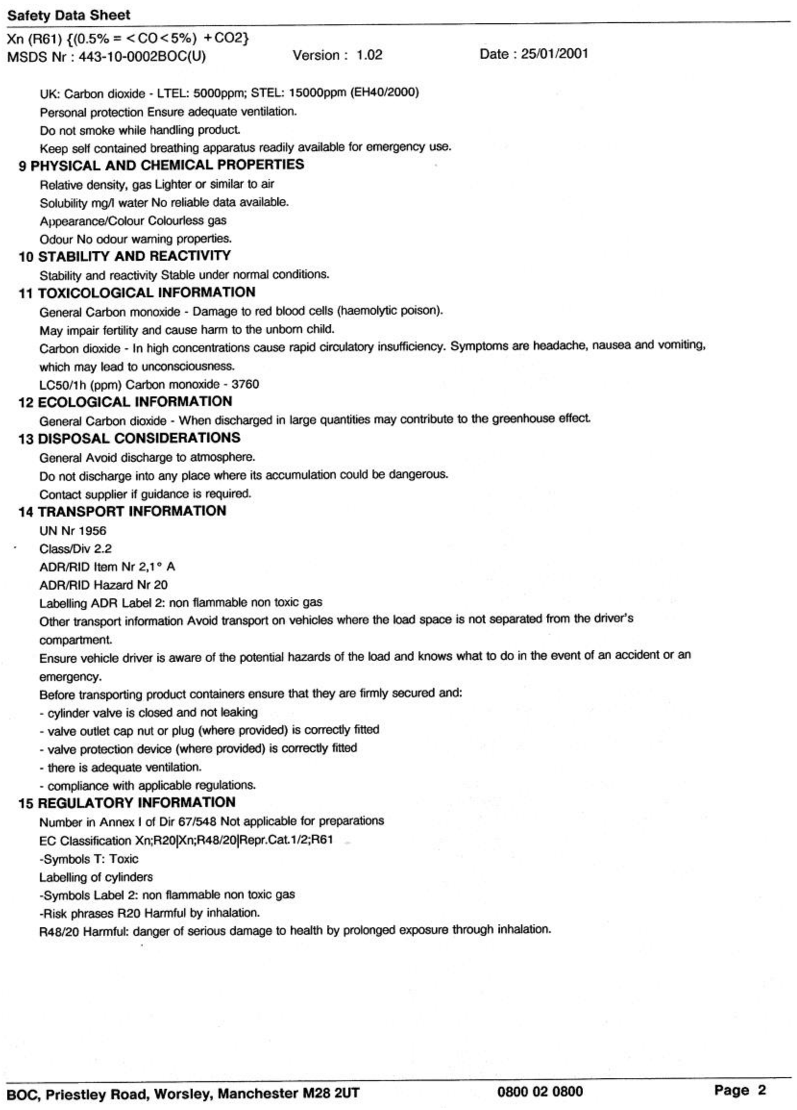
Keep container below 50°C in a well ventilated place.

8 EXPOSURE CONTROLS/PERSONAL PROTECTION

Exposure limit value for country UK: Carbon monoxide - LTEL: 30ppm; STEL: 200ppm (EH40/2000)

Germany: Carbon monoxide - MAK: 30ppm

France: Carbon monoxide - VME: 50ppm



UK: Carbon dioxide - LTEL: 5000ppm; STEL: 15000ppm (EH40/2000)

Personal protection Ensure adequate ventilation.

Do not smoke while handling product.

Keep self contained breathing apparatus readily available for emergency use.

9 PHYSICAL AND CHEMICAL PROPERTIES

Relative density, gas Lighter or similar to air

Solubility mg/l water No reliable data available.

Appearance/Colour Colourless gas

Odour No odour warning properties.

10 STABILITY AND REACTIVITY

Stability and reactivity Stable under normal conditions.

11 TOXICOLOGICAL INFORMATION

General Carbon monoxide - Damage to red blood cells (haemolytic poison).

May impair fertility and cause harm to the unborn child.

Carbon dioxide - In high concentrations cause rapid circulatory insufficiency. Symptoms are headache, nausea and vomiting, which may lead to unconsciousness.

LC50/1h (ppm) Carbon monoxide - 3760

12 ECOLOGICAL INFORMATION

General Carbon dioxide - When discharged in large quantities may contribute to the greenhouse effect.

13 DISPOSAL CONSIDERATIONS

General Avoid discharge to atmosphere.

Do not discharge into any place where its accumulation could be dangerous.

Contact supplier if guidance is required.

14 TRANSPORT INFORMATION

UN Nr 1956

Class/Div 2.2

ADR/RID Item Nr 2,1° A

ADR/RID Hazard Nr 20

Labelling ADR Label 2: non flammable non toxic gas

Other transport information Avoid transport on vehicles where the load space is not separated from the driver's compartment.

Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency.

Before transporting product containers ensure that they are firmly secured and:

- cylinder valve is closed and not leaking
- valve outlet cap nut or plug (where provided) is correctly fitted
- valve protection device (where provided) is correctly fitted
- there is adequate ventilation.
- compliance with applicable regulations.

15 REGULATORY INFORMATION

Number in Annex I of Dir 67/548 Not applicable for preparations

EC Classification Xn;R20|Xn;R48/20|Repr.Cat.1/2;R61

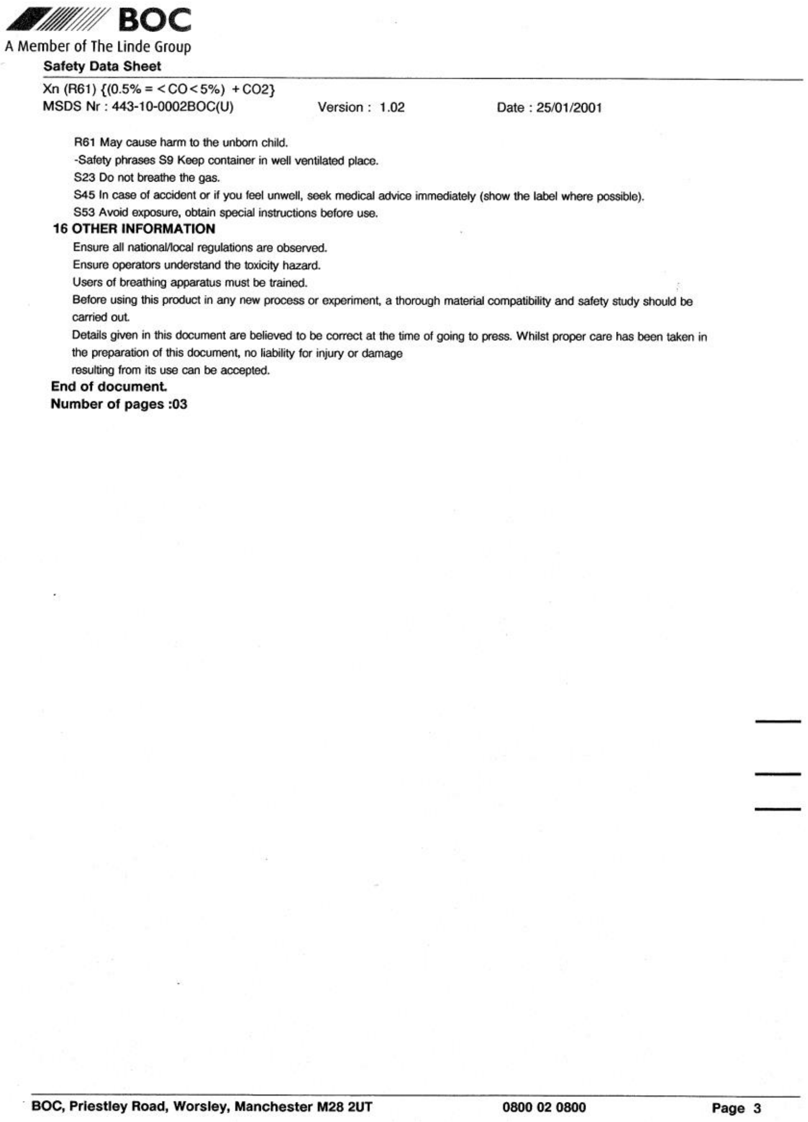
-Symbols T: Toxic

Labelling of cylinders

-Symbols Label 2: non flammable non toxic gas

-Risk phrases R20 Harmful by inhalation.

R48/20 Harmful: danger of serious damage to health by prolonged exposure through inhalation.



BOC
A Member of The Linde Group

Safety Data Sheet

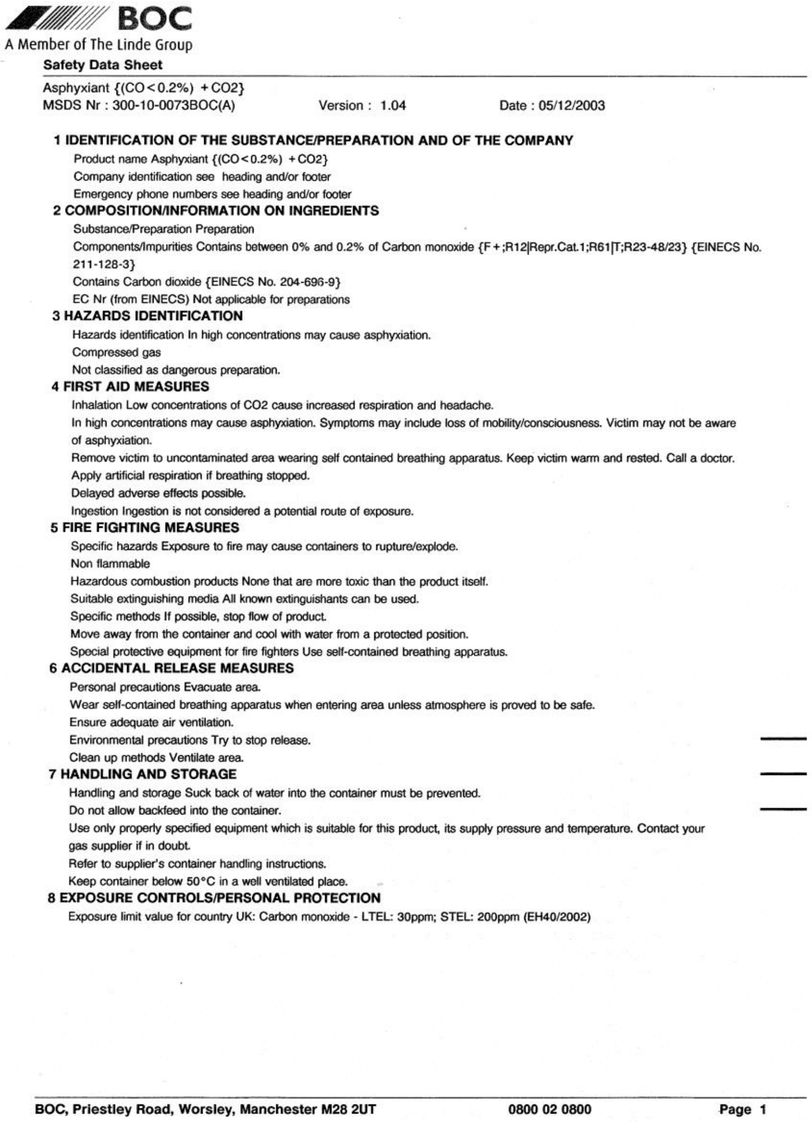
Xn (R61) {(0.5% = < CO < 5%) + CO2}
MSDS Nr : 443-10-0002BOC(U)   Version : 1.02   Date : 25/01/2001

R61 May cause harm to the unborn child.
-Safety phrases S9 Keep container in well ventilated place.
S23 Do not breathe the gas.
S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).
S53 Avoid exposure, obtain special instructions before use.

16 OTHER INFORMATION

Ensure all national/local regulations are observed.
Ensure operators understand the toxicity hazard.
Users of breathing apparatus must be trained.
Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out.
Details given in this document are believed to be correct at the time of going to press. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage
resulting from its use can be accepted.

End of document.
Number of pages :03



BOC
A Member of The Linde Group

Safety Data Sheet

Asphyxiant {(CO < 0.2%) + CO2}
MSDS Nr : 300-10-0073BOC(A)   Version : 1.04   Date : 05/12/2003

1 IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY

Product name Asphyxiant {(CO < 0.2%) + CO2}
Company identification see heading and/or footer
Emergency phone numbers see heading and/or footer

2 COMPOSITION/INFORMATION ON INGREDIENTS

Substance/Preparation Preparation
Components/Impurities Contains between 0% and 0.2% of Carbon monoxide {F+;R12|Repr.Cat.1;R61|T;R23-48/23} {EINECS No. 211-128-3}
Contains Carbon dioxide {EINECS No. 204-696-9}
EC Nr (from EINECS) Not applicable for preparations

3 HAZARDS IDENTIFICATION

Hazards identification In high concentrations may cause asphyxiation.
Compressed gas
Not classified as dangerous preparation.

4 FIRST AID MEASURES

Inhalation Low concentrations of CO2 cause increased respiration and headache.
In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation.
Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor.
Apply artificial respiration if breathing stopped.
Delayed adverse effects possible.
Ingestion Ingestion is not considered a potential route of exposure.

5 FIRE FIGHTING MEASURES

Specific hazards Exposure to fire may cause containers to rupture/explode.
Non flammable
Hazardous combustion products None that are more toxic than the product itself.
Suitable extinguishing media All known extinguishants can be used.
Specific methods If possible, stop flow of product.
Move away from the container and cool with water from a protected position.
Special protective equipment for fire fighters Use self-contained breathing apparatus.

6 ACCIDENTAL RELEASE MEASURES

Personal precautions Evacuate area.
Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe.
Ensure adequate air ventilation.
Environmental precautions Try to stop release.
Clean up methods Ventilate area.

7 HANDLING AND STORAGE

Handling and storage Suck back of water into the container must be prevented.
Do not allow backfeed into the container.
Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Contact your gas supplier if in doubt.
Refer to supplier's container handling instructions.
Keep container below 50°C in a well ventilated place.

8 EXPOSURE CONTROLS/PERSONAL PROTECTION

Exposure limit value for country UK: Carbon monoxide - LTEL: 30ppm; STEL: 200ppm (EH40/2002)

Germany: Carbon monoxide - MAK: 30ppm

France: Carbon monoxide - VME: 50ppm

UK: Carbon dioxide - LTEL: 5000ppm; STEL: 15000ppm (EH40/2002)

Personal protection Do not smoke while handling product.

Ensure adequate ventilation.

9 PHYSICAL AND CHEMICAL PROPERTIES

Relative density, gas Lighter or similar to air

Solubility mg/l water No reliable data available.

Appearance/Colour Colourless gas

Odour No odour warning properties.

10 STABILITY AND REACTIVITY

Stability and reactivity Stable under normal conditions.

11 TOXICOLOGICAL INFORMATION

General Carbon monoxide - Damage to red blood cells (haemolytic poison)./May impair fertility and cause harm to the unborn child.

Carbon dioxide - In high concentrations cause rapid circulatory insufficiency. Symptoms are headache, nausea and vomiting, which may lead to unconsciousness.

LC50/1h (ppm) Carbon monoxide - 3760

12 ECOLOGICAL INFORMATION

General Carbon dioxide - When discharged in large quantities may contribute to the greenhouse effect.

13 DISPOSAL CONSIDERATIONS

General Do not discharge into any place where its accumulation could be dangerous.

Contact supplier if guidance is required.

14 TRANSPORT INFORMATION

Proper shipping name COMPRESSED GAS, N.O.S.

UN Nr 1956

Class 2.2

ADR/RID Classification code 1A

ADR/RID Hazard Nr 20

Packing group None

Labelling ADR Label 2.2: non flammable non toxic gas

IMDG EmS codes F-C, S-V

IMDG Marine pollutant No

IATA passenger packing instruction 200

IATA passenger max. quantity/pack 75kg

IATA cargo packing instruction 200

IATA cargo max. quantity/pack 150kg

Other transport information Avoid transport on vehicles where the load space is not separated from the driver's compartment.

Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency.

Before transporting product containers ensure that they are firmly secured and:

- cylinder valve is closed and not leaking
- valve outlet cap nut or plug (where provided) is correctly fitted
- valve protection device (where provided) is correctly fitted
- there is adequate ventilation.
- compliance with applicable regulations.

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15 REGULATORY INFORMATION

Number in Annex I of Dir 67/548 Not applicable for preparations

EC Classification Not classified as dangerous preparation.

EC Labelling (Symbols, R&S phrases) No EC labelling required.

Labelling of cylinders

-Symbols Label 2.2: non flammable non toxic gas

16 OTHER INFORMATION

Ensure all national/local regulations are observed.

Asphyxiant in high concentrations.

Users of breathing apparatus must be trained.

Keep container in well ventilated place.

Do not breathe the gas.

The hazard of asphyxiation is often overlooked and must be stressed during operator training.

This Safety Data Sheet has been established in accordance with the applicable European Directives and applies to all countries that have translated the Directives in their national laws.

Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out.

Details given in this document are believed to be correct at the time of going to press. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted.

End of document.

Appendix IV: Safe Operating Procedure for Pyrolysis and Gasification Reaction Rig

Penny Challans, Angharad Beurle-Williams 10/06/2010

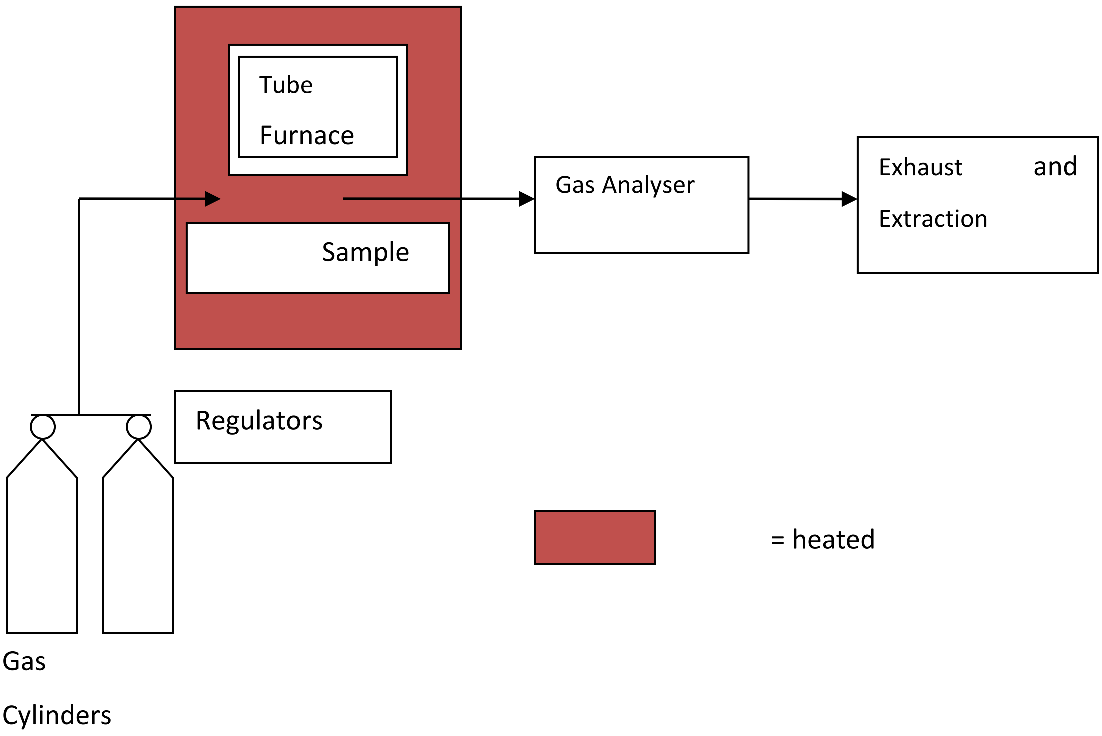
Description

This SOP is for the use of a “pyrolysis and gasification reaction rig” that heats up char and fuel samples in a controlled atmosphere. Nitrogen gas is passed through the box as a purge; after the devolatilisation stage, Oxygen gas is introduced. The gases that exit the reaction rig are analysed using a gas analyser.

Procedure

The char or fuel sample is weighed and loaded into the tube furnace. Nitrogen gas is purged through the system for pre-determined time to ensure volatile content is below 10%. After this devolatilisation time, Oxygen gas is introduced and exhaust gases are analysed. The sample is weighed after the process and undergoes leco testing to establish remaining carbon content.

Diagram



Preliminary Set-Up

1. Before using the equipment, this procedure document should be read carefully to ensure the methodology is understood.
2. Before beginning work with the reaction rig, the samples must be subject to proximate analysis and leco testing.
3. Check all gas cylinders before using the reaction rig to ensure that they are ready to use in accordance to the SOP for the appropriate gas cylinder in use.
4. Check the gas extraction system for blockages.
5. Check that the apparatus surfaces, especially heated ones, are all cool to the touch.
6. Connect the required thermocouples and temperature probes.

7. Switch on the furnace and allow it to heat to the required temperature.
8. Once at required temperature, switch on the extraction system.
9. Open Nitrogen valve and set regulator to required level to begin Nitrogen purge
10. Place sample in boat in the furnace and close door.

Testing Procedure

1. Once volatile percentage of sample is below the required level, connect the exhaust pipe to the gas analyser.
2. Check the furnace gas temperature thermocouple and monitor.
3. Open the Oxygen valve and set regulator to required level, allowing oxidant gas through the rig.
4. Take readings of gas composition from the gas analyser at pre-determined intervals during reaction time.
5. When Carbon Monoxide and Carbon Dioxide levels reach zero remove the sample boat using tongs and place on a cooling brick.
6. Close the Nitrogen and Oxygen valve.
7. Turn off extraction fan.
8. Re-weigh sample boat once cool.

Shutdown

1. Close the Nitrogen and Oxygen valves.
2. Remove any samples from the furnace.
3. Turn off the furnace and gas analyser.
4. Allow the apparatus to cool fully
5. If any equipment is left hot, it should be clearly marked as such.

Emergency Shutdown

1. If the room must be evacuated, switch off power to all the apparatus.
2. Close the Nitrogen and Oxygen valve if time allows.
3. Leave the room immediately.

Sample Handling

1. The char samples will be sourced from commercial char
2. Char will subsequently be processed by crushing, and mixing to ensure uniformity of samples.
3. Sub-samples will be taken and subject to proximate analysis. These will be kept in sealed containers prior to experimentation.
4. Once placed in furnace, the samples will be heated and devolatilised.
5. Once devolatilisation is complete and the percentage of volatiles in the sample is below the required level, the oxygen valve will be opened and the sample will undergo gasification.
6. After the process is complete, the samples will be removed, cooled and reweighed, before being leco tested and then disposed of.

Appendix V: Risk Assessment for Laboratory Testing

Risk Assessment Form

IMPORTANT: Before carrying out the assessment, please read the Guidance Notes

1. General Information

Department	ENGIN	**Building**	Combustion lab
Name of Assessor	P. Challans	**Date of Original**	30th June 2010

Status of Assessor: Supervisor ☐ Postgraduate ☒ Undergraduate ☐ Technician ☐ Other:

2. Brief Description of Procedure/Activity including its Location and Duration

Testing using laboratory scale pyrolysis reaction rig located in combustion lab, West Building from July 2010 to June 2013.

3. Persons at Risk Are they... Notes

Staff ☐ Students ☒ Visitor ☐ Contractor ☐	Trained ☐ Competent ☒ Inexperienced ☐ Disabled ☐	

4. Level of Supervision Notes

None ☒ Constant ☐ Periodic ☐ Training Required ☐	

5. Will Protective Equipment Be Used? Please give ***specific*** details of PPE

Head ☐ Eye ☒ Ear ☐ Body ☒ Hand ☒ Foot ☒	Safety shoes, gloves, goggles and lab coat will be worn when necessary.

6. Is the Environment at Risk? Notes

Yes ☐ No ☒	Extraction fan used, limited fumes and well ventilated area.

7. Will Waste be generated? If 'yes' please give details of disposal

Yes ☒ No ☐	All products resulting from the gas analysis will be analysed and then will exit the lab through the extraction fan. Any solid or liquid products will be small and will be disposed of down drain or combustion lab bin.

8. Hazards involved

Work Activity / Item of Equipment / Procedure / Physical Location	Hazard	Control Measures and Consequence of Failure	Likelihood (0 to 5)	Severity (0 to 5)	Level of Risk
Pipe work from Pyrolysis Unit	High temperatures, burns	Thermal gloves will be worn when handling hot materials.	2	1	2
Using electrical equipment	Electric shock	All equipment will be PAT tested.	1	2	2
Gas cylinders	Explosion	Cylinders will be used in accordance with cylinder regulations.	1	3	3
Moving around testing area	Trips/slips	Area will be kept tidy, any trip hazards will be indentified and made safe	1	2	2

9. Chemical Safety (COSHH Assessment)

Hazard	Control Measures	Likelihood (0 to 5)	Severity (0 to 5)	Level of Risk
Production of hazardous gases: Carbon Monoxide, Hydrogen and Hydrocarbon, risk of asphyxiation, poison or fire.	Ensure area is well ventilated during experimentation, CO detectors, masks to be worn if required.	1	3	3
Calibration gas: Hydrogen, Carbon monoxide, Carbon Dioxide, Methane, Ethane, Propane, N-Butane, Nitrogen	Stored in pressurised cylinder, used in accordance with cylinder regulations.	1	3	3
Isopropanol	Stored in suitable container, gloves to be worn.	2	1	2

Scoring Criteria for Likelihood (chance of the hazard causing a problem)
0 – Zero to extremely unlikely, 1 – Very Unlikely, 2 – Unlikely, 3 – Likely, 4 – Very Likely, 5 – Almost certain to happen

Scoring Criteria for Severity of injury (or illness) resulting from the hazard
0 – No injury, 1 – First Aid is adequate, 2 – Minor injury, 3 – "Three day" injury, 4 – Major injury, 5 – Fatality or disabling injury

10. Source(s) of information used to complete the above

11. Further Action

Highest Level of Risk Score	Action to be taken
0 to 5 ☒	No further action needed
6 to 11 ☐	Appropriate additional control measures should be implemented
12 to 25☐	Additional control measures **MUST** be implemented. Work **MUST NOT** commence until such measures are in place. If work has already started it must **STOP** until adequate control measures are in place.

12. Additional Control Measures – Likelihood and Severity are the values with the additional controls in place

Work Activity / Item of Equipment / Procedure / Physical Location	Hazard and Existing Control Measures	Additional Controls needed to Reduce Risk	Likelihood (0 to 5)	Severity (0 to 5)	Level of Risk

After the implementation of new control measures the procedure/activity should be re-assessed to ensure that the level of risk has been reduced as required.

13. Action in the Event of an Accident or Emergency

Report to supervisor / manager and emergency shutdown of apparatus, switch off power and close all gas valves.

14. Arrangements for Monitoring the Effectiveness of Control

Ad-hoc visual checks and regular inspection of equipment and procedures.

Appendix VI: Proximate analysis, total carbon content and calorific value results

	Moisture %			Ash, %			Volatiles, %			Fixed Carbon, %	
Component	1	2	3	1	2	3	1	2	3	Minimum	Maximum
Paper	3.7	3.7	4.3	11.3	11.4	11.0	77.6	77.9	77.2	6.3	8.1
Newspaper	5.1	4.8	5.3	9.3	9.2	9.3	79.4	79.8	80.0	5.4	6.6
Cardboard	5.8	5.9	5.3	4.2	3.7	3.8	81.1	80.6	80.9	8.7	10.4
PVC	2.0	1.8	1.8	0.5	0.6	0.6	88.9	88.9	88.7	8.5	8.9
HDPE	1.2	1.6	1.0	0.0	0.1	0.1	99.3	99.6	99.7	-1.4	-0.4
PET	9.6	9.4	9.6	0.0	0.0	0.0	90.9	90.7	90.8	-0.5	-0.1
Textiles	2.4	3.0	2.3	0.4	0.7	0.5	87.9	87.6	88.0	8.4	9.8
Food Waste	88.7	88.4	88.4	0.7	0.6	0.6	9.5	10.0	10.1	0.5	1.5

	Total Carbon, %			CV, MJ/kg		
Component	1	2	3	1	2	3
Paper	28.5	29.1	29.9	13.0	12.9	12.7
Newspaper	32.6	31.7	32.3	15.5	15.5	15.5
Cardboard	30.7	31.8	32.2	15.9	16.2	16.4
PVC	40.2	39.8	40.0	44.6	43.6	44.1
HDPE	86.2	84.9	87.0	47.1	45.1	46.8
PET	62.8	63.4	62.9	44.6	48.1	46.0
Textiles	46.1	46.0	45.3	28.3	27.9	28.2
Food Waste	41.8	41.3	40.0	16.9	15.9	16.6

Appendix VII: Mass Loss and Pyrolysis Products Results

Mass Remaining after pyrolysis, %

	Paper				Newspaper				Cardboard			
	Pyrolysis time, minutes				Pyrolysis time, minutes				Pyrolysis time, minutes			
	5	10	30	50	5	10	30	50	5	10	30	50
300°C	93.20	92.80	92.60	92.50								
	93.10	92.56	92.59	92.58								
	93.31	92.71	92.61	92.53								
400°C	78.91	65.91	62.10	62.01								
	78.20	65.78	62.13	62.02								
	78.64	65.24	62.21	61.98								
550°C	41.95	38.99	34.20	33.42	36.60	33.58	30.89	29.01	37.20	34.34	27.81	28.01
	42.60	38.70	34.50	33.20	36.40	33.09	31.06	29.78	36.98	34.01	27.98	27.98
	41.90	38.50	34.20	33.10	36.30	33.46	30.51	29.98	37.10	33.45	28.04	27.84
625°C	37.87	32.73	35.39	35.21	28.96	28.07	28.24	26.98	27.70	27.02	25.31	24.56
	38.20	33.46	34.70	35.01	27.90	27.45	27.61	27.81	27.40	27.31	25.01	24.06
	37.89	32.80	34.80	34.98	28.02	27.02	27.04	27.01	27.01	27.01	25.21	24.31
700°C	33.39	33.69	31.35	31.23	29.24	26.22	24.61	24.01	24.60	22.98	21.75	20.41
	32.14	32.50	30.89	31.01	29.42	27.07	24.14	24.10	24.09	22.67	21.64	20.35
	33.01	32.89	30.90	30.76	28.98	27.01	24.01	24.30	23.80	22.45	21.45	20.26
800°C	29.21	26.70	24.10	24.01								
	29.82	26.89	24.23	23.98								
	28.17	26.53	24.25	23.89								
900°C	28.10	26.90	23.01	23.31								
	29.21	26.48	23.24	23.02								
	27.61	25.43	22.48	22.46								

	Solid Products after 20 minutes, g		
Component	1	2	3
Paper	1.35	1.34	1.35
Newspaper	1.10	1.10	1.09
Cardboard	1.41	1.41	1.41
PET	0.56	0.57	0.57
HDPE	2.23	2.26	2.23
PVC	1.55	1.57	1.54
Textiles	1.33	1.30	1.30
Food waste	0.24	0.23	0.23
Paper 700C	0.91	0.93	0.92
PET 700C	1.13	1.16	1.19

Appendix VIII: Gas Analysis Results

	Total Gas Produced, litres							
Component	CO	CO2	H2	CH4	C2H6	C3H8	N2	O2
Paper	0.095	0.164	0.013	0.009	0.001	0.016	12.600	0.015
	0.095	0.166	0.013	0.009	0.001	0.016	12.600	0.013
	0.097	0.164	0.013	0.009	0.001	0.016	12.600	0.014
Newspaper	0.172	0.150	0.016	0.013	0.000	0.000	12.600	0.067
	0.171	0.149	0.016	0.013	0.000	0.000	12.600	0.061
	0.171	0.150	0.016	0.013	0.000	0.000	12.600	0.062
Cardboard	0.114	0.150	0.016	0.000	0.001	0.000	12.600	0.070
	0.113	0.150	0.016	0.000	0.001	0.000	12.600	0.070
	0.114	0.150	0.016	0.000	0.000	0.000	12.600	0.070
PET	0.212	0.306	0.010	0.000	0.017	0.002	12.600	0.024
	0.221	0.309	0.010	0.000	0.017	0.002	12.600	0.027
	0.214	0.310	0.010	0.000	0.017	0.002	12.600	0.027
HDPE	0.002	0.003	0.012	0.000	0.000	0.000	12.600	0.043
	0.002	0.003	0.011	0.000	0.000	0.000	12.600	0.043
	0.002	0.003	0.011	0.000	0.000	0.000	12.600	0.043
PVC	0.002	0.010	0.017	0.000	0.002	0.002	12.600	0.009
	0.003	0.009	0.017	0.000	0.001	0.002	12.600	0.009
	0.002	0.009	0.016	0.000	0.002	0.002	12.600	0.006
Textiles	0.046	0.071	0.003	0.004	0.001	0.017	12.600	0.028
	0.050	0.074	0.002	0.003	0.001	0.017	12.600	0.025
	0.050	0.073	0.003	0.003	0.000	0.017	12.600	0.027
Food waste	0.031	0.084	0.004	0.011	0.001	0.007	12.600	0.017
	0.031	0.084	0.005	0.012	0.001	0.006	12.600	0.016
	0.032	0.084	0.005	0.010	0.001	0.007	12.600	0.017
Paper 700C	0.508	0.230	0.408	0.039	0.003	0.003	12.600	0.027
	0.524	0.231	0.412	0.039	0.003	0.003	12.600	0.027
	0.509	0.241	0.399	0.039	0.003	0.003	12.600	0.027
PET 700C	0.453	0.299	0.079	0.024	0.011	0.002	12.600	0.027
	0.461	0.311	0.078	0.025	0.011	0.002	12.600	0.026
	0.432	0.299	0.078	0.025	0.011	0.002	12.600	0.026

Appendix IX: Commercial Rig 1 Results

Run 1: 100 % cardboard

Time from start of run (mins)	Chamber temperature, °C	Air Flow (l/min)	Produced Gas (% flow rate)							
			O_2	CO_2	CO	H_2	N_2	CH_4	C_2H_6	C_3H_8
0	20	8.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
15	91	8.0	20.520	0.430	0.420	0.140	75.710	0.000	0.000	0.317
19	140	8.0	19.580	2.710	1.710	0.200	73.730	0.496	0.000	0.313
24	228	8.0	19.210	3.280	0.000	0.150	73.410	0.463	0.000	0.334
27	235	8.0	18.695	3.750	0.000	0.130	73.280	0.388	0.000	0.356
34	239	8.0	20.704	0.380	0.180	0.090	75.120	0.000	0.000	0.293
38	234	8.0	16.537	6.360	3.080	0.110	72.080	0.274	0.000	0.350
42	276	8.0	20.020	2.700	1.620	0.110	72.450	0.275	0.000	0.363
46	291	8.0	16.329	9.690	0.000	0.190	65.400	0.893	0.045	0.412
51	329	8.0	20.662	0.540	0.220	0.090	74.730	0.187	0.000	0.288
55	327	16.4	20.953	0.080	0.000	0.080	75.050	0.000	0.000	0.262
59	323	24.9	10.373	9.540	0.000	0.720	72.570	1.442	0.058	0.386
63	353	31.3	9.382	10.040	4.090	1.690	71.480	1.480	0.055	0.381
66	374	38.2	20.890	0.100	0.010	0.110	75.020	0.001	0.000	0.328
70	399	55.0	18.648	2.130	1.010	0.220	74.100	0.874	0.038	0.324
74	445	84.7	10.913	8.950	2.130	0.520	74.850	0.973	0.030	0.339
78	450	126.3	10.496	9.500	0.000	0.520	75.160	0.691	0.000	0.329
82	468	126.3	20.979	0.050	0.000	0.070	74.910	0.000	0.000	0.301
86	478	56.1	17.501	3.160	0.610	0.470	74.470	0.243	0.000	0.354
90	514	101.5	15.783	4.280	0.980	0.800	74.300	0.361	0.000	0.351
98	569	74.6	20.934	0.080	0.000	0.070	74.860	0.000	0.000	0.325
101	578	128.0	20.825	0.330	0.000	0.070	74.790	0.000	0.000	0.369
106	578	35.6	20.975	0.050	0.000	0.070	74.920	0.000	0.000	0.270
109	575	61.5	19.330	2.150	0.050	0.070	75.110	0.000	0.000	0.339
114	580	64.5	20.797	0.400	0.060	0.070	74.900	0.000	0.000	0.300
124	563	64.5	20.930	0.180	0.010	0.070	74.900	0.000	0.000	0.282
128	537	128.0	20.834	0.400	0.010	0.080	74.820	0.000	0.000	0.319
132	505	128.0	20.925	0.190	0.020	0.070	74.900	0.000	0.000	0.308
136	463	128.0	20.951	0.180	0.010	0.070	74.870	0.000	0.000	0.322
140	469	128.0	20.983	0.080	0.000	0.070	74.950	0.000	0.000	0.297
143	482	52.5	20.984	0.050	0.000	0.070	74.960	0.000	0.000	0.308

Run 2: 33 % cardboard, 66 % PET

			Produced Gas (% flow rate)							
Time from start of run, mins	Chamber temperature, °C	Airflow, l/min	O_2	CO_2	CO	H_2	N_2	CH_4	C_2H_6	C_3H_8
0	97	0.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
7	97	0.0	20.900	0.000	0.120	0.050	75.030	0.000	0.000	0.284
11	101	0.0	20.993	0.000	0.050	0.070	75.180	0.000	0.000	0.261
16	215	0.0	20.165	0.752	1.050	0.080	74.870	0.000	0.000	0.372
20	241	0.0	20.486	0.362	0.710	0.070	75.090	0.000	0.000	0.332
25	241	0.0	19.624	0.783	1.550	0.070	75.120	0.000	0.000	0.329
29	234	0.0	20.639	0.193	0.370	0.070	75.260	0.000	0.000	0.324
33	237	0.0	18.423	2.492	2.920	0.080	74.650	0.000	0.000	0.340
36	276	0.0	15.514	6.176	6.730	0.090	73.060	0.199	0.000	0.308
41	284	0.0	14.411	6.861	7.430	0.090	73.220	0.206	0.000	0.322
48	297	0.0	19.437	2.042	1.910	0.090	74.420	0.206	0.000	0.331
52	341	8.4	20.924	0.000	0.070	0.080	74.930	0.000	0.018	0.308
56	346	20.8	13.296	6.929	7.060	0.140	74.260	0.448	0.020	0.373
59	352	26.4	10.717	7.766	8.770	1.180	72.520	0.957	0.031	0.354
63	352	40.3	17.728	1.943	2.830	0.410	74.460	0.376	0.000	0.356
67	363	64.8	10.180	6.128	9.380	1.460	72.950	0.751	0.020	0.337
70	374	99.2	14.721	2.840	6.000	0.580	74.440	0.286	0.000	0.325
74	359	118.3	15.812	2.226	4.990	0.520	74.440	0.275	0.000	0.339
78	343	118.3	19.147	0.700	2.100	0.140	75.010	0.000	0.000	0.341
81	364	118.3	20.609	0.143	0.540	0.070	75.080	0.000	0.000	0.349
85	385	118.3	20.962	0.000	0.090	0.070	75.080	0.000	0.000	0.366
89	389	118.3	20.964	0.000	0.100	0.070	75.040	0.000	0.000	0.417
93	411	118.3	18.186	1.395	2.720	0.190	74.830	0.224	0.000	0.348
96	430	118.3	20.115	0.564	0.990	0.130	74.060	0.000	0.000	0.427
100	435	118.3	18.014	1.623	2.990	0.240	74.530	0.269	0.000	0.343
103	455	118.3	15.255	4.746	4.730	0.270	74.530	0.445	0.000	0.324
107	492	48.1	20.299	0.724	0.700	0.090	74.710	0.222	0.000	0.390
111	576	111.4	20.336	0.744	0.660	0.090	74.560	0.213	0.000	0.413
114	579	120.0	13.948	7.437	6.420	0.270	73.160	0.932	0.078	0.345
118	574	52.1	14.888	6.073	5.930	0.230	73.290	0.915	0.000	0.356
121	568	36.4	13.766	8.701	7.290	0.370	71.480	1.751	0.020	0.340
125	566	27.6	3.463	15.230	16.310	0.370	70.140	2.419	0.020	0.368
129	571	20.3	10.362	6.093	11.300	0.200	73.290	0.793	0.057	0.369
132	569	45.7	13.266	1.467	7.650	0.440	75.840	0.248	0.000	0.361
136	549	41.3	14.682	1.899	5.990	0.440	75.020	0.316	0.000	0.380
140	537	78.8	15.261	1.621	5.310	0.360	75.260	0.230	0.000	0.371
143	523	120.0	14.567	2.494	5.410	0.510	75.090	0.243	0.000	0.374
147	510	48.1	15.412	2.165	5.160	0.360	74.450	0.000	0.000	0.365
151	498	120.0	21.008	0.000	0.070	0.070	74.960	0.000	0.000	0.385
155	509	120.0	21.012	0.000	0.050	0.070	75.080	0.000	0.000	0.315
158	513	61.3	19.629	0.561	1.420	0.120	75.100	0.000	0.000	0.384
162	509	120.0	21.002	0.000	0.050	0.070	75.070	0.000	0.000	0.304
166	497	120.0	17.179	1.952	3.850	0.150	75.060	0.000	0.000	0.398

Appendix X: Commercial Rig 2 Results

Repeat Number	Gas Produced, % flow rate							
	H_2	O_2	N_2	CH_4	CO	CO_2	C_2H_6	C_3H_8
1	6.169	8.992	53.764	1.375	10.788	5.200	0.368	0.341
2	6.776	8.466	51.754	1.460	12.581	5.519	0.363	0.389
3	6.719	8.469	51.822	1.628	12.473	5.677	0.436	0.421
4	6.076	9.575	53.059	1.456	11.428	5.181	0.364	0.420
5	6.754	9.956	50.809	1.419	10.214	3.839	0.330	0.340

Appendix XI: Risk Assessment for Testing on Commercial Rig 1

Risk Assessment Form

IMPORTANT: Before carrying out the assessment, please read the Guidance Notes

1. General Information

Department	ENGIN	**Building**	PyroPure Ltd, Bordon
Name of Assessor	P. Challans	**Date of Original Assessment**	30th Nov 2011

Status of Assessor: Supervisor ☐ Postgraduate ☒ Undergraduate ☐ Technician ☐ Other:

2. Brief Description of Procedure/Activity including its Location and Duration

Gas analysis testing including tar removal and gas cooling. This will involve connecting a tar trap, gas cooling system and gas analyser to PyroPure's pyrolysis unit. The testing will take place at PyroPure Ltd., Bordon from 7th – 9th December 2011.

3. Persons at Risk

3. Persons at Risk	Are they...	Notes
Staff ☐ Students ☒ Visitor ☐ Contractor ☐	Trained ☐ Competent ☒ Inexperienced ☐ Disabled ☐	

4. Level of Supervision

4. Level of Supervision	Notes
None ☒ Constant ☐ Periodic ☐ Training Required ☐	

5. Will Protective Equipment Be Used?

Please give ***specific*** details of PPE

Head ☐ Eye ☒ Ear ☐ Body ☒ Hand ☒ Foot ☒	Safety shoes, gloves, goggles and lab coat will be worn when necessary.

6. Is the Environment at Risk?

6. Is the Environment at Risk?	Notes
Yes ☐ No ☒	Extraction fan used, limited fumes and well ventilated area.

7. Will Waste be generated?

7. Will Waste be generated?	If 'yes' please give details of disposal
Yes ☒ No ☐	All products resulting from the gas analysis will be analysed. Waste produced by the PyroPure process will be disposed of in accordance with their procedures.

8. Hazards involved

Work Activity / Item of Equipment / Procedure / Physical Location	**Hazard**	**Control Measures and Consequence of Failure**	**Likelihood (0 to 5)**	**Severity (0 to 5)**	**Level of Risk**

Pipe work from Pyrolysis Unit	High temperatures, burns	Thermal gloves will be worn when handling hot materials.	2	1	2
Using electrical equipment	Electric shock	All equipment will be PAT tested.	1	2	2
Gas cylinders	Explosion	Cylinders will be used in accordance with cylinder regulations.	1	3	3
Moving around testing area	Trips/slips	Area will be kept tidy, any trip hazards will be indentified and made safe	1	2	2

9. Chemical Safety (COSHH Assessment)

Hazard	**Control Measures**	**Likelihood (0 to 5)**	**Severity (0 to 5)**	**Level of Risk**
Production of hazardous gases: Carbon Monoxide, Hydrogen and Hydrocarbon, risk of asphyxiation, poison or fire.	Ensure area is well ventilated during experimentation, CO detectors, masks to be worn if required.	1	3	3
Calibration gas: Hydrogen, Carbon monoxide, Carbon Dioxide, Methane, Ethane, Propane, N-Butane, Nitrogen	Stored in pressurised cylinder, used in accordance with cylinder regulations.	1	3	3
Isopropanol	Stored in suitable container, gloves to be worn.	2	1	2

Scoring Criteria for Likelihood (chance of the hazard causing a problem)
0 – Zero to extremely unlikely, 1 – Very Unlikely, 2 – Unlikely, 3 – Likely, 4 – Very Likely, 5 – Almost certain to happen

Scoring Criteria for Severity of injury (or illness) resulting from the hazard
0 – No injury, 1 – First Aid is adequate, 2 – Minor injury, 3 – "Three day" injury, 4 – Major injury, 5 – Fatality or disabling injury

10. Source(s) of information used to complete the above

11. Further Action

Highest Level of Risk Score	**Action to be taken**
0 to 5 ☒	No further action needed
6 to 11 ☐	Appropriate additional control measures should be implemented
12 to 25☐	Additional control measures **MUST** be implemented. Work **MUST NOT** commence until such measures are in place. If work has already started it must **STOP** until adequate control measures are in place.

12. Additional Control Measures – Likelihood and Severity are the values with the additional controls in place

Work Activity / Item of Equipment / Procedure / Physical Location	Hazard and Existing Control Measures	Additional Controls needed to Reduce Risk	Likelihood (0 to 5)	Severity (0 to 5)	Level of Risk

After the implementation of new control measures the procedure/activity should be re-assessed to ensure that the level of risk has been reduced as required.

13. Action in the Event of an Accident or Emergency

Report to supervisor / manager and emergency shutdown of apparatus, switch off power and close all gas valves.

14. Arrangements for Monitoring the Effectiveness of Control

Ad-hoc visual checks and regular inspection of equipment and procedures.

Appendix XII: Risk Assessment for Testing on Commercial Rig 2

Risk Assessment Form

IMPORTANT: Before carrying out the assessment, please read the Guidance Notes

1. General Information

Department	ENGIN	**Building**	QinetiQ Ltd, Farnborough
Name of Assessor	P. Challans	**Date of Original Assessment**	30th Nov 2011

Status of Assessor: Supervisor ☐ Postgraduate ☒ Undergraduate ☐ Technician ☐ Other:

2. Brief Description of Procedure/Activity including its Location and Duration

Gas analysis testing including tar removal and gas cooling. This will involve connecting a tar trap, gas cooling system and gas analyser to QinetiQ's pyrolysis unit. The testing will take place at QinetiQ Ltd., Farnborough on 16th May 2012.

3. Persons at Risk	Are they…	Notes
Staff ☐ Students ☒ Visitor ☐ Contractor ☐	Trained ☐ Competent ☒ Inexperienced ☐ Disabled ☐	

4. Level of Supervision	Notes
None ☒ Constant ☐ Periodic ☐ Training Required ☐	

5. Will Protective Equipment Be Used? Please give ***specific*** details of PPE

Head ☐ Eye ☒ Ear ☐ Body ☒ Hand ☒ Foot ☒	Safety shoes, gloves, goggles and lab coat will be worn when necessary.

6. Is the Environment at Risk?	Notes
Yes ☐ No ☒	Extraction fan used, limited fumes and well ventilated area.

7. Will Waste be generated?	If 'yes' please give details of disposal
Yes ☒ No ☐	All products resulting from the gas analysis will be analysed. Waste produced by the PyroPure process will be disposed of in accordance with their procedures.

8. Hazards involved

Work Activity / Item of Equipment / Procedure / Physical Location	**Hazard**	**Control Measures and Consequence of Failure**	**Likelihood (0 to 5)**	**Severity (0 to 5)**	**Level of Risk**

Pipe work from Pyrolysis Unit	High temperatures, burns	Thermal gloves will be worn when handling hot materials.	2	1	2
Using electrical equipment	Electric shock	All equipment will be PAT tested.	1	2	2
Gas cylinders	Explosion	Cylinders will be used in accordance with cylinder regulations.	1	3	3
Moving around testing area	Trips/slips	Area will be kept tidy, any trip hazards will be indentified and made safe	1	2	2

9. Chemical Safety (COSHH Assessment)

Hazard	**Control Measures**	**Likelihood (0 to 5)**	**Severity (0 to 5)**	**Level of Risk**
Production of hazardous gases: Carbon Monoxide, Hydrogen and Hydrocarbon, risk of asphyxiation, poison or fire.	Ensure area is well ventilated during experimentation, CO detectors, masks to be worn if required.	1	3	3
Calibration gas: Hydrogen, Carbon monoxide, Carbon Dioxide, Methane, Ethane, Propane, N-Butane, Nitrogen	Stored in pressurised cylinder, used in accordance with cylinder regulations.	1	3	3
Isopropanol	Stored in suitable container, gloves to be worn.	2	1	2

Scoring Criteria for Likelihood (chance of the hazard causing a problem)
0 – Zero to extremely unlikely, 1 – Very Unlikely, 2 – Unlikely, 3 – Likely, 4 – Very Likely, 5 – Almost certain to happen

Scoring Criteria for Severity of injury (or illness) resulting from the hazard
0 – No injury, 1 – First Aid is adequate, 2 – Minor injury, 3 – "Three day" injury, 4 – Major injury, 5 – Fatality or disabling injury

10. Source(s) of information used to complete the above

11. Further Action

Highest Level of Risk Score	**Action to be taken**
0 to 5 ☒	No further action needed
6 to 11 ☐	Appropriate additional control measures should be implemented
12 to 25☐	Additional control measures **MUST** be implemented. Work **MUST NOT** commence until such measures are in place. If work has already started it must **STOP** until adequate control measures are in place.

12. Additional Control Measures – Likelihood and Severity are the values with the additional controls in place

Work Activity / Item of Equipment / Procedure / Physical Location	**Hazard and Existing Control Measures**	**Additional Controls needed to Reduce Risk**	**Likelihood (0 to 5)**	**Severity (0 to 5)**	**Level of Risk**

After the implementation of new control measures the procedure/activity should be re-assessed to ensure that the level of risk has been reduced as required.

13. Action in the Event of an Accident or Emergency

Report to supervisor / manager and emergency shutdown of apparatus, switch off power and close all gas valves.

14. Arrangements for Monitoring the Effectiveness of Control

Ad-hoc visual checks and regular inspection of equipment and procedures.